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Zinc recovery from wastes and the environment at low concentrations.

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Zinc Recovery from Wastes and the Environment at Low Concentrations

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Abstract

This thesis concerns the selective recovery of low concentrations of Zn from waste materials using a number of integrated unit operations to produce a high purity material of high value. The emphasis of the processes investigated is to carry out these processes with high efficiency and low energy. A literature survey revealed that a promising hydrometallurgical approach was to concentrate Zn from low concentration using polymer enhanced ultrafiltration (PEUF) using polyethylenimine (PEI) as filterable metal chelator; followed by alkaline precipitation of the chloride salt to form $Zn(OH)_2$; the zincate salt in alkaline solution was then electrowon to give pure Zn metal.

Two practical areas of work central to this process were investigated with aims of devising mathematical descriptions of these processes to allow process prediction and optimisation of these operations. The first was to model the process using PEI, as water-soluble polymer that binds Zn efficiently. The process involved: the binding of zinc ions to polymer; concentration of the PEI-Zn complex; followed by decomplexation with acid to regenerate the polymer with alkali and concentrated zinc chloride solution. An MS Excel model based on mass balance, PEI-Zn binding phenomena and the separation of the polymer/zinc complex in the membrane system was developed. Each stage of the process was satisfactorily modelled and it was validated by a series of studies related to the complexation phenomena using Langmuir adsorption equilibria. A series of process variables were investigated to allow an assessment the affects of the zinc concentration and its decomplexation from PEI. The model showed a good agreement with observed data. The complex relationship between polymer concentration, complex concentration processes, washing and polymer regeneration on membrane productivity was then investigated and optimised. Under the conditions employed 6 g/L PEI concentration to give maximum $ZnCl_2$ production based upon membrane productivity. Increasing the washing feed/retentate ratio could decrease the membrane productivity and the final concentration $ZnCl_2$.

The electrowinning process of zinc from an alkaline zincate solution at stainless steel electrodes was then investigated. Alkaline electrowinning involved dissolving specific amounts of ZnO in 4 mole/L NaOH and the resultant solution was then subjected to a galvanostatic electrowinning process. The effects of initial zinc concentration, current density and NaOH concentration on the process were examined including electrical energy usage, zinc recovery and current efficiency relationships. The experimental results showed that the highest recovery rate could be obtained when varying current densities at 2000 A/m^2 and initial Zn concentration of 20 g/L. The experimental results were then used to test the predictions of concentration-time behaviour of an MS Excel based mathematical model of metal deposition kinetics. Reasonable agreement between experimental data and model predictions using a limited electrode surface area model was achieved. Based on the results obtained in this work, 88% of zinc from alkaline solution (20 g/L) with 95% current efficiency and energy consumption of 0.77 kWh/kg zinc were achieved.

Using these studies, an integrated zinc recovery process from low grade zinc tailings was investigated further with primary aim of determining the economics and impacts of the process. The leaching efficiency; metal oxide dissolution and other operation to reduce waste (electrodialysis) were incorporated into an MS Excel model so that the overall process could be evaluated. The process was capable determining the production rate at break-even point based on extraction efficiency and Zn ore content. For example, a profit of about £1.22 M/year was made over 2.2 years with an extraction efficiency of 50% from an ore input of 1000 t/day containing 2% Zn. This model provides a tool for further analysis of the process and will provide good targets for process development and improved process feasibility.

Declaration

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

Signed ....

Date ....

Emadeddin Hassan Gejam

Statement 1

This thesis is the result of my own investigation, except where otherwise stated. Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended.

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ACKNOWLEDGMENT

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Chapter 1

1. INTRODUCTION

This project concerns the recovery and purification of metals from low concentrations that are commonly found in waste streams or contaminated environments. One of the main challenges for the future will be the recovery of metals from dilute environments either for recovery of the metal or as a clean up procedure for polluted water or soils.

It is now becoming quite clear that the world is becoming resource limited as the major economies of the world develop. In addition, huge centres of population in China, India and South East Asia and South America are now developing rapidly and desire the lifestyles of Western Europe and North America. This in turn is putting a major stress on the supply of energy and material to drive these developments. At the same time land use is also changing as food and alternative sources of energy such as bio-fuels are developed.

Indicative of these new demands, the prices for metals have increased substantially and now are beginning to be an important factor in the development of countries like China and even threaten developments and economic stability in Europe. These pressures are leading to a drive for sustainable development which in turn means that security of energy and materials supply becomes an important issue for long term political and economic stability.

The discovery and extraction of metals from the environment was at the root of the industrial revolution and today it still represents a significant challenge. Although the early industrialists had little care for the environment this issue has come to the fore as the human activities on the planet are having a significant impact on the environment in the form of diminished resources, pollution, loss of habitat and climate change.

As a response, governments are striving for improving environmental standards enforced by increasingly strict legislation and economic incentives.

In the UK and the rest of the world the use of resources is being driven by greater environmental awareness and by their limitation. There are now strong environmental policies making traditional methods of disposal of waste non-viable, e.g. landfill (Environmental Protection Agency, 2003). At the same time governments are making it more worthwhile to recycle materials by increasing the costs of disposal and making the recycled materials more valuable.

Kiely (1997), listed some industrial producing metal wastes in table 1-1. Disposal of the waste was a viable option until the value of land and the number of suitable sites has become ever more limited as the environmetal impact of these systems was realised.

Table 1-1: Industries producing metals waste.

Industrial type	Hazardous substance
Batteries	Li, Cd, Pb, Ag, Zn, Ni
Chemical manufacturing	Cr, Cu, Pb, Hg
Electrical/electronic	Cu, Co, Pb, Hg, Zn, Se
Printing	As, Cr, Cu, Pb, Se
Electroplating	Co, Cr, Cn, Cu, Zn, Ni
Textile	Cr, Cu
Pharmaceutical	As, Hg
Paints	Cd, Cr, Cu, Co, Pb, Hg, Se
Plastics	Co, Hg, Zn
Leather	Cr

Another important aspect associated with metals is that heavy metals can be toxic. Toxicity depends on two factors. These factors are:

Concentration: some heavy metals, such as copper and zinc, are required in trace concentrations because they can be toxic in large quantities. On the other hand, metals like lead, aluminium and mercury have no known physiological role since

they are highly toxic to organisms. Generally, it is important that all these metals have to be in a form that can be taken into the organism before they become toxic, (i.e. bio-available) (Karabulut et al., 2000). This depends on the chemical form of the metals.

Chemical form: A complete examination of the form of the metal must be established in any pollutant before its toxicity can be determined. This conclusion is based on much research over the past 50 years and the research carried out by Howells (1999) illustrates this. Howells (1999) studied stream pH levels in which a particular form of aluminium called labile monomeric aluminium can occur. This component is believed to be toxic to fish in streams.

The toxic substances produced by metal industries and derivatives, such as metal plating facilities, mining operations, and tanneries, can directly affect the health of all living systems. For example, Hettiarachchi and Pierzynski (2004) stated that lead, Pb, is toxic to humans and affects virtually every system in the body. Many environmental sources, such as contaminated soil, household dust and industrial wastes, are typical sources of Pb exposure for humans (Karabulut et al., 2000). The metals listed in table 1-1 have maximum permissible values in different environments and there are still proposals to achieve values below these limits (Crommentuijn et al., 1997).

Gungor and Surendra (1999) pointed out three main reasons for the recovery of material and recycle of products to be carried out. These are: hidden economic value of solid wastes, market requirements, and governmental regulations. Therefore, metal recovery from waste streams is becoming increasingly important and potentially viable.

Fortunately, heavy metals are not destroyed and tend to accumulate in waste streams in dilute forms where it may be possible to recover them. Sustainable development is defined as "development that meets the needs of the present without compromising the ability for future generations to meet their own needs" (Gungor and Surendra, 1999). Sustainable development is based on three important factors: economic development, social consequences and development, and environmental protection. The sustainability of production and processing systems including technology for

recycling are important to cover the regulations of waste materials, which have been put in order to identify the extent of the environment problems and take corrective actions. As a consequence of that, two forms of optimal primary objectives have been employed in the real industries (Gungor and Surendra, 1999):

- Creating environmentally friendly products (i.e. green products).

- Developing techniques for product recovery and waste management.

Mining and refining charges vary with supply and demand in the market and the costs of energy. Consequently, the mining and refining share of the metal price varies considerably. Treatment processes for metal recovery include smelting, chemical precipitation, membrane filtration, ion exchange, carbon adsorption and electrowinning. Some techniques, like smelting are now becoming very expensive with long costly operating conditions and they are also environmentally unfriendly compared to the alternatives. In addition, wastes containing heavy metals are treated to remove them from water resulting in a solid waste containing a relatively high concentration of metals. This results in these solid materials being toxic with the consequence expensive costs of disposal.

Therefore there is considerable interest in the development of cost effective technologies for the recovery of metal ions from effluent streams. Selective recovery of metals is seen as one method of improving the economics of the operation. This is because the technology recovers relatively high purity metals, which have considerable value, and can be reused at the same time, so reducing demand on new materials from the environment and possibly reducing imports of such materials. Also, the remaining waste of such a technique should be detoxified so making it cheap to dispose or to become recyclable itself. These metal recovery processes will drive the system towards greater sustainability, reducing our needs to import materials, making systems more self sufficient.

1.1. The Project Aim:

The aim of this project is to investigate the viability and utility of integrated zinc recovery processes from relatively low concentrations. Also, the potential for reprocessing wastes on site and at a relatively small scale is required. There are a

number of objectives: Assessment of current technology and its ability to reprocess real industrial wastes, assessment of selected targets for reprocessing such as metal electroplating and experimental investigation of specific targeted processes

Zinc metal has important markets in the brass and construction industries and in chemicals. Also, zinc forms an important nutritional element. Zinc is used in galvanised steel, protective coatings for steel, and die-casting. Zinc compounds are used for luminous dials, cosmetics, plastics, rubber products, soaps and inks. The increased demand for galvanised products is reflected in the growth in demand for zinc. Meanwhile, the higher zinc prices encourage increased mine output and waste treatment. Therefore, the project presents an experimental examination of polymer enhanced ultrafiltration processes of zinc solution and electrowinning behaviour. A design model for an integrated zinc recovery plant using low concentration feed solutions was constructed and the effect of extraction efficiency and amount of solids fed to the system were investigated to determine the optimum operation values for the plant under a given set of conditions.

1.2. Structure of the Thesis:

Chapter 2 is a survey of the relevant literature. This consists of several topics, viz. current metal recovery technologies used by industry, an overview of metal in the environment and methods of treatments used to extract metals from the environment. Also, a review of previous experimental work is discussed for metal recovery through operating conditions, design and relevant operating strategies.

Chapter 3 presents the experimental methodology for the study of both the electrowinning and polymer enhanced ultrafiltration processes. Chapter 3 also explains the apparatus and experiments of each process and the materials employed for these particular systems. The proposed integrated zinc recovery process is also outlined

In chapter 4, the results of polymer enhanced ultrafiltration experiments are presented. Optimum operation and number of washing times is concluded in the second section of this chapter. Also, this chapter presents the mathematical simulation in relation to the volume concentration factor as a function of permeate flux and this is used to evaluate the optimum flux with the strategy of achieving the

optimum PEI concentration that results in maximum membrane productivity of the whole membrane system.

The results of the zinc electrowinning for both the acidic and alkaline system design and the optimisation procedure are shown in Chapter 5. It is found that alkaline electrowinning can provide better performance and less energy usage than the acidic process. The Alkaline cell was hence selected in order to carry on examining the effect of varying the parameters and coding a model that could predict the performance of such a process. Further suggested development to improve the deposition efficiency of zinc is also explained employing limited surface metal deposition model.

The principle findings regarding the zinc recovery system design and operation and economic aspects of the plant are discussed in Chapter 6, whereas Chapter 7 draws conclusions from the results obtained and describes ways in which the project may be extended in the future.

Chapter 2

2. LITERATURE REVIEW

Many publications have considered heavy metals recovery, reprocessing principles and technologies. Only directly relevant work is reviewed here to provide general background to the viability and utility of individual and integrated metal recovery processes.

2.1. Metal Recovery from Mining Ores:

2.1.1. Overview:

Mining is the first and main source of metals and with most metals being found in complex form called ores. Mining is a major economic activity and takes place all over the world, and is a huge contribution to the economic and industrial development. Mined materials are central to large scale civil engineering and contribute to many other sectors of the economy, for example the construction of roads and other transport infrastructure, to build automobiles and houses, to make computers and satellites, to generate electricity, and to provide many other goods and services (Hayes, 1993).

Mining begins with exploration, continues through production, and ends with closure and post-mining land use. Most metallic ore deposits are formed through the interaction of an aqueous fluid and host rocks. At some point along the fluid flow pathway, the fluids encounter changes in physical or chemical conditions that cause the dissolved metals to precipitate as salts. The focus has traditionally been on the location of metal depositions, that is, the ore deposit. Consequently, the process of mining commonly exposes ore to more rapid oxidation, which naturally affects the environment. Therefore, understanding the movement of fluids through the Earth, for example, through enhanced hydrologic models, will be critical for future mineral exploration, as well as for effectively closing mines that have completed their life cycle (Hayes, 1993).

After a mineral deposit has been identified through exploration, the industry must make a considerable investment in mine development before production begins. Further exploration near the deposit and further development drilling within the

deposit are done while the mining is ongoing. Typically on site as well as recovering the deposits by blasting, the ores are exposed to a series of processes that make concentrates. The operations include; the breaking of rock to facilitate the separation of ore minerals from waste typically by crushing and grinding (processing steps (Hayes, 1993) followed by enrichment of the ore by flotation of sedimentation.

2.1.2. Metal Ores:

Ore can be defined as a mineral or association of minerals that may be worked commercially for the extraction of one or more metals (Hayes, 1993). In addition, ore is a mixture of minerals one or more of which can be economically exploited to become a source of supply of a particular material. On the other hand, all metals that have no economical value to the process under consideration are referred to as gangue. Generally, several metals like gold, silver, platinum and copper could be found in any quantity in nature as pure metals. However, some of these could consist of very small particles dispersed in the surrounding rock. Other metal ores could contain a relatively high percentage of gangue materials and a relatively small percent of metals. For example, zinc mining sphalerite, ZnS, contains 67% gangue comparing to 10% or less of zinc after mining (Kuopanportti et al., 1997).

Each metal could be found and extracted in relatively high percentage compared to other metals in the same ore. Tables 2-1 to 2-7 present lists of ores for each metal (Dennis, 1965). Metals like cobalt do not exist in sufficient concentration in ores to make their extraction possible at an economic price. Nevertheless, their recovery as a by-product could be possible within reasonable cost. Cobalt is usually associated with other metals such as copper, lead and nickel.

Table 2-5 presents the type of ores that contain cobalt associated with copper and other metals. Gold and silver could be mainly found in native form or alloyed, more or less with each other. Gold could be associated with sulphides such as pyrite and aresenopyrite. Tables 2-6 and 2-7 present the type of ores for both gold and silver respectively.

Table 2-1: Copper ores

Ore Type	Ore Name	Chemical Structure
Sulphide ores	Chalcopyrite	$CuFeS_2$
	Chalcocite	Cu_2SCuS
	Covellite	$Cu_2S.CuS.Fe.S$
	Cuprite	Cu_2O
Oxidation ores	Carbonate Malachite	$CuCO_3.Cu(OH)_2$
	Azurite Sulphate	$2CuCO_3.Cu(OH)_2$
	Brochantite Silicate	$CuSO_4.3Cu(OH)_2$
	Chrysocolla	$CuSiO_3.2H2O$

Table 2-2: Zinc ores

Ore Type	Ore Name	Chemical Structure
Sulphide	Sphalerite	ZnS
	Calamine	$Zn(OH)_2.SiO_3$
Oxidation	Smithsonite	$ZnCO_3$
	Zincite	ZnO
	Marmatite	$(ZnFe)S$

Table 2-3: Tin ores

Ore Type	Ore Name	Chemical Structure
Sulphide	Stannite	$SnS_2.FeS.Cu_2S$
Oxide	Cassitrite	SnO_2

Table 2-4: Nickel ores

Ore Type	Ore Name	Chemical Structure
Sulphide	Pentlandite	$(FeNi)S$
Hydrous	Garnerite	$((NiMg)SiO_3.H_2O$

Table 2-5: Associated cobalt ores

Ore Type	Ore Name	Chemical Structure
Sulphide	Linnarite Carrollite	Co_3S_4 $CuCo_2S_4$
Arsenide	Smaltite Cobaltite	$CoAs_2$ $CoAsS$

Table 2-6: Associated gold ores

Ore Type	Ore Name	Chemical Structure
Combined ores (with Tellurides)	Calaverite Sylvanite	$AuTe_2$ $((AuAg)Te_2)$

Table 2-7: Associated silver ores

Ore Type	Ore Name	Chemical Structure
Sulphide	Argentite	Ag_2S
Chloride	Chloride	$AuCl$
Combined ores (with Tellurides)	Hessite Naumannite	Ag_2Fe $((AgPb)Se)$

2.1.3. The Physical Treatment of Ores for the Enrichment of Metals:

The quantity of metals in ores varies depending on the location from where the ore was obtained. Ores go through several treatments (physical or pre-treatment processes) before extracting metals from them.

The physical processing involves separation of mineral grains from an ore in order to recover particular minerals. This includes recovery of elements contained within those minerals and removal of unwanted materials from the mining feed. The process does not result in any change to the chemical properties of the individual phases present in the process streams. Physical processes can be performed in individual stages. These include: size reduction of the particles and selection of the desired

component from the mixture. These processes are energy intensive and the value of metal content determines the viability of these processes.

Of the enrichment processes used in metal recovery, flotation is one of the most widely employed techniques. This process has been shown to be effective in selecting the desired particles from ore mixtures. The desired particles move with gas bubbles to the surface of the liquid forming a froth (see figure 2-1). Both froth and the suspended particles are separated from the slurry by skimming the froth from the surface of the liquid. The mineral particles remaining in the slurry are then removed in a separate process, such as hydrometallurgical units. The low value gangue materials which do not attach to the bubbles, sediments and is discarded.
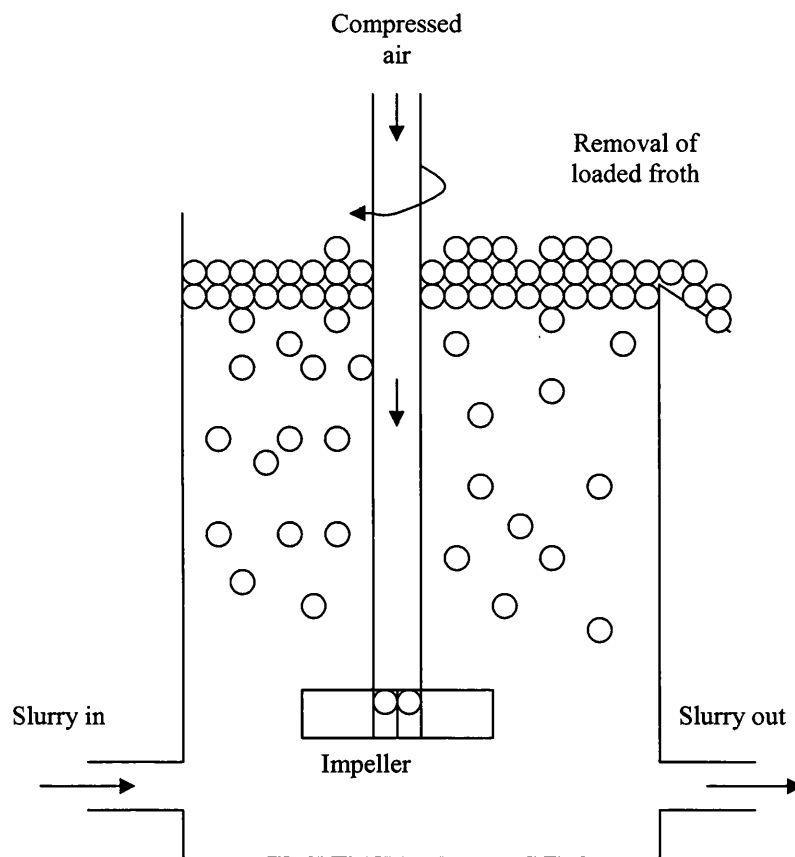
Figure 2-1: The flotation of mineral particles in a typical flotation cell

Generally, sulphide ores, which are the most common materials, are concentrated by flotation. Meanwhile, oxidized minerals could be floated with less recovery at certain concentration grades. It is also important to separate specific minerals from other mineral in the ore. Consequently, several reagents could be employed in order to achieve the task. There are specific kinds of reagents used during the flotation. The first types, which bind to undesired minerals in order to prevent them temporarily or permanently being floated, are called depressants. However, few minerals need depressants since they normally remain un-floated. There are other types of reagents called activators. These reagents behave opposite to depressants and are required to liberate the depressed minerals from the slurry in order to separate the minerals desired. The modifying agents are utilized to adjust the environment of the flotation processes. They act as pH regulators, controlling the alkalinity of the pulp and counteracting the interfering effects of negative substances and soluble salts. These agents affect the rate of floatation and should be used depending on the process requirements.

Fairthorne et al. (1997) conducted research to study the interaction performance of thionocarbamate, (O-isopropyl-N-ethyl thionocarbamate (IPETC) and O-isobutyl-N-ethoxycarbonyl thionocarbamate (IBECTC)) and thiourea, (butyl ethoxycarbonyl thiourea (BECTU)) reagents with sulphide minerals, chalcopyrite, pyrite and galena ores, in order to find out the most suitable and efficient selective agent, (or collector), for each ore. They used low conductivity water that is produced by reverse osmosis, two stages of ion exchange, high purity nitrogen and two stages of activated carbon prior to final filtration. Potassium chloride, (0.01 mol/dm^3 KCl), was used as a conditioner in their experiment and the mineral dispersion was transferred to a water-jacketed vessel and conditioned for 20 minutes in the presence of N_2 and at several pH values. The minerals then were passed through a modified microflotation Hallimond tube and floated with nitrogen gas. They concluded that the reagents are more selective for chalcopyrite than for galena and pyrite. In addition, the flotation using these collectors increases with the collector concentration and decreasing pH values.

Similar work has been published by Shen et al. (2001) who aimed to study the flotation mechanism of the flotation process of sphalerite and pyrite using sodium

sulfite as depressants. Moreover, the effect of sodium sulphite on copper activated pyrite flotation was documented in their paper alongside the separation of sphalerite in mildly alkaline conditions, (i.e. pH = 8.5), as it corresponds to the pH values used in the copper circuits. The work concluded that the separation of sphalerite from pyrite could be improved when adding sodium sulphite with oxygen as the conditioning gas. The authors also recommended adding xanthate immediately after sodium sulphite addition. The UV-visible infrared and XPS spectroscopy analysis employed in their study showed that the selective depression of the flotation of pyrite with sodium sulphite is the result of an increased oxidation of the pyrite surface, mainly as copper hydroxide which inhibits collector adsorption.

Further work conducted by Guang-yi et al. (2006) has compared the collecting performance of ethoxycarbonyl thionocarbamates, (ECTC), with dialkyl thionocarbamates and xanthates in order to separate copper sulphide minerals from iron sulphide minerals. The main copper bearing minerals were chalcopyrite, chalcocite, covellite, bornite and the main iron bearing minerals were pyrite and marcasite. The operating pH was 8.5. The experiment resulted in poor selectivity of xanthates due to its ability to react with metal cations on the surfaces of copper and iron sulfide minerals through forming normal covalent bonds. Dialkyl thionocarbamates were more selective for copper sulphide flotation, particularly against gangue iron sulphides. The interaction of ECTC for copper sulphide minerals and their selectivity against iron sulphide minerals showed better performance at the same time. This means this collector could be the best choice for floatation of copper ores.

Kelebek (1996) suggested the use of sulphur dioxide in combination with diethylnetriamine, (DETA), at moderate pH in order to depress pentlandite and pyrrhotite from pyrrhotite, pentlandite and chalcopyrite ores mixture. The last ore is believed to have a highly floatable nature and the authors were concerned with improving the separation process of chalcopyrite from the other two ores. This means no collectors are needed when separating this particular ore. However, the separation of the other two ores could be achieved with retreatment of tailings. This required more grinding since these minerals are intimately associated with each other. Collectors were also needed when splitting these ores from each other.

It can be concluded from the above literature that the success of flotation processes depends directly on the type of ores, depressors and conditioning reagents. The works of the above researches show some examples of how to manipulate and adjust the process conditions depending on the ore type and hence, the collectors employed. Clearly, an understanding of the colloidal properties of the particles and their interaction with these reagents is key for their selection and the conditions of application. Most of these researches run their experiments at a roughly similar pH value, which is within the range of 8-9. However, further work is required in order to standardise the above factors to suit a particular flotation system and suit the recovery of specific metal ores. Also, this kind of process involves the use of expensive complex components that might harm the environment.

2.2. Current Industrial Technologies for Metal Recovery by Reprocessing:

Most of the methods employed in this stage were invented during the mining revolution. After the physical process, minerals go to chemical treatments, where some change to the physical or chemical properties of the individual phases occurs. This could involve several operations that might lead to a high metal purity. However, some of these processes are not useful because they are not cost effective or have significant environment impacts.

In order to extract metals, two major types of techniques dominate chemical processes and these are smelting (thermal) and hydrometallurgy processes and these methods are used in the latest technologies either as individual stages or in combination. The broad concept of reprocessing of waste and consumed products can be applied to many situations in industry making the current processes safer and more viable. For example, the importance of recycling and reprocessing batteries and consumed electronic devices cannot now be ignored.

2.2.1. Smelting or Pyrometallurgical Processes:

Pyrometallurgical processes are smelting (or melting and separation), based processes employed to remove metals. The high temperature processing is widely used in the treatment of metals to achieve chemical and structural changes. Smelting processes are carried out using one of several types of furnaces, which are refractory structures designed to stand the effect of the heat released by the combustion of fuel

and the corrosive effects of slag and metals. These processes have high production rates and use massive amounts of energy. However, the high temperature process can cause major environmental problems that come from the gases evolved during the process, such as sulphur dioxides (SO_x), nitrogen oxides (NO_x), carbon dioxide (CO_2) and fine particulate solids. To avoid these problems expensive gas cleaning processes are required, with their efficiency depending on the size of the particles to be removed. Removing small particles increases the process capital and operating cost (Kuopanportti et al., 1997, Dennis, 1965). Also, high concentration of metal in ores is essential to smelt economically reducing financial and environmental costs. It is generally not suitable for treating ores with low metal concentrations.

The approach of a combined hydrometallurgy and pyrometallurgy process was proposed during 1990's in order to reduce the cost of the smelting process. Rabah (1998) published a paper explaining how pyrometallurgical treatment involves melting with a carbon/alkali borate flux at 1150-1300°C. This is done after utilization of hydrogen peroxide and ammonia as leachate solutions to dissolve copper and lead selectively. However, the process could still be costly and might increase the risk of producing toxic solutions.

2.2.2. Hydrometallurgy Processes:

This process is defined as the use of chemical treatment with aqueous and organic solutions where the majority of the processes rely on the chemical properties of the dissolved metals. The process involves the selective transfer of species in liquid/liquid and liquid/solid systems. These processes are generally more environmental friendly and less expensive than the smelting process. The hydrometallurgical treatment procedures of ores or other metal source is shown in figure 2-2 (Dennis, 1965).

Hydrometallurgical processes start from the process of leaching, which involves the extraction of a metal from a mineral or concentrate by means of a suitable solvent followed by the removal of the resulting solution from the unwanted material. It can be seen from figure 2-2 that the essential operation in leaching is only one in a series of operations, which could be formulated as follows (Dennis, 1965): preparation of ore involving crushing and grinding and/or roasting, leaching the metal from the ore,

separation of the metal solution from the gangue material and recovery of metal from solution.

Safarzadeh et al. (2007) presented a review of cadmium recovery from different resources, such as zinc and zinc-lead ores and Ni-Cd batteries, using different schemes of hydrometallurgical methods. They also outlined steps starting with leaching the media by sulphuric acid to dissolve metals, precipitating cadmium from solution by adding zinc powder and leaching cadmium from the mixture again using sulphuric acid. The solution obtained was then used as an electrolyte in an electrowinning cell.
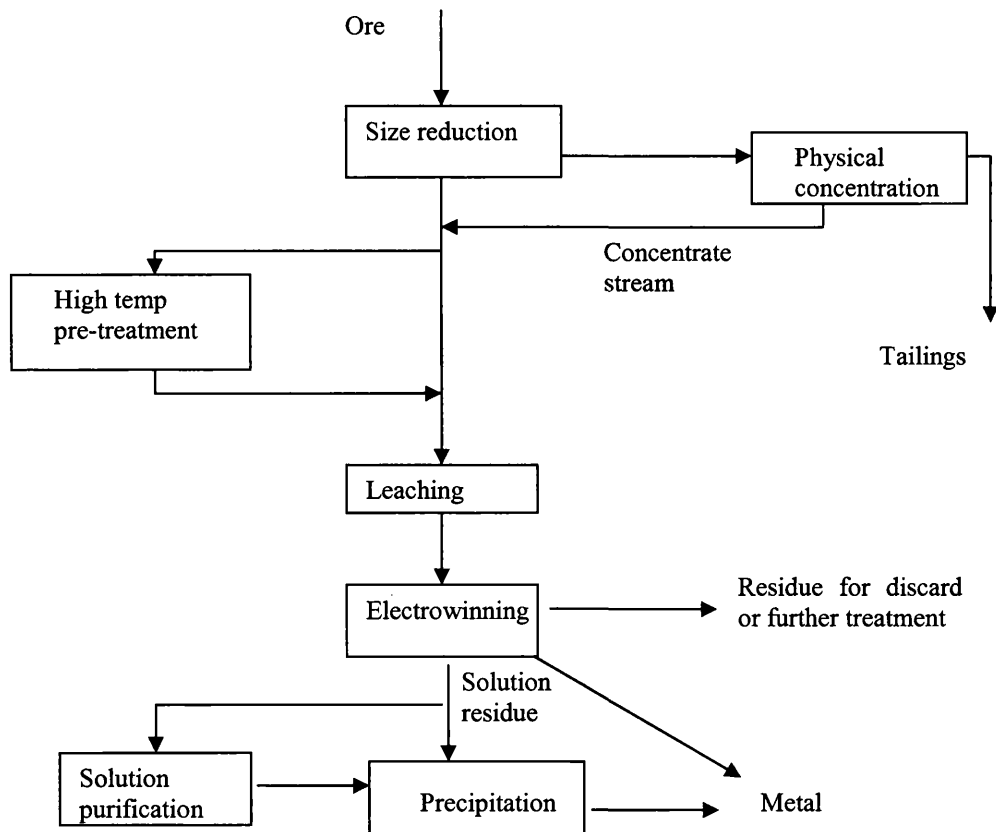
Figure 2-2: Typical sequence of processes undertaken in hydrometallurgical processing of ores.

The above procedures can be applied to different kinds of environments and materials that contain cadmium. Hydrometallurgy processes for recovering metals from their solutions after leaching were carried out using chemical precipitation, solvent extraction, ion exchange or ultrafiltration.

1) Chemical Precipitation:

Chemical precipitation involves the formation of an insoluble solid using a specific reagent. This process is not widely employed as the sole recovery method. The process of copper separation is carried out industrially in long canals filled with scrap via the following reaction:

$$CuSO_4 + Fe \leftrightarrow FeSO_4 + Cu$$

(2.1)
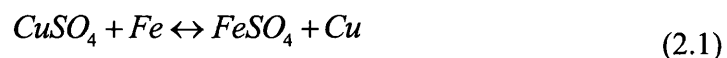
Reaction (2.1) can be slow and long treatment times are usually required before the final step of recovery of copper can take place. The purity of metal recovered by this method is low , i.e. ranging from 50 to 75 per cent (Dennis, 1965). In addition, the separation of these metals could be difficult by filtering and smelting the resultant precipitate.

Lee et al. (2006) studied chemical precipitation methods used to treat wastewaters containing heavy metals in Taiwan. They found that they could remove heavy metals from wastewaters efficiently but the resultant heavy metal sludge was classified as a hazardous solid waste creating another environmental problem. Safari and Bidhendi (2007) indicated that the effect of lime could increase the pH of the leachate in the mechanism for removal of zinc and magnesium metals by the metal precipitation.

2) Solvent Extraction:

Solvent extraction can be used to remove unwanted substances from a metal solution or to transfer the purified metal to an environment more suitable for isolation. This is based on the use of an immiscible solvent in which the component (metal or unwanted materials) is completely dissolved. The component can distribute itself between the appropriate organic solvent and aqueous media, depending on the relative solubility in the two phases.

It is important to select the correct solvent in order to extract a particular metal. Typically the solvent must have a high selectivity for that particular metal (Fairthorne et al., 1997). However, the presence of gangue materials is another issue which is important when considering the choice of the solvent.

Dilute sulphuric acid (H_2SO_4), is one of the most widely used solvents. This solvent is found to be efficient and is used extensively in the leaching of zinc, oxidised copper ores and cobalt. Ammonia at ordinary temperatures and pressure can also be used to recover copper from oxidised ores. On the other hand, the above solvent is employed at elevated temperatures and pressures for leaching copper-nickel-cobalt-ores. TBP (tri-*n*-butyl phosphate), LIX, (a hydroxyl-oxime complex chelating compound), and Cyanex, which are commercial sulphur-containing extractants, are widely used in solvent extraction for separation of various zinc metal ions.

The solvent can be non aqueous and contain additives that chelate with the metals, for example, Gilchrist (1989) stated that about 10-15% of chelate would be dissolved in kerosene. Sarangi et al. (2007) reported the separation of metal ions using solvent extraction for the separation of iron, copper and zinc ions present in the solution using TBP, LIX 841 and Cyanex 923. The recovery of iron from the leach liquor was conducted in two counter-current stages at equal phase ratios, (see figure 2-3).

The result of 0.004 kg/m^3 iron in the raffinate could be removed by stripping of the iron loaded organic phase with distilled water using TBP, LIX 841 and Cyanex 923 in kerosene. Hence, copper was separated from the Fe-free raffinate in three stages at Aqueous: Organic ratio of flows of 1:2. This could be achieved by using 70% LIX 841 in kerosene. Hence, zinc was separated from the Fe and Cu free raffinate using 0.05 M Cyanex 923 in kerosene at Aqueous: Organic ratio of 2:1. The quantitative stripping of iron loaded TBP, and zinc loaded Cyanex 923 were also carried out with distilled water, but stripping of the copper loaded LIX 841 was carried out with H_2SO_4 solution.

O unit volumes of solvent containing

O unit volumes of extract containing

O_{yn+1} grams solute from stage n+1

O_{vn} grams solute leaving stage n

Stage n

A unit volume of raffinate containing

A unit volume of feed containing

A_{xn} grams solute leaving stage n

A_{xn-1} grams solute from stage n-1
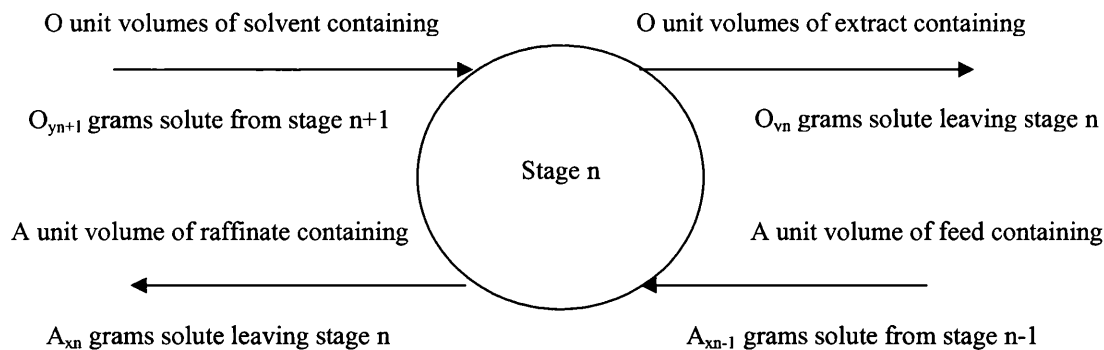
Figure 2-3: Continuous counter-current extraction circuit around stage n

Other work has been conducted by Kongolo et al. (2003) concerning the extraction of cobalt and zinc by simultaneous solvent extraction followed by their selective stripping from the organic phase. The method mainly consists of selective copper extraction with LIX 984, iron removal by precipitation with $CaCO_3$, simultaneous cobalt and zinc extraction with D2EHPA followed by their separation by selective stripping with H_2SO_4 of different concentrations. More than 95% copper has been recovered from the pregnant solution typically containing 1.0 g/L Co, 2.0 g/L Cu, 12.60 g/L Zn and 8.4 g/L Fe. Cobalt and zinc recoveries were on an average of 90% each in their respective individual solutions.

Alam et al. (1997) published a paper comparing the solvent extraction performance of SFI-6R, (dihexyl sulphide), MSP-8, (di (2-ethylhexyl) monothiophosphoric acid), Cyanex 302, (di (2,4,4_trimethylpentyl) monothiophosphinic acid) and Cyanex 301, (di (2,4,4-trimethylpentyl) dithiophosphinic acid) to recover silver from chloride media. The above solvents are found to be efficient because of the nature of silver as a soft acid. However, no further work concerns the performance of some of the above solvents when extracting other metals.

It can be seen from the above review that solvent extraction could be a good choice for the recovery of metals from many different environments. However, many potential hazardous solutions are produced and the cost of such reagents is relatively high.

3) Ion Exchange:

Ion exchange is a chemical characteristic of the metals and the ability to associate with organic counter ions. It is a suitable method for separation of low concentration of ionic materials from dilute rinse-water and minerals. The principles of the process are similar of solvent extraction but the non-aqueous phase is a solid substance of extensive surface area on which the metal can be collected via chemisorption processes or by ion exchange. Furthermore, the process of ion exchange can be outlined in three stages (Kuopanportti et al., 1997, Tzanetakis and Scott, 2004): the absorption stage, in which the metal ions in solution undergo exchange with ions of the same sign in the resin contained in a column, so that as the solution percolates down the column the resin becomes saturated and the solution becomes depleted in metal ions, removal of the retained ions in the resin by a suitable solution known as the eluate and washing of the resin free of eluate.

Agents employed in this method can be classified into natural inorganic and organic, such as clay, zeolites and ultramarines, and synthetic resins. Synthetic ion-exchange resins have long been used in commercial scale applications for the softening or demineralisation of water. However, such resins often suffer from a lack of selectivity. Therefore, many researches have been directed towards improving this selectivity. Another significant problem in the process is the kinetics of absorption where the diffusion of the metal often becomes limiting especially at low concentrations.

Simpson and Laurie (1999) studied the removal of zinc from zinc-rich industrial waste liquor and from model zinc-rich solutions using ion exchange resins chosen to cover a range of the different types available, i.e., strong and weak acid cation exchangers. The study recommended the use of ion exchange resins over solvent extraction in connection with zinc electrowinning since the removal of the carry-over of any organic reagents or impurities to the electrowinning cell is reduced down to an acceptable level. This approach came after a previous study of McLay and Reinhard (1996) who aimed to review the technologies employed in the metal finishing industry. They identified problems associated with operating ion exchangers in that it is difficult to separate recovered metal salts and excess re-generate acid in the plating bath.

The cation exchange process appears as the main mechanism responsible for Cd, Zn and Ni sorption. The use of zeolite sorbant depends on the controlled desorption characteristics. For example, Moreno et al. (2001) used a specific kind of synthetic zeolite, NaP1, generated from hydrothermal alkaline activation of fly ash from a power station of Teruel in Spain. The work concluded that each targeted metal was recovered under individual pH values in their experiment for each resin. The work concluded that precipitation of metal hydroxides is much more likely on synthetic zeolite than on natural zeolite. This is because natural zeolite tends to decompose irreversibly in acid solutions (Dennis, 1965). Consequently, the use of synthetic zeolite could be costly.

2.3. Selective Separation Techniques:

Several separation methods, such as physicochemical treatment, (i.e. flocculation, precipitation and filtration), ion exchange resins, vacuum evaporation, solvent extraction, electrowinning and membrane technologies, could achieve selective separation of a specific metal ion from a mixture, (see figure 2-4). The electrowinning process is considered to be the last unit in a complete system that recovers a high degree of purity of metals from waste streams (Simpson and Laurie, 1999).

Simpson and Laurie (1999) pointed out three key factors required for any separations developed to be commercially viable. First, the method should be robust enough to cope with variations in impurity ion levels between batches of waste liquor. Second, the separation process should produce the metal in a form that is commercially useful. Third, the overall process should be cost effective, taking into account the balance between the cost of recovery against the cost of conventional disposal and the market value of the recovered metal.

	Ultrafiltration
	Complex Polymer-metal
	Low cost

Selective Separation

Solvent extraction
More residue produced.
More expensive.
Involves many additives which are not disposable and must be treated.

Electrowinning
Widely used in the industry.
less cost required.

Ion exchange
Suitable for the metals recovery from wastewater.

Absorption
Used to treat mine ores.

Alkaline precipitation
Based on the separation of MOH from solution contain several metal ions.
Efficient method.

Cementation
Produces cemented waste that could be difficult to be treated.

Figure 2-4: Examples of the principle metal separation processes

This section presents some of the most efficient techniques involved in the recovery of heavy metals.

2.3.1. Electrometallurgy:

Electrochemical reactions are heterogeneous chemical processes involving transfer of charge to or from an electrode that could be metal or a semiconductor. Electrochemical processes for electrolytic recovery and refining of metals have been established for many years (Janssen and Koene, 2002, Juttner et al., 2000). Generally, these processes deal with the conversion of electrical energy into chemical energy (Kuopanportti et al., 1997). It is well known that in the extraction process the metal is plated from its solution onto the cathode, whereas the anode is an insoluble conductor. Electrolysis is maintained by simultaneous processes at the anode and cathode immersed in electrolyte and in contact via an external circuit, (see figure 2-5).
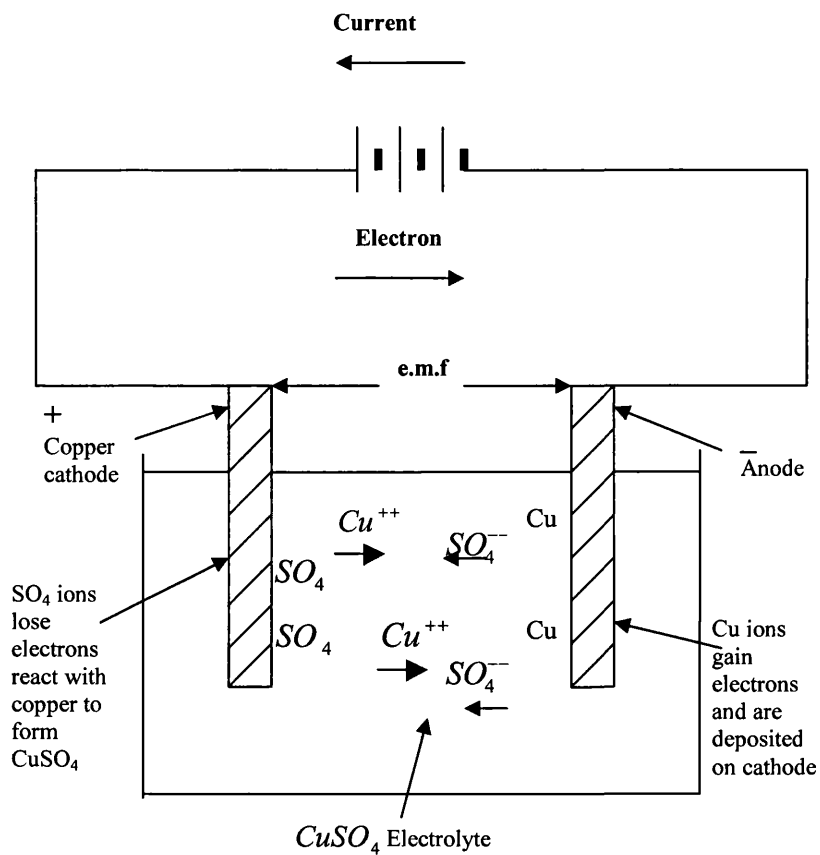
Figure 2-5: Electrowinning process of copper

Positively charged ions (cations) pass towards the cathode and cations take up electrons and become uncharged atoms. The non-metallic negatively charged ions (anions) go towards the anode and the anions lose electrons and become neutral radicals. Ions carry a number of charges equal to their chemical valance. An example of this process can be represented by the following electrochemical equations for the dissociation of a copper sulphate solution:

$$CuSO_4 \rightarrow Cu^{++} + SO_4^{2-} \tag{2.2}$$

$$SO_4^{2-} \rightarrow SO_4 + 2e \tag{2.3}$$

$$Cu^{++} + 2e \rightarrow Cu \tag{2.4}$$

Several authors described electrowinning units as open cells of concrete tanks linked with rubber or plastic (Kentish and Stevens, 2001, Kuopanportti et al., 1997, Dennis, 1965, Fornari and Abbruzzese, 1999). The lines of cathode and anode plates are placed alternately with separation spaces of 5 to 15 cm (Kuopanportti et al., 1997). It is important to use insoluble anodes and the compound of the targeted metal decomposes with the deposition of pure metal at the cathode. Operating conditions are dependent on the impurity content of the electrolyte.

2.3.1.1. Electrometallurgy Classification:

It is important to understand the principles of electrometallurgy as one of the technical approaches employed in metals recovery and processing in the industry. Figure 2-6 represents electrometallurgical methods and their procedures.

1. **Electrowinning** involves the extraction of metals by electrodeposition from aqueous solutions or melts of their salts. It is used for extraction of electronegative elements that cannot be electrodeposited from aqueous solutions, such as aluminium and magnesium, as well as pure copper, zinc and cadmium by electrodeposition from aqueous solutions of the metal salts (Pletcher, 1982).

2. **Electrorefining** is the purification of metals by electrolysis. The impure metals are dissolved anodically and pure metal is deposited cathodically, while the impurities are left as anode sludge or as ions in the solution. Many metals are electrorefined, such as copper because of conducting applications and precious metals because of their cost. Electrorefining is also a part of processes in recycling of metals. However, large electrolytic plants for metal production are heavy consumers of electric energy (Kentish and Stevens, 2001, Kuopanportti et al., 1997).

3. **Electroplating** is defined as a treatment that modifies the surface of a metal or occasionally a non-metal, without changing its bulk properties in order to improve the appearance of a surface, to decrease the corrosion and abrasion resistivity, etc. Metal objects are often electroplated. In addition, the most important application of electroplating technology is the manufacture of electronic components (circuit breakers and contacts). Electroplating can be

performed from molten salts, non-aqueous solutions but most frequently from aqueous solutions. The conditions depend on the nature of electrodeposited metal.
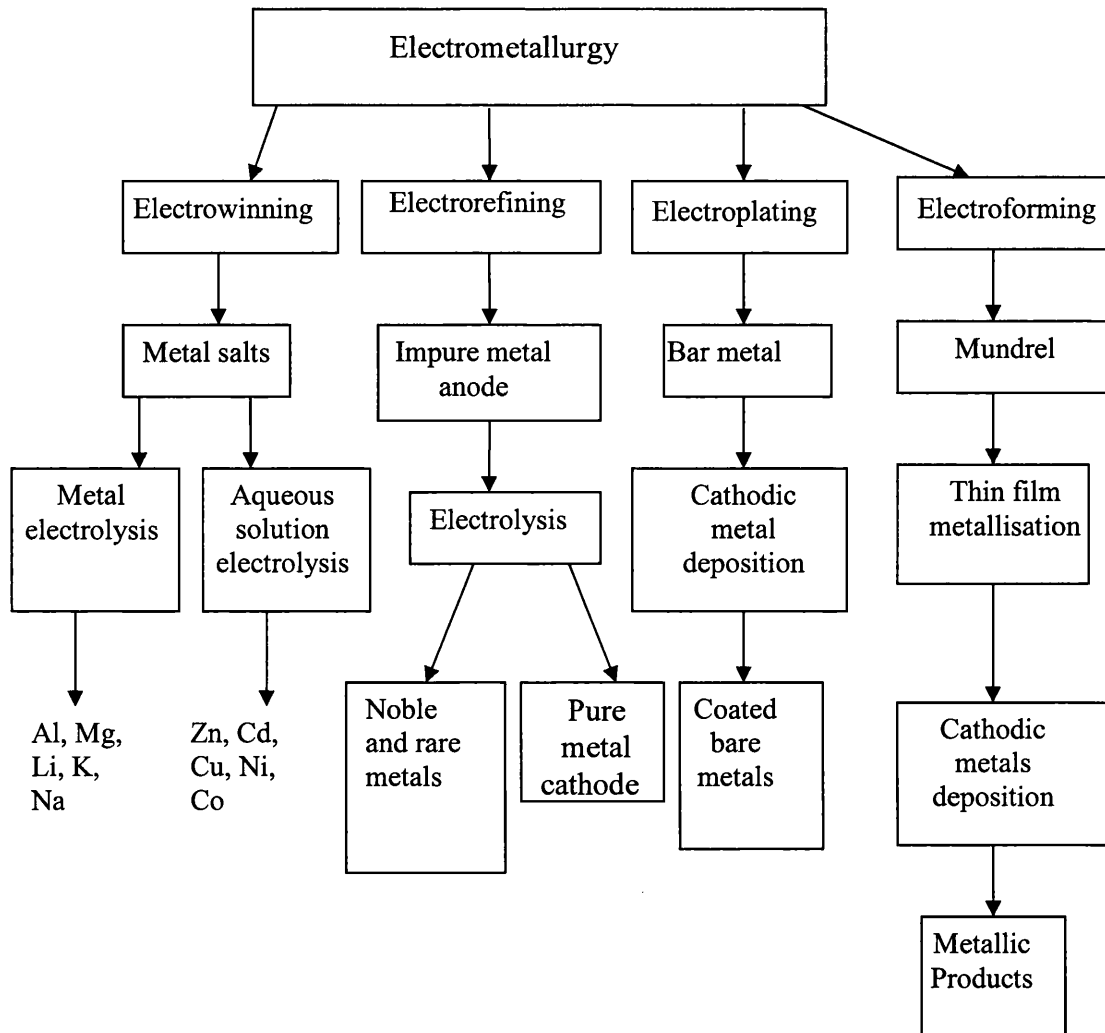
Figure 2-6: A classification electrometallurgy processes

4. **Electroforming** deals with the manufacture of articles by electrodeposition. If a deposit is good from the electroplating point of view except adhesion, and can be removed from the cathode as an entity in itself, it has been electroformed. Electroforming is a branch of electroplating technology, but involves some additional steps including aqueous solutions production, preparation and extraction of the desired metals.

The main requirements in metal electrorefining and electrowinning are to produce pure and compact deposits. This is typically done at lower current densities. Powder electrodeposition can also be treated as a kind of electrowinning or electrorefining, which produces the metal deposits in forms suitable for sintering and various different applications. Electrowinning methods are the main concern in this project and can be employed to achieve the purpose of the work. Therefore, it is required to understand more about the basic principles of the electrode reactions of the above methods.

2.3.1.2. Metal Recovery by Electrowinning:

Electrowinning has been addressed in the literature and widely employed industrially to treat solutions contaminated with metals, such as mining ores, electroplating processing, mine tailings and waste electronics. Pletcher (1982) described several electrochemical processes, which were employed in order to remove and recover heavy metals form dilute solutions within the range of 1 to 1000 ppm. The feed to these processes might result from different chemical operations such as plating or photography rinse water, etching processes, or mine workings. The author also recommended these processes since they have a major advantage in that the metal could be recovered in its most valuable form.

An example of this kind of cell was described by Pletcher (1982) as eco-cell process use and development. The process consists of a rotating cylindrical cathode surrounded by an anion exchange membrane and concentric anode. The cell is also designed with a high ratio of electrode surface area to catholyte volume. The cell design plus the use of conditions that are highly turbulent, which could be introduced by the rotation of the cathode, are important factors in order to achieve an acceptable rate of metal removal. A number of cells could be run in series in order to achieve complete stripping of the metal ion. However, the last few cells are inefficient and limited by the concentration of the metal and might only be responsible for the removal of 10% of the metal ions while costing the same as the first two cells to install and operate. This economically could result in a high capital investment and running cost.

Another type of cell also discussed by Pletcher (1982) is called the Chemelec cell. This cell is designed with a series of closely spaced gauzes or expanded metal

electrodes; alternating with beds of non-conducting beads separating the anode and cathode. This type of cell was designed in order to remove several metals from wash water and was developed in the electroplating industries. This cell exposes large surface areas to the solution; however, this unit is still not suitable for the treatment of solutions with very low concentration of metals because the electrical conversion efficiency is reduced at low concentrations.

Pletcher (1982) has also mentioned another approach in his book. A process based on the fluidised bed cathode that has been developed by the Akzo Zout Chemie Company. The cathode is employed as a turbulence promoter in this unit. The process is capable of maintaining high apparent current densities and rates of metal removal. This process has a high mechanical strength and resistance to chemical attack but a low hydrodynamic permeability and electrical resistance.

Pletcher (1982) emphasised that each application in table 2-8 requires different deposit thickness and characteristics hence a different bath formulation and electrolysis conditions. These could be temperature, electrical current, additives, and the type of application. However, this process could result in different kinds of inert electrolyte, which contains different types of heavy metals, although the amount of the metal content could be relatively small compared with other types of metals sources.

Many authors have considered the removal of metals from electroplating wastewater with respect to economic reviews using several techniques. Applications of electroplated metals are presented in table 2-8. Further improvements have been added on an electrowinning cell to improve its performance (Pickett, 1979).

Bolger and Szlag (2002) mentioned a problem associated with the production of hydrogen ions at the anode due to water electrolysis. Amara and Kerdjoudj (2002) gave a general view of the problem. They stated that some cations are able to be transferred freely when their mobility is high and, as a result, the cell becomes more ineffective because of competition between ions and the predominating flux of hydrogen ions.

Table 2-8: Some applications of electroplated metals (Pletcher, 1982).

Electrodeposited metal	Application
Tin	Protective coating for steel cans used for food packaging. Electrical contacts for soldering
Nickel	Protection and decoration of household items. Protection and repair of engineering components. Undercoat for Cr plating. Protection of chemical plant.
Copper	Contacts and circuitry in the electronics industry. Undercoat for Ni and Cr plating. Decoration of consumer goods.
Chromium	Decoration and protection of household items, car components, screw, etc. water-resistance surfaces in tools, machine parts and valves.
Cadmium and zinc	Corrosion protection of steel and iron base alloys
Silver and gold	Decoration, Mirrors and reflectors. Electrical contacts

Bolger and Szlag (2002) suggested two options in order to neutralise hydrogen ions. The first option is to pass the electrolysis solution through a weak base anion exchange column to replace the sulphate and chloride anions in the rinse water with hydroxide ions. However, Bolger and Szlag (2002) criticized this option in that it could bring more expense to the treatment when recovering base rinse water. Nevertheless, this idea has been reviewed by Szlag and Dilhoff (2000) who focused on the environmental and economic positive outcome of this technique. The above approach could be efficient when treating other metal rinses, such as gold and silver.

The second option involves the addition of either an anion exchange membrane, (AEM), or a cation exchange membrane; (CEM). This idea is becoming more popular in laboratory and industrial scales. McLay and Reinhard (1996) defined the ion exchange membrane as ion permeable and selective, permitting ions of a given electrical charge to pass through. Moreover, anion exchange membranes allow only anions, such as sulphates or chlorides, to pass through. Similarly, cation exchange membranes allow only cations, such as copper or aluminium, to pass through. Amara and Kerdjoudj (2002) introduced cathodic exchange membranes, CEM and anodic exchange membranes, AEM, to their experiments. CEM contains sulfonic acid

groups in a polymer matrix, and an AEM containing quaternary amine groups in a polymer matrix were used for the electrodialysis. Their work showed that a number of advantages, such as a good water solubility, high content of functional groups and chemical stability. Also, the electrodialysis process using membranes selective to monovalent ions was strongly recommended for the treatment of effluents containing nitrate or chloride ions.

Bolger and Szlag (2002) and Oztekin and Yazicigil (2006) suggested employing AEM as a second option in order to separate the cathode and the anode in the cell. The principle is to place nickel on the cathode and excess anions in the catholyte migrate across the anion exchange membrane to the anode compartment to maintain electro-neutrality. The authors summarised the benefit of this option in that dual electrode use could permit recovery of the metal from the rinse water at the cathode and generating an acid mixture at the anode that can be used in cleaning metal parts before plating. The above-modified cell is shown in figure 2-7. Amara and Kerdjoudj (2002) supported the above approach in that neutralisation of effluents and concentration of acids in the concentrate compartment may be achieved completely by electrodialysis when the current density is high (using a low resistance membrane) and the experiment duration is long.

Oztekin and Yazicigil (2006) compared the electrodeposition method performance with other methods conducted by Johnson et al. (1972) and concluded that chelating agents could be oxidised into many components. This makes the traditional hydrometallurgical methods less efficient in order to separate metals from chelating agents. Consequently, there was a need to employ CEM membrane for better recovery.

Watts nickel
rinse water
out

Anolyte out

Membrane,
AEM/CEM

H_3BO_3

Ni^{++}

SO_4^-

SO_4^-

$O_2 + 4H^+$

Cl^-

Cl^-

Ni

$2H_2O$

Anode

Cathode

Anolyte in

Watts nickel
rinse water in
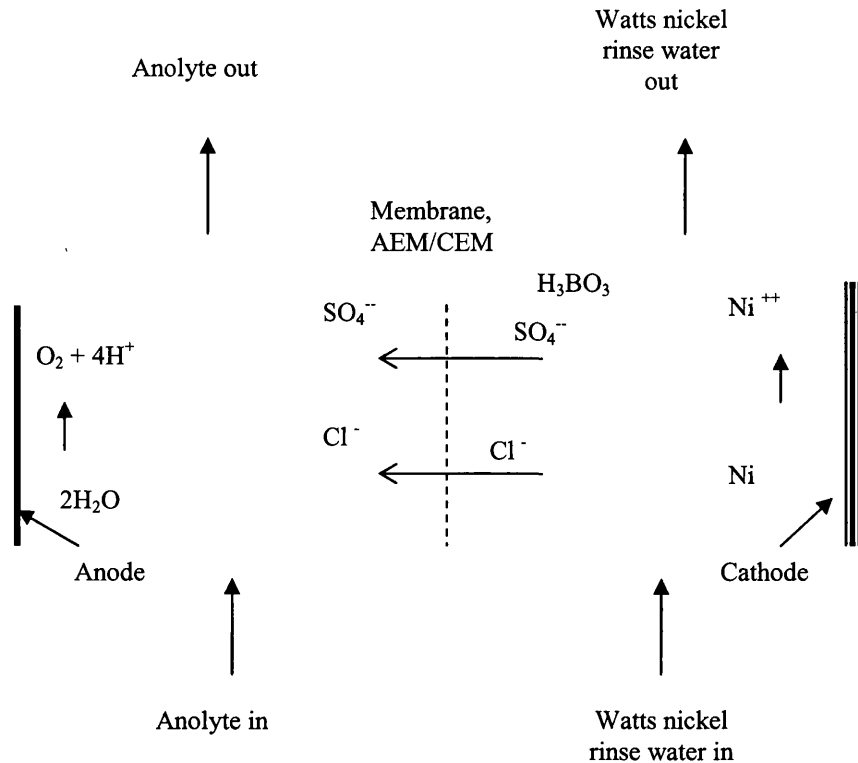
Figure 2-7: Process treatment of watts nickel using AEM/CEM electrowinning/electrodialysis cell

Lemos et al. (2006) found out that CEM membrane could be used to avoid the anodic oxidation of the cyanide ions released during cathodic reduction of the copper or gold cyanide complexes. In addition, Lemos et al. (2006) conducted several electrowinning tests with copper in a flow-by cell with a reticulated vitreous carbon, RVC, cathode separated from the anode by a cation exchange membrane. They concluded that the above approach could give a recovery of 99.6% of copper with the liberation of 99.4% of the cyanide as free ions for recycling. However, the low current efficiency applied caused an increase in resistivity of the RVC cathode, which promotes an uneven current distribution throughout the cathode thickness. This would lead to a dramatic increase in energy consumption. Stavart et al. (1999) emphasized the importance of the nature of the separator between the anodic and cathodic compartments and that it has to be optimised when the process requires it. Cifuentes and Simpson (2005) stated that the use of anion membranes was a good option to permit the separation of a ferric anolyte, which is generated when using

graphite bar anodes that could transfer the ferrous to ferric ion reaction, from a copper electrowinning type catholyte. This means that this kind of membrane might perform better when separating ferric ions from other non-ferric once.

According to McLay and Reinhard (1996) and Amara and Kerdjoudj (2002) the advantages of the above option are: low energy consumption, the ability to produce a highly concentrated stream for recovery and the ability to recover only ionic materials. This means all the undesired impurities could be retreated and rejected.

Although, the above technology could dramatically improve the efficiency of electrowinning cell, this kind of separation requires a clean feed, careful operation and periodic maintenance, in addition to the energy consumed.

2.3.1.3. Cell Components and Design:

Generally, an electrochemical circuit consists of a current source, metallic connecting wires, an electrochemical cell, current and voltage measuring instruments and a circuit breaker. A steady current flow in such a circuit can only be maintained if there is a change of charge carrier at the metal-electrolyte interfaces by a chemical transformation involving the transfer of electrons across these interfaces.

There are several rules to be followed when designing a cell. These can be listed as follows (Greef et al., 1985):

1. The process should meet the requirements in the simplest and cheapest way possible. Therefore, all kind of separators, solution flow and stirring should be minimised.

2. The unit must operable alongside other operations, such as leaching.

3. In case of the need to employ electrolyte flow or stirring, it is recommended to consider the transport regime at the early stages of design.

4. The potential distribution over the electrode surface should be uniform. This can be achieved by simple electrode geometry.

5. The cell should have only a small gap between the cathode and anode.

6. The material of construction in the cell should be compatible with the electrolyte and the products.

It should be pointed out that the selection of the cell type depends on metal in the feed, the form of the product and the level of purity required. Once this specification has been established, the characterisation of both the electrolytes and electrode could be specified (De Francesco and Costamagna, 2004). This of course is accompanied by specifying the cell design limitations.

1. Electrolysis:

Electrolysis can be defined as the conductors that allows the passage of a current, which is accompanied by a simultaneous migration of material. Conduction in electrolytes is driven by elementary electronic charges, (electrons) that move and give rise to the electric current. Several parameters affect electrolysis (Pak et al., 2001). These are:

- **Electrode potential:** This determines the absolute rate of electron transfer reactions and its type.

- **Electrode material and structure:** The electrode material should be totally stable in the electrolysis medium but allow the desired reaction with high current efficiency at low overpotential.

- **The concentration of electroactive species:** This is another major factor that determines the maximum feasible current density and optimum time yield. In other words, the higher the concentration is, the more the current density obtained.

- **Type of electrolysis medium:** This parameter is related to the choice of solvent, electrolytes and pH and complexing agents and other additives.

- **Temperature and pressure:** It is desired to operate an electrochemical cell under atmospheric pressure. In addition, it is not recommended to vary the pressure (Kargl-Simard et al., 2003). On the other hand, the effect of temperature can have a significant influence on the performance of the cell as diffusion and reactivity are temperature depend.

- **Mass transport regimes:** The transport of materials within the electrolyte medium are involved including both diffusion and convection and can vary from unstirred to high turbulent conditions, produced by rapid stirring and pumping. However, all forms of pumping and stirring will add more cost and complexity to the system and produce problems of interaction of the anode and cathode product

- **Cell design:** The factors described above all effect the electrolytic performance and hence the design of the cell. These are reflected in how the presence or absence of a separator and its type, the mass transport regime, the arrangement of electrodes and the anode-cathode gap, the potential distribution at both electrodes and the materials of construction are chosen.

The above parameters should be considered when designing any kind of electrochemical cell at experimental or industrial scale. Each parameter has a different way to be defined and/or estimated.

2. Electrodes:

Electrodes can be defined as the metallic end of external circuit and are immersed in the electrolytes. Ions which are material carriers of the electrical charges could be divided into cations which are positively charged and migrating towards the cathode, the negatively charged electrode and anions which are negatively charged and migrating towards the anode, the positively charged electrode.

The most common electrode materials used in the real world of electrometallurgy is presented in table 2-9 (Pletcher, 1982). Electrodes also could take different geometries, i.e. flat plate, rotating cylinder, low- and high-porosity three-dimensional materials (Panzer and Elving, 1972, Panic et al., 2006b). It is known that electrode materials may be involved in the electrochemical reactions. The materials could be consumed or deposited from the solution or they may remain inert to provide an interface at which the reduction/oxidation may occur. To minimise potential problems here, the power applied to and consumed by the process has to be carefully controlled (Panic et al., 1999). To achieve this, electrodes should have several properties of a good electrical conductor material, that is: have low activation overpotential at the electrode; have high exchange current density for the produced

species; the electrodes should be passive during cell operation, i.e. it should not react to form any compound that could reduce the efficiency of the cell on the electrode surface; be easily manufactured, resistant to corrosion by elements in the cell, have good dimensional stability, strength and be low cost.

The choice of the anodes for the direct processes is complex since the reaction mechanism is strongly dependent on the electrode properties. In the non-selective scheme, where electrodes are prepared by the heating of metal plates, it is require that the oxygen transition is slower than hydroxyl production. These anodes should not have oxygen vacancies (i.e. a high oxidation level or oxygen excess, also in combination with doping with other metals); on the contrary, the presence of oxygen vacancies is preferable for the anodes for the selective process. For these reasons tin oxide (SnO_2) shows a non selective behaviour and platinum and titanium coated with IrO_2 are selective electrodes (Kentish and Stevens, 2001, Doulakas et al., 2000, Armelao et al., 2003, Panic et al., 2006a).

Table 2-9: Electrode materials

Cathodes	Anodes
Hg, Pb, Cu, Ni	Pt, Pt/Ti, Ir/Ti
Graphite and other forms of C sometimes treated thermally or with organics to modify porosity, density, and corrosion resistance.	Graphite or other forms of C
Steels	Ni in alkaline media
Coating of low hydrogen overpotential materials on steel (Ni, Ni/Al, Ni/Zn)	Dimensionally stable anode (RuO_2 on Ti) Oxide coating ($CuxCO_3$-xO_4, Iro_2 on Ti) Magnetite Fe_3O_4

2.3.1.4. The Nature of Electrochemical Reactions:

The oxidant and reductant in electrolyte solutions reach the electrodes via one of three mass transfer processes (Koene and Janssen, 2001, Crow, 1988, Milazzo, 1962):

- **Migration:** This process occurs due to electrical charges of the species. It involves the movement of cations and anions through the solution under the

influence of an applied potential between two or more electrodes placed in that solution.

- **Diffusion:** Where an electrode reaction decreases the concentration of oxidant or reductant at an electrode surface and produces a concentration gradient on the surface. This process occurs for both charged and uncharged species.

- **Convection:** This involves the movement of the fluid by thermal and stirring equipment.

When the metal ions in the solution are the same type as in the electrode metal lattice and electron transfer reaction can occur at metal electrolyte interface and lead to the generation of a potential difference. The electron transfer takes place until the process reaches a dynamic equilibrium state. The above process starts with either the deposition of ions from solution onto the metal electrode, (where the electrode is more positive than the solution at equilibrium), or with the dissolution of the metal electrode, (where the electrode is more negative than the solution at equilibrium).

The nature of electrode reaction can be explained by considering two completely stable and soluble species, O, (the oxidized state that accepts n electrons), and R, (the reduction state or the donor of electrons), in an electrolyte medium containing an excess of electrolyte which is electroinactive. The following reaction could occur:

$$O + ne \rightarrow R \qquad (2.5)$$

It is required to maintain a current in order to supply reactant to and remove the product from the electrode surface and for the electron transfer reaction at the surface to occur. Therefore, the above electrode reaction could be carried out in three steps:

$$O_{bulk} \xrightarrow{\ MassTransfer\ } O_{electrode} \qquad (2.5a)$$

$$O_{electrode} \xrightarrow{\ ElectronTransfer\ } R_{electrode} \qquad (2.5b)$$

$$R_{electrode} \xrightarrow{\ MassTransfer\ } R_{bulk} \qquad (2.5c)$$
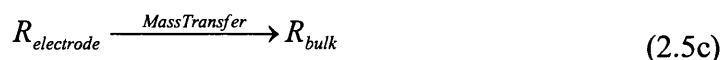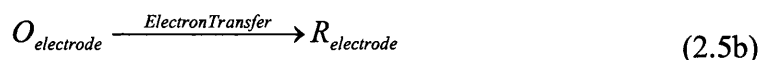
In addition, it is important to point out that the rate of reduction and/or cathodic current could be determined by the rate of overall reaction, which depends on the rate of the slowest step of the process.

Meanwhile, electrode reactions could involve multiple electron transfer by three other steps. These steps are:

- **Chemical Reactions:** The species resulting from the electron transfer step are not stable in the electrolysis medium since they act as an intermediate in order to cause chemical change. Two possible types of reactions could occur, homogeneous processes where species R is transported away from the surface and heterogeneous processes where R is adsorbed on the surface.

- **Adsorption:** This process is considered to be very important in electrode reactions. It is responsible for the success of electrochemical processes. In electrocatalysis, such as platinum, Pt, adsorption of intermediates on the surface could provide alternative lower energy pathways.

- **Phase Formation:** Electrowinning processes involve the formation of a new phase. This step requires both nucleation and subsequent growth, where as crystal growth could involve surface diffusion and lattice growth.

The reversible electrode potential of a reaction at equilibrium state can be described mathematically using Nernst equation. For reaction (2.5), the Nernst equation can be written as (Farrington and Daniels, 1979):

$$E_{O/R} = E^{\theta}_{O/R} + \frac{RT}{nF} \ln \frac{a_O}{a_R}$$

(2.6)

where $E_{O/R}$ is the equilibrium electrode potential, $E^{\theta}_{O/R}$ is the standard electrode potential, a_O, a_R are the activities of the electron acceptor and donor respectively, T is bath temperature, F is Faraday's number, (96500 A/s), n is number of electrons transferred in the cell reaction and R is the gas constant.

According to equation (2.6), when the cell is connected to a high impedance voltmeter, the equilibrium concentration of elements in the more negative electrode

will be larger than it is in the more positive one. On the other hand, if the cell is connected with a low impedance ampero-meter, the oxidation process will take place on the more negative electrode and the reduction process will occur on the more positive electrode and become an electron source. This transformation at the two interfaces provides electrons available for external use. This results in a complete removal of positive ions.

The reversible reduction potential calculated form the Nernst equation assumes each electrode to be in equilibrium with its local environment. In addition, the Nernst equation states that it should be possible to decrease metal ion concentration in solution to an arbitrarily low level, if the potential, E, of the metal/metal ion electrode is maintained sufficiently negative with respect to the standard potential. However, the equation does not provide any information regarding the reaction rate in the cell.

2.3.1.5. Electrowinning Process Conditions:

The performance of the electrowinning process has been the subject of much research (Szpyrkowicz et al., 2005, Szpyrkowicz et al., 2000) and includes the improvements of electrowinning cell design and operating conditions. For instance, it has been reported that the purity of copper could reach around 99.5% when the electrolyte temperature is between 40 to 60 degrees, current density of 15 to 150 mA/cm^2, (the intensity of electrolysis current over the electrode surface area), cell voltage of -1.9 to -2.5 V and at a current efficiency of 80 to 96% (Kuopanportti et al., 1997). However, the conditions can be changed depending on metal type, the degree of purity and the recovery required. Also, other conditions, such as type of electrolyte solution, its pH (acidic or alkaline), for acid or alkali type, initial concentration of metals, type of anode and cathode materials and the process kinetics have been involved in studying the performance of this process.

Ramachandran et al. (2004) explored the process of zinc recovery from zinc ash using an iridium oxide, IrO_2 catalytic anode. The performance of both an IrO_2 catalytic anode and traditional lead anode where compared in their work. Ramachandran et al. (2004) stated that zinc ash contained a large amount of chloride, (around 3.0 g/L) which could result in heavy contamination of the zinc sulphate solution with chloride ions and would affect the traditional lead anode during the

electrowinning process. Consequently, the authors demonstrated the high performance of an IrO_2 catalytic anode in that this anode can resist the attack of chlorine and oxygen evolved as a part of anodic reaction. However, their work did not consider the effect associated with hydrogen liberated as a side reaction. This might cause problems regarding the morphology and reduce the recovery percentage of zinc.

Another interesting work by Sharma et al. (2005) concerned the recovery of cobalt, from its sulphate solution by electrowinning. They studied the effect of hydrogen generated on the process variables. They stated that when the pH of the electrolyte drops, the Co strength of the electrolyte will be depleted. Sharma et al. (2005) suggested a method called restoring pH, in order to regenerate the bath with respect to the pH and Co concentration. This could be done by adding cobalt hydroxide, $Co(OH)_2$. However, other side reactions, such as the generation of Co^{3+}, could occur:

$$Co^{2+} \rightarrow Co^{3+} + e^-$$

(2.7)

This problem has also been pointed out by Lakshminarayanan et al. (1976) and Pradhan et al. (2001) who stated that most of the Co^{3+} ions could deposit at the anode as a black oxide or hydroxide powder which is hard to ignore once they reached the cathode as it affects electrode performance. Despite this, Sharma et al. (2005) recommended neglecting the above reaction because the amount of Co deposited at the anode was only a small fraction of Co deposited at the cathode.

Based on the above discussion, the effect of metal ions concentration, amount of additives, temperature, pH, and cathode current density on metal recovery from synthetic solutions is addressed in this review.

1.   Effect of Initial Metal Concentration:

Several papers have been concerned with the effect of metals concentration on the efficiency of electrowinning cell. Sharma et al. (2005) started their study by varying the cobalt concentration, (from 20 g/L up to 70 g/L), at a sodium sulphate concentration of 15 g/L, temperature of 60°C, pH4, and current density of 400 Am/m^2 during acidic electrowinning. The experiment showed that increasing the initial cobalt concentration could increase the current efficiency and decrease the

energy required for the deposition. This is due to higher conductivity, improved transport phenomena within the metal solutions and competition at the electrodes. However, at low concentrations of cobalt less deposition of cobalt due to a high hydrogen ion evolution rate resulted.

Similar results were also achieved by previous work conducted by Elsherief (2003) who concluded that the cathodic efficiency of cobalt deposition from solutions containing cobalt was increased when the initial concentration increased. In addition, current efficiency increased from 94% to 97% with increased cobalt concentration (60 g/l at 20°C). Elsherief (2003) gave more explanation in that as the cobalt concentration is increased, the area covered by the anodic curve is increased, and the charge related to anodic stripping is increased. Oztekin and Yazicigil (2006) concluded the same and added that the recovery efficiency of the process could also vary depending on the type of targeted metal.

Holm and O'Keefe (2000) aimed to determine the effects initial nickel concentration on the current efficiency. Nickel concentration was varied from 20 to 60 g/l for an electrolyte containing 150 g/l sodium sulphate at constant pH 2.5 at 40°C. The work reported poorer deposit quality when the nickel concentration was 20 g/l compared to the deposit from 60 g/l Ni electrolyte.

It can be seen from the above review that increasing the metals initial concentrations could increase the performance of the electrowinning cell. However, it is still required to introduce other approaches in order to recover metals that exist at low concentrations. McLay and Reinhard (1996) suggested two options in order to reduce the effect of electrode polarization. First, by adding heat to the process, but this is not recommended because it could increase the cost of the process. The second option could be performed by delaying plate-out of metal from these low concentration solutions. This could be done alongside strong air agitation to provide adequate mechanical mixing. However, McLay and Reinhard (1996) again criticised this option because it could remove heat from the system, thus reducing operating rates. Air agitation may also add to the load on air pollution control equipment.

2.   Effect of Temperature:

Many papers have emphasised the effect of bath temperature on the performance of an electrowinning cell. Work has been conducted by Fratesi et al. (1997) to study the deposition of Zn-Co alloys from a chloride bath. They found out that an increase in temperature caused a dramatic decrease in the cobalt amount recovered when applying high current density. According to the results achieved by Elsherief (2003), increasing the electrolyte temperature should enhance the deposition reaction but the author also found out that the hydrogen evolution reaction occurs more readily at higher temperature. This supported the conclusions of Fratesi et al. (1997). Holm and O'Keefe (2000) concluded that higher temperature has the most impact on the quality of nickel deposition when maintaining solution pH and nickel concentration.

Sharma et al. (2005) obtained similar results when increasing the temperature from 27 to 70°C under constant electrolyte composition of 60 g/L cobalt and 15 g/L sodium sulphate. They found out that higher temperature up to certain point provided a higher quality and more adherent deposition. At high temperature, high current efficiency may also be due to increased ionic mobility. However, the researchers emphasised on the fact that optimum temperature should be specified as detachment of the deposit occurs at very high temperature.

Most of the above mentioned work recommends that the optimum temperature should be within the range of 50-60°C for high quality deposition.

Another work conducted by Cifuentes and Simpson (2005) reviews the effect of temperature on several kinetic parameters for the copper electrowinning reaction. They present two equations derived in order to estimate the relationship between current densities of both cathodic and anodic reactions:

$$|i_c| = \frac{i_{0c}\,|i_{Lc}|}{i_{0c} + |i_{Lc}|\exp(\dfrac{\alpha_c F}{RT}\eta_c)}$$

(2.8)

$$|i_a| = \frac{i_{0a}\,|i_{La}|}{i_{0a} + |i_{La}|\exp(\dfrac{\alpha_a F}{RT}\eta_a)}$$

(2.9)

where i_{0c}, i_{0a} are cathodic and anodic exchange current densities, A/m^2, i_{Lc}, i_{La} are cathodic and anodic limiting current densities, A/m^2, α_c, α_a are cathodic and anodic charge transfer coefficients, η_c, η_a are cathodic and anodic overpotentials, Volt, F is the Faraday's constant, 96,500 C/eq, R is the gas constant, 8.314 J/mol K and T is temperature, K.

The equations above show that both the exchange current density for the Cu^{2+}/Cu^0 reaction and the limiting current density for the Cu^{2+}/Cu^0 reaction both increase by increasing the temperature. However, the charge transfer coefficient for the Cu^{2+}/Cu^0 reaction does not significantly change with temperature. The authors recommended employing a temperature-dependent mathematical model derived in their work for the operation of the electrowinning processes in order to study the temperature effects on electrowinning. However, further work is required to study the effect of temperature on the recovery of other metals, such as cobalt and nickel.

3.   Effect of Electrolyte pH and Electrolyte Type:

The type and pH of the electrolyte employed in the electrowinning method can have an important effect on the process. The study of the effect of pH is important in conjunction with the initial concentration of metal(s) in the electrolyte. Furthermore, the type of electrolyte plays an important role when the initial concentration of metal is very low. Other reasons, such as hydrogen generation, which could effect on the recovery performance, are also important to consider in this study.

Many papers have considered the behaviour of electrolyte solution and the effect of its pH during the recovery process. Sharma et al. (2005) studied the effect of pH on the current efficiency of the unit, by varying the value of pH from 2 to 5. Therefore, their work concluded that when pH was increased, the efficiency increased. However, the efficiency of the unit stabilised when the pH value was between 3 and 4 but when the pH was greater than 5, the efficiency dropped to the minimum value. Hence, at lower pH value, the higher hydrogen ions concentration could reduce the current efficiency of the unit. This was confirmed by Fornari and Abbruzzese (1999) who stated that decreasing of pH could also increase energy consumption for unit weight of metal by more than 3.4%. When the pH was greater than 5, a small amount of hydrogen ions were discharged at the cathode (Sharma et al., 2005). This caused

the production of metal hydroxide which could result in very poor quality plating. Similar results were also achieved by Casas et al. (2000) who referred to the fact that in sulphuric acid solutions, mainly copper sulphate complexes were generated. This complex is more stable than copper hydroxide. Fratesi et al. (1997) agreed with the fact that increasing pH value could result in the formation and precipitation of nickel hydroxide on the cathode, which decreases the current efficiency.

Lupi and Pasquali,(2003) found that the optimum electrolyte pH was within the range of 3 - 3.2. The authors also stated that pH could be more effective at lower current densities. Jeffrey et al. (2000a) and Bolger and Szlag (2002) recommended the same. Jeffrey et al. (2000a) stated that when increasing pH; the current efficiency could be increased due to both the enhancement of cobalt deposition and the reduction in hydrogen evolution. However, the pH of the solution cannot be increased too much, as the solution resistance becomes high.

Tsuru et al. (2002), Yin and Lin (1996) and Lupi and Pilone (2001) recommended the use of boric acid and ammonium sulphate as a buffer to control electrolyte pH. They found that the pH adjacent to the plating metal surface was maintained at a value close to that in the bulk solution, so that the deleterious effects of hydrogen co-deposited during electroplating on the development of high internal stresses in the resulting nickel films are greatly reduced. However, Ji et al. (1995) criticised this approach in that other components may be formed and could interrupt the metal deposition reaction.

4. Effect of Current Density:

Many electrowinning processes are run under the galvanostatic scheme, (under constant current density). Faraday's law is used in calculating current density for the deposition process. The mathematical formula of the law is:

$$I = \frac{nF}{AM} \frac{dm}{dt}$$

(2.10)

where n is the number of moles of electrons transfer per mole of metal deposited, F is faraday's number, (96500 A/sec), M is atomic mass of the metal deposited, A is surface area, dm is the change of electrode mass and dt is time difference.

The current density calculated could be employed in the design of an electrowinning cell. However, it is difficult to estimate the real amount of metal deposited particularly when other side reaction, such as evolution of hydrogen and chlorine gases, occurs.

Sharma et al. (2005) found out that the effect of varying current density could be clearly apparent when recovering cobalt. The percentage recovery of cobalt under certain fixed experiment parameters was increased when increasing the current density up to certain value, however, beyond this value; the efficiency decreased due to the generation of hydrogen gas. Elsherief (2003) concluded that hydrogen evolution could cause a loss of useful current density. Hence, he suggested maintaining the pH at 4 to solve this problem. Also, Amara and Kerdjoudj (2002) pointed out that decreasing the pH could decrease the current density. This could decrease the efficiency of the process. Consequently, there is a need to use other methods, such as adding boric acid as a buffer in order to control pH without affecting the optimum current density. Oztekin and Yazicigil (2006) found in their study that increasing the current density at different pH values could increase the copper recovery. In addition, current density could have an effect on the structure of metal deposition. This supports a previous study conducted by Fratesi et al. (1997) whom concluded that increasing current density might give more uniform structure to the targeted metal.

Jeffrey et al. (2000a) suggested the use of a rotating electrochemical quartz crystal microbalance, (REQCM), which has been highly recommended in previous work conducted by Jeffrey et al. (2000b) in order to distinguish the current density, which is due to metal deposition and hydrogen evolution since, hydrogen evolution often occurs simultaneously with the deposition reaction during metal deposition. The above device was employed to evaluate the electrode mass change at several intervals. Jeffrey et al. (2000b) stated in his paper that REQCM could also achieve good results when removing copper from cyanide solutions. However, the above process could be complicated by the fact that there are several possible discharging species, including $CuCN$, $Cu(CN)^{-2}$, $Cu(CN)_2^{-3}$ and $Cu(CN)_3^{-4}$ that might reduce the cell efficiency Moreover, the equilibrium of these possible dischargeable species in the diffusion layer may be different from that of the bulk solution.

5.   Effect of Impurities and Other Chemical Additives:

The effect of the presence of common plant impurities, such as nickel, copper, iron, lead and zinc, has been the concern of many researchers. Jeffrey et al. (2000a) studied the effect of zinc presence on the cobalt deposition process. They found that when the zinc concentration exceeded 10 ppm, the current density increased. Also the amount of hydrogen evolved decreased. Jeffrey et al. (2000a) described the presence of zinc as a co-deposited metal with copper since this leads to suppression of hydrogen evolution. However, further increase in zinc concentration hindered cobalt deposition. The same conclusion was made by Fratesi et al. (1997) when recovering cobalt from a zinc-cobalt alloy.

Elsherief (2003) also studied the effect of zinc, copper and iron on cobalt recovery. He made a similar conclusion stated by Jeffrey et al. (2000a) regarding the presence of zinc in that it interferes with the purity and efficiency of the recovery process. Moreover, Elsherief (2003) also found that increasing the copper amount increases the efficiency of the deposition with no apparent copper concentration limitation. On the other hand, it was recommended to remove iron from deposited solution since it reduced the current efficiency of the cell and increased hydrogen evolution. The effect of chemical additives on metal deposition has also been studied in the literature. Jeffrey et al. (2000a) used boric acid and sodium lauryl sulphate, (SLS), in his study. Both substances are found to reduce hydrogen evolution at low current density. However, increasing current density could result in less electrowinning potential and less efficiency when these additives are present (Tsuru et al., 2002, Fratesi et al., 1997).

Other chelating additives like citrate, nitrilotriacetic acid, (NTA) and ethylenediaminetetraacetic acid, (EDTA), could also effect metal electrowinning. Oztekin and Yazicigil (2006) concluded that the recovery of copper could be varied depending on the chelator used. These chelators might improve the efficiency of electrowinning since they have the ability to reduce side reactions.

Sharma et al. (2005) recommended the addition of sodium sulphate, Na_2SO_4, to increase the efficiency. This could increase current efficiency and lower hydrogen evolution, resulting in higher metal recovery and reduced energy consumption.

2.3.2. Separation by Absorption:

Adsorption processes have been widely used to achieve a better metal recovery from electroplating wastewater (Al-Asheh and Duvnjak, 1997, Taty-Costodes et al., 2003, Balkose and Baltacioglu, 1992). It has been recommended to use sorbents that are obtained from natural materials available in large quantities, or certain waste products from industrial or agricultural operations (Moreno et al., 2001, Peternele et al., 1999). This is because of their low cost and deposition without expensive regeneration. However, a sorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry.

Bailey et al (1999) presented a review paper with a list of sorbents used in the literature and provided a summary of available information on a wide range of low cost sorbents. Sciban et al (2007) studied the adsorption of copper, zinc and cadmium from electroplating effluent using wood sawdust, (a solid metal obtained from mechanical wood processing). The authors mentioned the advantages of this sorbent in that it has an extremely low cost, is widely available and has a good mechanical stability. The work showed an increase in the efficiency of sawdust adsorption with an increase in the amount of the sawdust. Also, the efficiency of the adsorption depended on the type of the metal recovered and the amount of that metal. However, the selectivity of metal removal using this method did not show satisfactory results. Bailey et al (1999) also related the sorbant low cost to the degree of processing required and local availability. Hence, improved sorption capacity may compensate for the cost of additional processing. Meena et al (2005) stated that the presence of agricultural materials may provide a good performance in removing heavy metals from effluent solutions. This is due to the adsorption on the surface and pores, in addition to complexation by these materials. Sorption data could be effectively described by a Langmuir model (Meena et al., 2005).

The removal of heavy metal ions using carbon aerogel adsorbent has been proposed by Meena et al (2005). The work also concerned the effect of other factors, such as concentration, pH, contact time, temperature and etc. The pH was found to be a most effective variable in this kind of adsorption. Moreover, the experiment showed almost 100% adsorptive removal of heavy metal ions under certain conditions.

However, the work was aimed mainly to reduce the metal content of the solution rather than the recovery and reuse of these metals. Furthermore, carbon aerogels are expensive to manufacture and use.

Alvarez-Ayuso et al (2003) studied the sorption behaviour of natural and synthetic zeolites with respect to heavy metals, such as Cr, Ni, Zn, Cu and Cd, commonly present in metal finishing wastewaters. Four wastewater samples were used from an electroplating wastewater and were from: acid zinc electroplating, cyanide zinc electroplating, typical chromium electroplating after reduction of Cr(VI) to Cr(III) with $Na_2S_2O_5$ and a typical nickel electroplating process (Watts bath) sample.

The selection of the type of unit depends on its efficiency and economy. Moreover, absorption processes can only be used within a given concentration range and are not viable for treating large volumes of effluents containing low concentrations of metal cations (Yordanov and Roundhill, 1998, Baticle et al., 2000). The following section discusses one of the most efficient units that could achieve the above task with low cost.

2.3.3. Polymer Enhanced Ultrafiltration, (PEUF):

The concept of PEUF has been well documented in the literature (Singh et al., 2000, Jones, 2005, Coulson et al., 1999, Juang and Liang, 1993b, Canizares et al., 2002, Aliane et al., 2001). The improvements in commercial ultrafiltration membrane technology over the last 10-15 years have made the use of water-soluble polymers with UF a more reliable and cost-effective approach for separations. The process works in a similar way as the absorption method described by Bailey et al. (1999), Sciban et al.(2007) and Meena et al. (2005) but instead of using solid particles a soluble high molecular weight polymer that can selectively bind metal ions is used (Kaliyappan and Kannan, 2000). By far the most effective approach is to use a compound that forms a complex with the metal of interest.

An appropriate complexing agent must complex specific metal ions satisfactorily in order to ensure the complete rejection of the metal before the membrane. However, the complexation must be reversible so that the complexing agent can be easily regenerated for recycling to reduce costs. Some polymers, such as polyethyleimine, can be highly selective to particular metals.

The main steps and principles of the process are illustrated in figure 2-8. The first step, complexation, is where water-soluble polymer with the ability to selectively chelate metal ions is added to a solution containing metal ions. This generates a complex of targeted metal ions with the polymer under specific conditions, such as pH. The macromolecular complex is then retained by the membrane while the non complex metal ions pass through the membrane to the permeate stream.

The next step involves dissociating the polymer-metal ion complex. This can be done by acidification of the component in order to lower solution pH so that the polymer becomes protonated and the metal complex breaks up. A secondary ultrafiltration separates the polymer from the metal ion, and the permeate produced from this stage will be a concentrated metal ion solution suitable for recovery of metal by electrowinning.

Some polymers are highly selective for copper ions over zinc ions (Singh et al., 2000). However, Jones (2005) mentioned that the investigation of PEUF using various commercially available water-soluble polymers was required since there are no chelating agents, as yet, developed specifically for this type of separation. Polyethylenimine, (PEI) has been shown to be a good metal chelator, (that contain selective ligand groups and is termed a "polychelatogens"), and has been used in combination with membrane filtration (Jones, 2005). It is believed that PEI has a number of advantage that are required for a successful polychelatogen. These include high density for functional groups (hence high binding capacity), good water solubility, chemical stability and metal selectivity (Singh et al., 2000, Geckeler and Volchek, 1996). Consequently, PEI is used for the experimental work performed in this project.

Several kinds of PEUF modes can be used. These are: Batch, Permeate recycle, washing method with variable ionic strength, washing method with constant ionic strength and enrichment methods. Jones (2005) has recommended the use of either the batch or the enrichment technique in order to treat wastewater, which is also the subject of this work.

Targeted & non
targeted ions
solution

Complexing
polymer

Complexation

+

Decomplexation

**Primary
ultrafiltration**

Retentate

Solution of non
targeted ions for
disposal, recycle or

**Secondary
ultrafiltration**

Concentrated
solution of
free polymer

Solution of targeted
ions for downstream
recovery
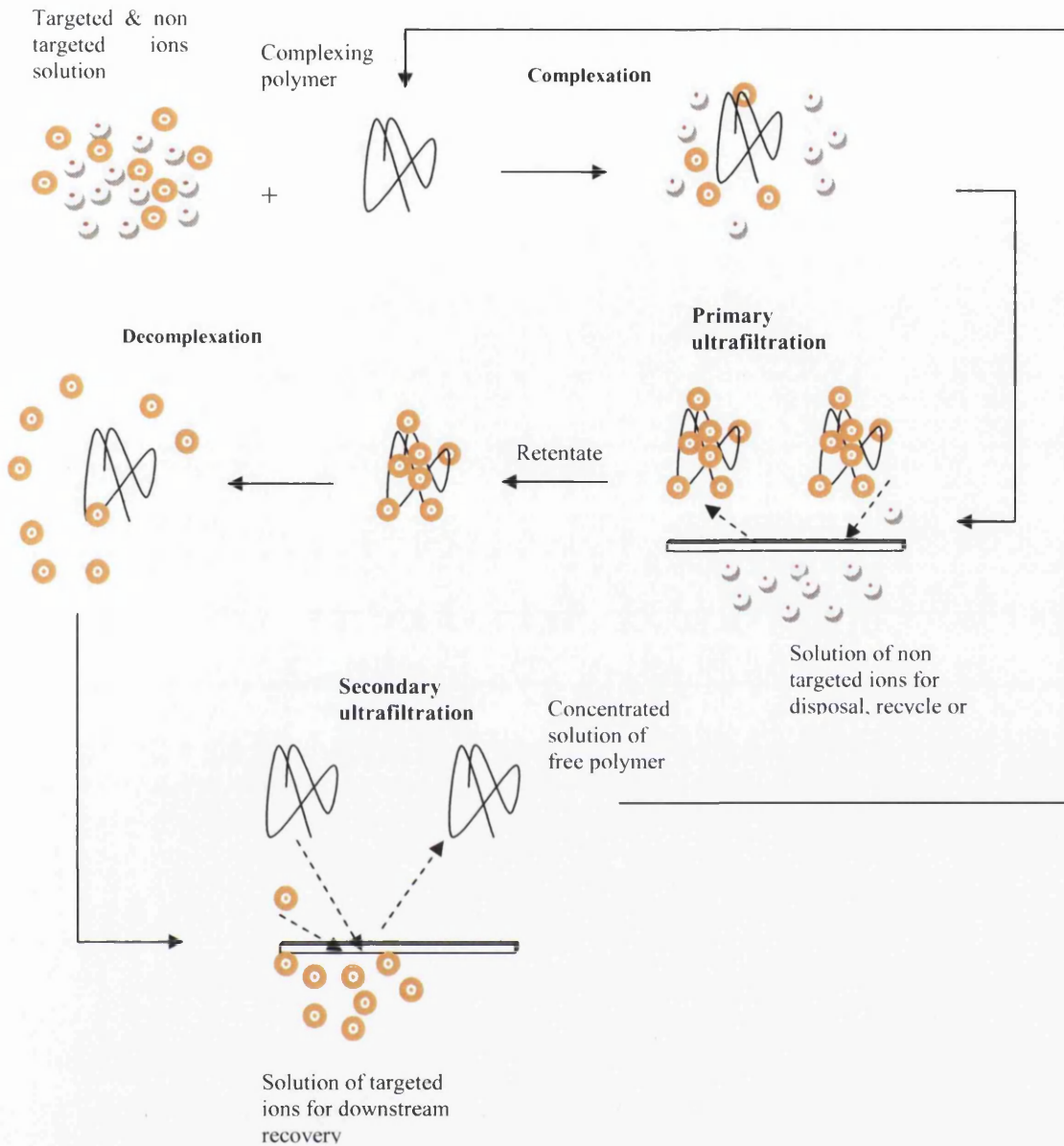
Figure 2-8: Metal separation using and Ideal PEUF process stages. The diagram, shows the specific stages of the process and the recycling of the polymer to allow its reuse. Two streams are obtained, one contains a specific ion selected from the original solution and the second stream which is now depleted in the ion.

2.3.3.1. PEUF Parameters:

Some parameters have been shown to influence metal ions separation in PEUF. The parameter of ionic strength of the solution, can cause precipitation to occur. The

formation of metal salts should be avoided since it inhibits complexation of target metal ions by compression of the electric double layer around the polymer. It also reduces the overall thickness of double layer. It also may affect the interaction of the polymer with the membrane surface as this is typically negatively charged at neutral pH. The sensitivity of water-soluble polymer can be expressed by the following equation (Coulson et al., 1999):

$$\varphi = 0.5 \sum [I] z^2 \qquad (2.11)$$

where, φ is the ionic strength of solution, (mol/L), $[I]$ represents the concentration of ion in solution, (mol/L) and z is the ion valence. The relationship between ionic strength and the overall thickness of the double layer can be shown as following:

$$x = \left[DT / 8\pi [I] e^2 z^2 \right]^{0.5} \qquad (2.12)$$

where x is the depth of electric double layer, D is the dielectric constant, e is ion size, (or electronic charge) and T is the system temperature.

It is importance to point out that the electric double layer can reduce electrostatic attraction between metal ions. Increasing polymer/metal ion loading, or loading ratio can increase retention. The loading ratio can be shown in the following relationship:

$$L = C_p / \sum_{i=1}^{i=m} C_i \qquad (2.13)$$

where L is loading ratio, C_p represents polymer concentration, g/L and C_i is concentration of metal i, g/L. Jones (2005) found out that increasing polymer concentration can lead to a decrease in the permeate flux and the retention of metal ions. His statement was based on previous work by Geckeler and Volchek (1996) who referred to the high viscosity and concentration polarization at the membrane surface associated with the increase in polymer concentration. On the other hand, Geckeler and Volchek (1996) pointed out that increasing ion strength could increase repulsion between like charge groups. This could reduce the size of macromolecules and therefore, reduce retention of metal ions.

Increasing operational pH in the acidic region (i.e. from 2 to 6) increased the metal retention in the presence of PEI (Jones, 2005, Juang and Liang, 1993b). However, metals could form insoluble hydroxide of sufficient size to be retained by the membrane when pH exceeds a certain value. Nevertheless, pH sensitivity of metal – polymer complexation can vary significantly between different metals. Based on the above, Jones (2005), Baticle et al. (2000), Canizares et al. (2002), Juang and Liang (1993a) and Aliane et al. (2001) suggested the control of pH which could offer the possibility of selectively binding metal ions. The retention values of various metal cations over a range of pH using PEI as polychelatogen is listed in table 2-10 (Jones, 2005).

Table 2-10: Membrane retention of metal ions by PEI at different pH levels. PEI concentration was 1% by weight and initial metal concentration of 10 ppm were used (Jones, 2005). Polyvinylidene fluoride (PVDF) membrane was used.

pH	Retention%						
	Co	Ni	Zn	Cd	Cu	Mg	Na
2.1	1.2	0.1	1.0	0.1	86.3	-	-
3.2	16.3	21.3	0.5	0.7	99.0	-	-
4.0	93.1	99.0	-	98.1	99.0	-	-
5.3	99.0	99.0	99.0	99.0	99.0	0.1	0.1

High cross flow feed rate could also reduce concentration polarization and improves permeate flux rates. However, a high feed velocity invokes high shear which in turn could degrade polychelatogen. According to Geckeler and Volchek (1996), this could result in a reduction of molecular weight and permit the polymer to pass through the membrane.

After the metal ions are complexed with the polymer and selectively separated from non targeted ions, it is required to decomplex these ions and regenerate the chelating agent without excessive damage. Two methods have been reported in the literature, the first is to use electrolysis by Geckeler and Volchek (1996) where ions could be

separated in cells similar to the one discussed in section 2.3.3.6. However, Juang and Chiou (2000) criticised this approach because of the anodic oxidation that could cause excess damage to the polymer. The second method of chemical decomplexation has been recommended by Baticle et al. (2000), Geckeler and Volchek (1996) and Jones (2005) as an efficient strategy. This operation typically depends on the addition of chemicals to adjust pH. Metal-polymer dissociation can be specific and so a sequential release of metals is possible if the environment is manipulated carefully. Consequently, this process can offer the possibility to selectively separating metal ions during decomplexation (Jones, 2005).

The retention of solutes by membranes can be defined as the fraction of a solute in the feed solution retained by the membrane. This can be expressed as:

$$R_i = 1 - \left(\frac{C_{if}}{C_{ia}} \right)$$

(2.14)

where R_i = retention of solute i, C_{if} = Concentration of metal i in the permeate, mg/L and C_{ia} = Concentration of metal i in the feed solution, mg/L.

The retention of metal ions can be used as an indication of the degree of the formation metal-polymer complexes with the assumption that only metal ions complexed with polychelatogen are retained by the membrane while non-complexed metal ions pass through the membrane (Jones, 2005).

Langmuir and Freundlich isotherm equations have been employed to describe the complexation process via retention values (Jones, 2005, Moreno-Villoslada and Rivas, 2002, Moreno-Villoslada and Rivas, 2003, Almutairi, 2008). The investigation showed the retention data fitted the linearised form of each isotherm with a coefficient of correlation, R^2 greater than 0.9. Therefore, the isotherm could be employed to model these processes. However, Jones (2005) and Almutairi (2008) concluded that the Langmuir equation provided the better description of the system as this has a strong theoretical background being reliant on the number of specific binding sites and the affinity of materials to bind to such sites. The Langmuir equation can be given by (Jones, 2005, Moreno-Villoslada and Rivas, 2002, Moreno-Villoslada and Rivas, 2003, Almutairi, 2008):

$$Q = \frac{Q_{max} \cdot C_{iu}}{K_L + C_{iu}}$$

(2.15)

where Q is the amount of metal complexed, mg metal/mg polymer, Q_{max} is the maximum capacity of polymer, mg metal/mg polymer, C_{iu} represents the metal residual concentration in solution, mg/mL solution and K_L is the dissociation constant, mg/mL. The above equation can be linearised by taking reciprocals of both sides of the equation and becomes:

$$\frac{1}{Q} = \frac{K_L}{Q_{max}} \frac{1}{C_{iu}} + \frac{1}{Q_{max}}$$

(2.16)

If plotting the reciprocal of Q against the reciprocal of C_{iu} yields a straight line, then the system follows the Langmuir model and the intercept of the resulting line is equal to $1/Q_{max}$ and the slope is K_L/Q_{max}. These parameters give important information as to the metal binding characteristics with the polymer

2.4. Metal Recovery from Wastes and the Environment

Many technologies have been designed and developed to suit the type of metal to be recovered or removed, (i.e. base, precious or strategic), and the environment (water, soil or consumed products). Therefore, many authors have addressed these technologies that suit the phase and type of waste inputs. The above environments will be discussed in the following sections.

2.4.1. Recovery of Metals from Soil:

Soil is one of the main repositories of metals from wastes and as such could yield relatively large amounts of metals. The migration of heavy metals into soil depends on the solubility of the original metal source, (for example ore). The movement of metals in soils is heavily dependent on the nature and chemistry of the metal. To move rapidly is must end up in a soluble form and typically this is as a chelated form associated with organic materials and residues (proteins, peptides, humic and fulvic acids etc). Landfill leachates, in particular, are good examples of solubilised metals associated with organic soluble materials. The metal content of leachates being heavily dependent on the materials that they are co-disposed with them. He et al.

(2006) mentioned that the estimated amount of the leached heavy metals from methanogenic landfill were 0.13%, 1.8%, 0.15%, and 0.19% of Cu, Cd, Pb, and Zn, respectively of the total present. These values where obtained from two wells drilled in Hangzhou Tianziling landfill, in China. Flyhammar (1995) found in his research that the leachate from methanogenic landfill in Sweden contained low concentrations of heavy metals.

Many papers have considered the recovery and removal of heavy metals from the polluted soil environment. According to Hodson et al. (2000), decontamination techniques, such as solidification and stabilisation off-site, and soil washing are expensive and disruptive. Consequently, phytoextraction has been suggested by Cunningham and Berti (2000) to translocate the lead from the soil into plants, and remove by plant harvesting. Hettiarachchi and Pierzynski (2004) criticised this proposal in that low solubility of lead, Pb in soil may cause unavailablity of Pb for plant uptake, poor Pb translocation into plants, and the high degree of Pb toxicity to plants and tissues (Demirbas, 2004). Hettiarachchi and Pierzynski (2004) found out that in situ (i.e. in the original place instead of being moved to another place) stabilisation seems to be the most economical and attractive alternative currently available for remediating Pb contaminated sites.

Hettiarachchi and Pierzynski (2004) also presented a review of soil lead bioavailability, (i.e. the portion of Pb in a soil that is available for absorption into living organisms, such as the human blood stream), which depends on the solubility of the lead solid phase and other site-specific soil chemistry. They suggested the use of the physiologically based extraction test, (PBET) known as vito, in order to predict the bioavailability of lead metal from a solid mixture. The test was performed earlier by Ruby et al. (1996) and included the influence of other parameters such as simulated gastric solution and appropriate temperature. The review also discussed several in situ stabilization methods of reducing Pb bioavailability, such as the process of adsorbing Pb onto surfaces of freshly precipitated manganese and iron oxides. McKenzie (1980) emphasised the fact that immobilisation of metals ions by synthetic manganese oxides and three synthetic iron oxides was due to strong specific adsorption. However, Hettiarachchi and Pierzynski (2004) found out that

this process could be irreversible and other kinds of complex components could be formed and suggested the use of phosphate, P in situ stabilization of soil Lead.

2.4.2. Recovery Metals from Water:

Water is one of the most important entities in the environment. Water has been used intensively during the industrial activities in order to improve the quality of products. Consequently, water pollution has been one of the biggest environmental issues and many researchers have been concerned with the removal of pollutants from this environment.

Heavy metals have been released into the environment in a number of different ways, such as coal combustion, automobile emissions, mining activities, sewage wastewaters, the utilization of fossil fuels, electroplating processes, etc, and metals like Pb, Cd, Cu, Hg, Cr, Ni, and Zn can be found in large amounts in water. Therefore, removal, separation and enrichment of heavy metal ions in aqueous solutions play an important role for the environmental remediation of wastewater.

Selective separation is one of the most widely hydrometallurgical techniques used in the recovery and removal of heavy metal ions from water. It has been given a huge interest and concern by many publications because it somehow covers both environment and economic requirements. In addition, it showed the economically feasible alternative method for removing trace metals from wastewater and water supplies (Van Erkel, 1992).

Adsorption of heavy metals by different kinds of agricultural materials, such as palm kernel husk (Hawthorne-Costa et al., 1995), modified cellulosic material (Elik et al., 2004), corn cobs (Lalvani et al., 1997), residual lignin (Gharaibeh et al., 1998), apple residues (Raghuwanski et al., 2003), olive mill products (Garcia et al., 2003), pine bark (Consolin Filho et al., 1996), sawdust (Zhang et al., 2000), etc., have been reported for the removal of toxic metals from aqueous solutions. Doyurum and Celik (2006) investigated the removal of Pb and Cd from wastewater using olive cake as an adsorbent. They described an olive cake which is a waste from olive factories and is usually used as heating, fertilizer and feeding material. According to Garcia et al. (2003), the structure of an olive cake contains organic compounds like lignocellulosic material, polyphenols, amino acid, protein, oil, and tannins.

Meena et al. (2005) stated that adsorption of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compounds, which have metal binding functional groups, such as carbonyl, hydroxyl, sulphate, phosphate, and amino groups. Hence, Doyurum and Celik (2006) emphasised the fact that olive cake has an extensive surface area and may be used as an adsorbent material.

Peternele et al. (1999) found that adsorption increases with increasing temperature when using sugar cane bagasse, which was extracted sequentially with n-hexane, ethanol and water in a soxhlet system. Their work was based on research conducted by Consolin Filho et al. (1996) who suggested the use of lignin from sugar cane bagasse as a low cost copper adsorbent. Peternele et al. (1999) concluded that cheap materials such as lignin from sugar cane bagasse can be easily modified in order to obtain new materials able to adsorb heavy metals ions. However, the absorbent used in their experiment can adsorb Pb selectively rather than Cd under specific conditions (pH 6.0, 30°C and ionic strength of 0.1 mol dm^{-3}), when both ions are present in the mixture.

Although adsorption processes can achieve a high level of water cleaning at low cost, the process can not be considered to be efficient in recovering high purity of an individual metal, which is an important aim of this project. Therefore, the extractions of metals by PEUF and electrochemical processes provide a route to high purity metal recovery as previously discussed.

2.4.3. Metals from Industrial Products:

All industrial products reach the end of their product life cycle for a number of reasons, such as becoming obsolete, increasingly strict health and safety and environmental standards or technology, innovation and development driving changes or simply increasing maintenance costs. This leads to an accumulation of the old redundant products like batteries, computer hardware and electronics scrap metals etc. The above products contain relatively large amounts of heavy metals that could be recovered.

Huisman et al. (2004) stated that the end-of-life processing could serve several goals. These are: reduction of materials going to landfill in order to minimise landfill volumes and their impact, recycling of materials in order to keep maximum

economical and environmental value and so avoiding dilution, preventing new material extraction and reduction of emissions of environmentally relevant substances. This includes leaching from landfill sites and incineration slag, etc. Huisman et al. (2004) also reported that cellular phones could contain relatively high amounts of precious metal, (between 320 ppm and 385 ppm of gold, 187 ppm to 222 ppm palladium and 500 ppm to 800 ppm of other metals). On the other hand, the precious metal content of the cordless phones varies from 8 ppm to 183 ppm for gold and 23 ppm to 135 ppm palladium.

Nogueira and Delmas (1999) listed the main features of the hydrometallurgical process in the sulphate medium for spent Ni–Cd battery recycling. These are: mechanical processing by shredding and separation of battery fractions, leaching of electrode fractions with sulphuric acid as a cheap reagent and less corrosive than other acids, cadmium, cobalt and nickel separation by solvent extraction, metals recovery from the separated streams by electrodepositing or crystallisation as sulphates and separation of case materials like nickel, iron and plastic.

The following subsections will mainly focus on the current technologies employed in the literature in order to recover heavy metals form certain end of life products that might contain significant amount of metals.

2.4.3.1. Metals from Batteries:

Batteries are classified as primary and secondary. This classification depends on the particular type of their application. Primary batteries were predominantly zinc-anode-based systems. These batteries have been widely spread and other metals have been added to form more efficient primary types, such as zinc oxide, alkaline manganese dioxide and silver oxide. Primary batteries are used extensively in a wide range of applications, such as road hazard lamps and intruder alarm circuits. The secondary type has higher gravimetric density than the primary type. These kinds of batteries have been designed in order to provide the advantages of being recyclable, extended shelf life prior to use, remote activation, adjustment in load current with minimum voltage variation and operation under extreme temperature conditions (Barr and Hestrin, 1999, Tzanetakis and Scott, 2004).

The recovery of heavy metals from batteries has been intensively discussed in the literature (Linck, 1998). Nogueira and Delmas (1999) proposed the method of solvent extraction for the recovery of cadmium, cobalt and nickel from batteries in the pure and marketable forms from sulphate solutions. The paper also reviewed previous publications of several authors in order to recover these metals from different types of batteries. Processes such as the SAB NIFE (Hanewald, 1998), the SNAM (Bartolozzi et al., 1995) and the INMETCO (Lyman, 1994) are considered to be pyrometallurgical processes. According to Nogueira and Margarido (2004), these processes are in fact very efficient concerning the management of Ni–Cd residues since they are capable of solving the main related environmental problem (i.e. the release of the contained cadmium) but have less potential to recover cobalt and nickel. Furthermore, the above processes are strongly energy consuming and some emissions of dust and gases would be expected.

Alternatively, several hydrometallurgical processes have been developed for the treatment of spent primary and secondary batteries. Solvent extraction is therefore used as the most efficient separation technology for the treatment of wasted batteries (Pletcher, 1982).

TNO is a primary process described by Van Erkel (1992) employed in order to remove Ni and Cd from Ni–Cd batteries using hydrochloric acid leaching followed by the separation of cadmium chloride complexes using tributyl phosphate, TBP as a solvent. The process is followed by the recovery of nickel and cadmium separately by electrowinning. Another approach proposed by Bartolozzi et al. (1995) was to mechanically remove the external case and the metal supports of the battery and then use a hydrometallurgical process to acid leach the metals from the electrode powder and then recover the metals by electrowining. The above approach showed good results in order to recover about 99% of cadmium. However, nickel recovered as $NiCO_3$ was of the purity of 98% of the nickel, which was of a lower purity than expected. Di (2-ethylhexyl) Phosphoric Acid, (DEHPA) solvent was used by Lyman (1994) in order to investigate the recycling of nickel–metal hydride batteries.

Zhang et al. (2000) presented hydrometallurgy treatment alternatives for the recovery of metal from lithium-ion and nickel–metal hydride spent batteries, which are used as electrical supplies for mobile phones. Hydrochloric acid, HCl, was found to be the

most suitable solvent among the other three reagents used in their experiment. In addition, leaching extraction efficiency of around 99% of cobalt and lithium could be achieved when a solution of 4 M HCl was used at a temperature of 80°C and a reaction time of 1 h.

It can be seen that the process of heavy metals recovery from batteries involves several steps in order to achieve maximum purity of these metals for future reuse. The type of the solvent used also depends on many factors, such as temperature, pH, initial concentration, and type of the recovered metal. The recovery of heavy metals from batteries is a very important issue considering our reliance of batteries to power personal electronics and the potential use in automobiles either as electric powered cars or as hybrid systems

2.4.3.2. Metals from Electronic Wastes:

Electronic waste or E-Waste is one of the fastest growing components of municipal trash. Therefore, many authors, organisations and individuals have warned of the potential problems of E-waste. According to the SVTC, consumer electronics in the United States already account for 70% of the heavy metals, including 40% of the lead, found in landfills (Pletcher, 1982). The impact of these kinds of wastes can result in significant deleterious effects to the environment and the loss of valuable materials that should be recovered and reused.

Yadong Li et al. (2006) pointed out the fact that E-waste already constitutes 1% of the municipal solid waste. Therefore, the recycling and reuse of the obsolete electronic products is strongly encouraged. However, only 9% is recovered for recycling and the vast majority ends up in landfills. According to Smith et al. (1996) the cathode ray tubes (CRTs) in computer monitors and TVs contain about 8% lead (Pb) by weight. Lee et al. (1998) and Lee and Hsi (2002) concluded that this kind of products could also contain small amounts of other toxic substances, such as barium, Ba, cadmium, Cd, chromium, Cr, copper, Cu, and zinc, Zn.

Personal computers (PCs) are the most significant component in the E-waste stream. Printed wiring board (PWB) is the foundation both literally and figuratively for all electronics in the world. It is the platform upon which electronic components such as integrated circuit chips and capacitors are mounted. The PWB, or printed circuit

board (PCB) provides both the physical structure for mounting and holding electronic components as well as the electrical interconnection between components. A PWB consists of a non-conducting substrate (typically fibreglass with epoxy resin) upon which a conductive pattern or circuitry is formed. Copper is the most prevalent conductor, nickel, silver, tin, tin-lead, and gold may also be used as etch-resists or top-level metal.

Pyrometallurgical and hydrometallurgical processes have been employed and applied to achieve metal recovery from waste PWBs. Kinoshita et al. (2003) reviewed these processes and their efficiencies to recover metals from PWBs. He criticised methods proposed by Iji and Yokoyama (1996a) and Iji and Yokoyama (1996b) whom suggested carbonising or thermally decomposing the resin substrates and recovering the remaining metals by a physical method. Physical methods might be considered when treating large quantities with no concern to energy consumption.

The hydrometallurgical process has been widely applied in the field of metal recovery from industrial wastes, due to its advantages of being flexible, environmentally friendly and energy efficient (Alvarez-Ayuso et al., 2003). According to Kinoshita et al. (2003), hydrometallurgical processes have been efficient in terms of selectively leaching of nickel and copper from non-mounted printed wiring boards, along side recovering solid flakes of gold at high purity using nitric acid. In addition, the work achieved the optimum leaching performance, which was evaluated under various experimental parameters, such as concentration, temperature and solid–liquid ratio.

Cathode ray tubes (CRTs) in television and computer monitors are one of the most common components of discarded electronics in the solid waste stream. CRTs in computer monitors and televisions may contain barium, cadmium, copper, lead, zinc, and several rare earth metals. Jang and Ownsend (2003) published a paper concerning leaching tests using MSW leachates from lined landfills in Florida in order to examine lead leachability of PWBs from computers and colour CRTs from computer monitors and televisions. The work was based on a previous attempt performed by Musson et al. (2000) who concluded that the cost of hazardous waste management is much greater than MSW management and recycling becomes a more cost-effective alternative.

It is clear, from the literature that a substantial amount of work has been done to investigate the selective recovery of metal ions from aqueous solutions, such as solvent extraction, ion exchange, electrowinning and ultrafiltration processes. However, the safety of the environment and production cost still poses severe problems. Thus, there is scope for further research in this field in order to design more effective integrated zinc recovery systems with the general strategy of optimising the economy of such a unit.

Chapter 3

3. MATERIALS AND METHODS

This chapter presents the materials and methods used in the experimental work. Zinc was chosen in this study for its importance as a commodity metal. The optimum conditions of zinc electrowinning were investigated through a series of lab-scale alkali and acidic electrowinning experiments. PEUF was performed at different operating conditions of applied pressure, initial solution concentration and solution pH.

3.1. Materials:

3.1.1. PEUF Materials:

In PEUF experiments, two types of solution sets were prepared. The first consisted of 2.0 g/L $ZnCl_2$, (Fischer Scientific Chemicals, laboratory grade) in deionised water. The solution pH was maintained at 3 using 0.5 mol/L HCl solution. The second set was a series polyethylenimine (PEI) solutions at a variety of concentrations, (molecular weight of 750,000) received as 50% solution from Aldrich, (cat. No.: 18, 197-8, lot: 06885-452, CAS: 68130-97-2). These were typically made up with deionised water.

Stock hydrochloric acid, HCl, solutions of 0.5 mol/L were prepared by the addition of 20.9 mL Fischer Scientific laboratory reagent grade, (37% solution) HCl to 1 L of distilled water. NaOH stock solutions were produced by the addition of 40 g NaOH pellets from Fisher chemicals to 1 L of distilled water. Certified solutions of 10 ppm Zn^{2+} in 7.5 mL, 0.1 mol/L acetic acid solution were supplied by Fisher Chemicals in order to calibrate polarographic analysis.

Prior to UF, the two solutions were mixed and stirred for 2 h, in which the pH was adjusted by adding a small amount of HCl or NaOH. Aqueous solutions of zinc metal were produced in a range of concentrations so as to produce a series of metal to polymer ratios (or polymer capacity). This was done so as to maintain a constant polymer concentration of 1 g/L. In addition, eight solutions of each polymer to metal ratio were produced over a range of pH's from 2 to 6. Those solutions were produced by the addition of various volumes, i.e. from 0.05 to 2.5 mL of required 9.59 g/L zinc

ion solution and 10 mL of 10 g/L PEI stock solution to distilled water using suitable size of glass pipettes. Solution pH was altered as needed using 0.5 mol/L HCl or 0.5 mol/L NaOH. Sufficient distilled water was then added up to the final volume of 100 mL.

About 50 mL of each sample was subjected to batch ultrafiltration using a stirred cell apparatus described later in this section. The results of polarographic analysis (see section 3.3.2) of feed and permeate samples for zinc allowed the calculations of the respective retention values using equations (2.13), (2.14) and (2.15).

UF experiments were performed in a batch cell (Amicon 8050). It was used to perform batch ultrafiltration procedures. The construction of such a cell was sufficient to withhold operation under the conditions required, with manufacture's recommendations of 75 psi maximum pressure, 85 $^{\circ}$ C maximum temperature and 2-10 pH range. The cell was stirred at 300 rpm by a magnetic motor. The unit was sufficiently robust to with stand operation under the conditions required, with the manufacturer's recommendations (Al-Amoudi et al., 2007, Al-Amoudi and Lovitt, 2007, Bowen et al., 2003).

The pressure can be controlled using a nitrogen gas stream and the temperature can be fixed at a constant value using water passed from a thermostat through an outside jacket surrounding the cell. The minimum and the maximum process volume are 2.5 and 50 mL respectively, the membrane diameter was 44.5 mm and the membrane surface area is 13.4 cm^2. The cell can be dismantled for ease of maintenance and cleaning, (see figures 3-1, 3-2 and 3-3).

The membranes used were Intersep Nadir polysulphone of 30,000 molecular weight cut off, (MWCO). The values of water flux, J_w were measured before and after UF and only the membranes with a deviation of J_w smaller than 5% were used. A compressed gas cylinder, (200 bar) containing high purity nitrogen from British Oxygen Company was used to control the pressure and provide a driving force for the ultrafiltration experiment. A polarographic analysis unit was used to determine the concentration of metals in aqueous solutions (see section 3.3.2).

Figure 3-1: Amicon 8050 ultrafiltration cell.
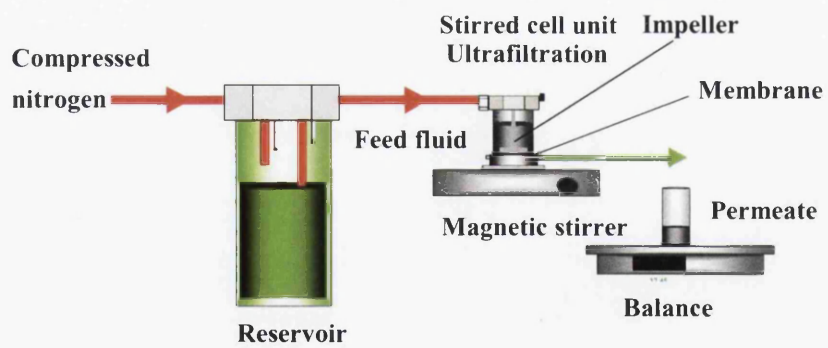
Figure 3-2: Diagram and experimental set up for stirred ultrafiltration cell.

1. Cap
2. Pressure relief valve
3. Pressure tube fitting assembly
4. Top o-ring, provides seal to maintain pressure in the unit
5. Magnetic impeller (provides cross flow conditions)
6. Main body of the stirred cell, and constitutes reservoir wall.
7. Bottom o-ring, provides seal to maintain pressure in the unit, and prevent loss of sample.
8. Membrane disc
9. Base with outlet for permeate/filtrate
10. Screw in bottom to secure base in the main body (3)
11. Filtrate / permeate tube
12. Retaining stand prevents displacement of cap when pressure is applied to the unit

Figure 3-3: Schematic diagram of stirred cel (Amicon cell) used in the experiments.

3.1.2. Methods for the Study of the Electrowinning Process:

Acidic zinc electrowinning experiments were carried out using solutions prepared from analytical grade reagents. Zinc chloride, $ZnCl_2$ and sodium hydroxide, NaOH purchased from Fisher Scientific (Bishop Meadow Road, Loughborough, Leichestershire, Le11 5RG), were used to prepare standards, (from 5 g/L to 30 g/L zinc ion concentrations). Zinc hydroxide $Zn(OH)_2$ slurry was prepared by the addition of 4 mol/L NaOH to 80 g/L $ZnCl_2$ solutions. The resulting slurry was then filtered and washed using distilled water.

Zinc oxide, ZnO powder was obtained from Sigma & Aldrich (The Old Brickyard, New Road, Gillingham, Dorset, SP8 4XT). 2.8 g to 5.6 g of ZnO were dissolved in several NaOH concentrations ranging from 1 up to 8 mol/L. These Zincate solutions where subjected to alkaline electrowinning.

The optimum conditions of zinc electrowinning have been investigated through a series of lab-scale alkali electrowinning experiments. Electrowinning operations

were performed by varying the experiment parameters of initial zinc concentration (from $\left[Zn^{2+}\right]$ = 7.5 to 30 g/L), NaOH concentration, (from 1 to 8 mol/L) and current density, (500 to 2500 A.m^{-2}), in order to estimate the optimum parameters. 2.8 g to 5.6 g of zinc oxide (ZnO), obtained from Sigma & Aldrich (The Old Brickyard, New Road, Gillingham, Dorset, SP8 4XT), were dissolved in several volumes of NaOH concentration to form a total value of 150 mL for each zinc concentration at specified conditions. The resulting solutions were then subjected to electrolysis using a 200 mL glass constructed cell cased with its own outer shell water jacket. Stainless steel electrodes were employed in each experiment. Solutions were stirred using a Bibby B211 electromagnetic stirrer, (see figure 3-4).

Current values were calculated and maintained on the basis of the geometrical cross-sectional area of the electrode at various current density values. The cell voltage was recorded using TTi EX355P power supplier. The data obtained are employed and analysed and the cathode was removed, washed thoroughly with water, dried for 24 hr and weighed. Each experiment was run for an average of 75 min.

The concentration of zinc ions was measured by analysing samples from the electrolyte at various time intervals using a polarographic cell at a scan rate of 100 mV/sec and cell potential between -1500 to 1500 mV. Each sample was diluted by adding 0.1 mL into 15 mL of 0.05 M of acetic acid to provide the solution within the zinc detectible pH of 2.5 (Moneeb, 2006). The system was then deaerated by passing oxygen-free nitrogen gas through the solution for 5 min (Moneeb, 2006, Somer and Unal, 2004, Renuka et al., 2001), (see section 3.3.2 below for details of the analysis).

RuO$_2$/Ti anode was prepared by painting 1.5 × 6 cm^2 titanium plate with ruthuim chloride, (purchased from Fisher Scientifics), dissolved in isopropyl alcohol and then heated up to 450 °C for 1 hr. The above anode type is capable to resist chlorine and oxygen attacks evolved during acidic electrolysis of the process. Stainless steel electrodes were prepared with the equal size to the anode area. All zinc electrowinning experiments were carried out in an electrochemical batch reactor as shown in figure 3-4.

The system consists of a 200 mL glass constructed cell cased with its own outer shell water jacket, stainless steel cathode, and RuO$_2$/Ti anode, TTi EX355P DC supplier to

provide the sufficient e.m.f and record cell voltage and current, Bibby B211 electromagnetic stirrer and external wires.
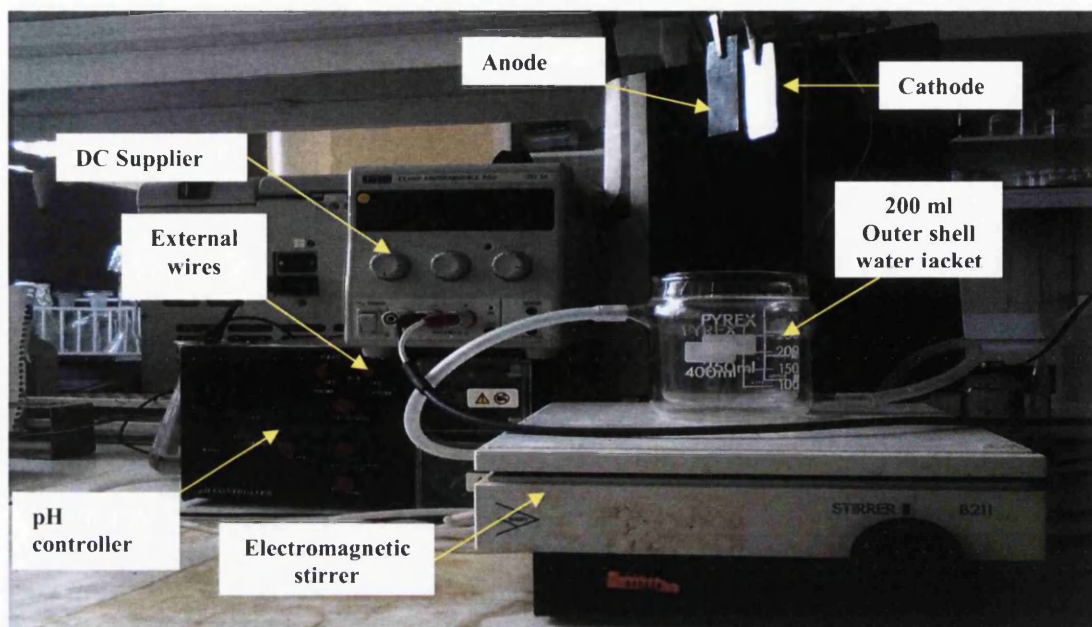
Figure 3-4: Typical laboratory scale electrowinning cell.

Electrowinning of zinc may be represented by the following reactions:

for acidic electrowinning at the cathode surface:

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad (3.1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3.2)$$

and at the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (3.3)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (3.4)$$
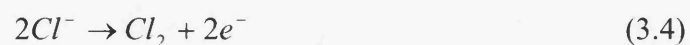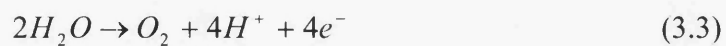
and for alkaline electrowinning at the cathode surface:

$$Zn(OH)^{2-} + 2e^- \rightarrow Zn + 4OH^- \qquad (3.5)$$

with the same reaction of the anode as shown in equation (3.3)

3.2. Methods:

3.2.1. PEUF Operation:

3.2.1.1 Polymer Titration Curve:

The polymer titration curve presented in figure 3-5 was obtained by recording pH values of PEI solutions of 10, 5 and 1.5 g/L after the addition of 0.5 M HCl solution. The figure was prepared to determine the amount of HCl required to maintain the PEI pH at required values for PEI-Zn complexation and/or decomplexation process (Kobayashi et al., 1987).
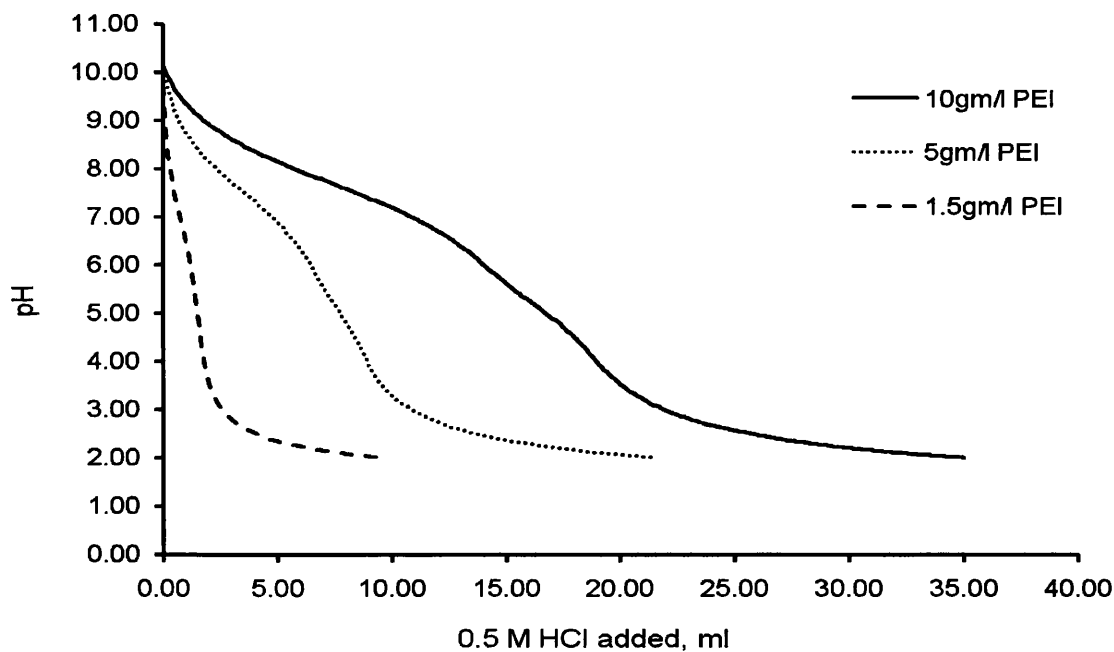
Figure 3-5: The effect of polymer concentration on the titration curves of 40 mL polymer solutions using 0.5 mol/L HCl .

3.2.1.2 Complex Zinc-Polymer Batch Mode Ultrafiltration:

To study the zinc-polymer complexation, aqueous solutions of zinc metal were produced to investigate the polymer binding capacity. The polymer concentration of 1 g/L was kept constant. In addition, eight solutions of each polymer to metal ratio

were produced over a range of pH from 2 to 6. Those solutions were produced by the addition of appropriate volumes, i.e. from 0.0 to 50 mL of required 2 g/L zinc ion solution and 50 to 0.0 mL distilled water to 50 mL of 10 g/L PEI stock solution up to a final volume of 100 mL using a suitable size of glass pipettes. Solution pH was altered as required using additions of 0.5 mol/L HCl or 0.5 mol/L NaOH.

Solutions of fixed pH and polymer capacity were prepared by varying both polymer and $ZnCl_2$ solution concentrations in order to study the hydrodynamic membrane conditions. The polymer concentration ranged between 0.5 to 20 g/L; and zinc ion concentration was between 50 to 2000 mg/L respectively. The polymer in each solution was at concentration of 10 greater than that of the zinc ion at pH = 5.5, see chapter 4. The above solutions were prepared by the addition of 50 mL of each polymer concentration to apropriate volumes (from 2.5 to 50 mL) of 2 g/L stock $ZnCl_2$ solution using glass pipettes. The solutions pH was then altered to pH 5.5 using 0.5 mol/L HCl and/or 0.5 mol/L NaOH. Sufficient distilled water was added to give final volume of 100 mL.

All polymer metal complex concentration experiments, after the polymer-metal complexation stage, were performed by applying about 50 mL of above each sample to batch ultrafiltration using the stirred cell apparatus mentioned in section 3.1.1. The runs were conducted at different pressures of 5, 10, 15, 20, 25 and 30 psi. The desired pressure was maintained across the membrane via Nitrogen gas stream and valves attached to the system. The results of polarographic analysis of the feed and the permeate samples for zinc allowed the calculations of the respective retention values using equation (2.15).

3.2.1.3 Decomplexation and Batch Ultrafiltration:

After studying the effect of experiment parameters on the complexation and concentration of ultrafiltration units described above, it was required to separate the decomplexed metal from the polymer using the UF unit to give a permeate of zinc ions for electrowinning recovery.

The decomplexing stage was performed at pH 2.5. The amount of acid was specified by the calibration curve prepared to present the polymer dissociation at several pH values. After concentrating of polymer-zinc complex, (by filtering from 50 mL to 5

mL), the final concentration of the retentate solution increased up to 10 g PEI /L solution. 2.8 mL HCl were then added, the resultant volume (7.8 mL) was filtered till the volume of permeate was 2.8 mL. An additional volume (2.8 mL of HCl) was added and the washing operated repeated several times as required. The number of times needed to recover a certain amount of zinc will be discussed in chapter 4.

3.2.1.4 Membrane Preparations and Cleaning:

Intersep-Nadir polysulphone membranes were employed with a molecular weight cut off, (MWCO) of 30K Dalton. These membranes are supplied in a sheet form and can be used up to a maximum temperature of 50 $^{\circ}$C and in a pH range from 1 to 10. The membrane was cut into appropriate area of 0.00134 m^2 and kept in distilled water for 24 hrs to allow it to become fully hydrated.

Before each experiment, the membranes were subjected to compacting and washing with 50 mL deionised water at range of pressure values, (from 5 to 30 psi). Once the water flux became steady with no further decrease, the hydraulic resistance (R_m) was obtained at each pressure value. The membrane was washed thoroughly with deionised water after each run with metal polymer solution to remove the deposited layer. This was followed by clean water runs to determine the extent of fouling as membrane resistance.

3.2.2. Zinc Electrowinning:

The aim of electrowinning experiments was to investigate the operating variables, which could effect on the electrowinning performance, and determine the optimum parameters that results in maximum current efficiency and metal recovery with minimum electrical usage. The above system can be run under two different modes of current supply (galavanic or potentiostatic). Experiments were operated under constant current conditions, (or so called galvanostatic mode).

For acidic electrowinning, the bulk pH values were adjusted and controlled by addition of either NaOH (first case) or Zn(OH)$_2$ (second case). The volume of zinc hydroxide added to the system was also recorded. Several electrolytic experiments were carried out at a given solution pH ranging from 3.65 to 5 using a pH titrator/controller. For each experiment, a 40 g/L zinc chloride solution was prepared and 150 mL volume of solution was subjected to electrowinning. The current was

recorded at set time intervals during the experiment. The cathode was removed, washed thoroughly with water, dried for 24 hours and then weighed.

The alkaline zinc electrowinning was carried out using specified amounts of ZnO dissolved in 150 mL, 4 mol/L NaOH. Both experiments were run under the following range of conditions: initial zinc concentration, (from $[Zn^{++}]$ = 2.5 to 40 g/L), cell voltage of 4 volts, current density for galvanostatic mode, (between 500 to 2500 A/m^2) and NaOH concentration, (from 1 to 6 mol/L). After an individual experiment was carried out, the cathode was removed, washed thoroughly with water, dried for 24 hours and then weighed.

5 mL volume samples were taken every 5 min during each electrolysis experiments for analysis of Zn content. Zinc concentration was measured using a polarographic method described in the following section. All the equipment used was thoroughly washed and cleaned after every use. This is due to the sensitivity of zinc measurements.

3.3. Zinc Analysis:

3.3.1. Polarographic Analysis:

Assessing all experiments relies on the measurement of several parameters (Meena et al., 2005, Somer and Unal, 2004). The amount of zinc in samples was determined by means of a polarographic method, the equipment was a BAS Epsilon electrochemical system shown in figure 3-6.

The Polarographic cell was used to perform cyclic voltammetry analysis by measuring the current at the working electrode during the potential scan. Three electrodes, platinum auxiliary electrode, Ag/AgCl reference electrode and working electrode were used. The working electrode was made from polished steel plate supported by plastic syringe barrel as shown in figure 3-7. High purity N_2, (supplied by British Oxygen Company) was passed through each solution for deoxygenating the solution at least 5 min prior to each run. The voltage is then held at the initial potential of -700 mV where no electrolysis occurs and hence no faradic current flows. As the voltage is scanned in the positive direction, so the reduced compound is oxidised at the electrode surface. At a particular set value of 1500 mV, the scan direction is reversed and the material that was oxidised in the outward excursion is

then reduced. Once the voltage is returned to the initial value, the experiment can be terminated. In conformity with normal practice, cathodic (reduction) current are shown as positive and anodic (oxidation) current as negative.

Figure 3-6: Polarographic system for zinc concentration measurement

Figure 3-7: Stainless steel working electrode.

The calibration curve was plotted using the current recorded for 15 mL of up to 11 standard solutions at a pH maintained at 3 using 0.1 mol/L of acetic acid for acidic electrowinning and 0.05 mol/L with 0.1 mL of 4 mol/L NaOH for alkaline process. Both were run with a scan rate of 100 mV/sec. The calibration gives a straight line of the current, which is measured by polarographic system, as function of zinc

concentration. Acidic and alkaline calibration curves of zinc were obtained as shown in figure 3-8.

a

Current (mA)

y = 0.0035x + 1.2914
R² = 0.9876

mg/l Zinc

b

Current (mA)

y = 0.0003x + 0.0784
R² = 0.9875

mg/l zinc
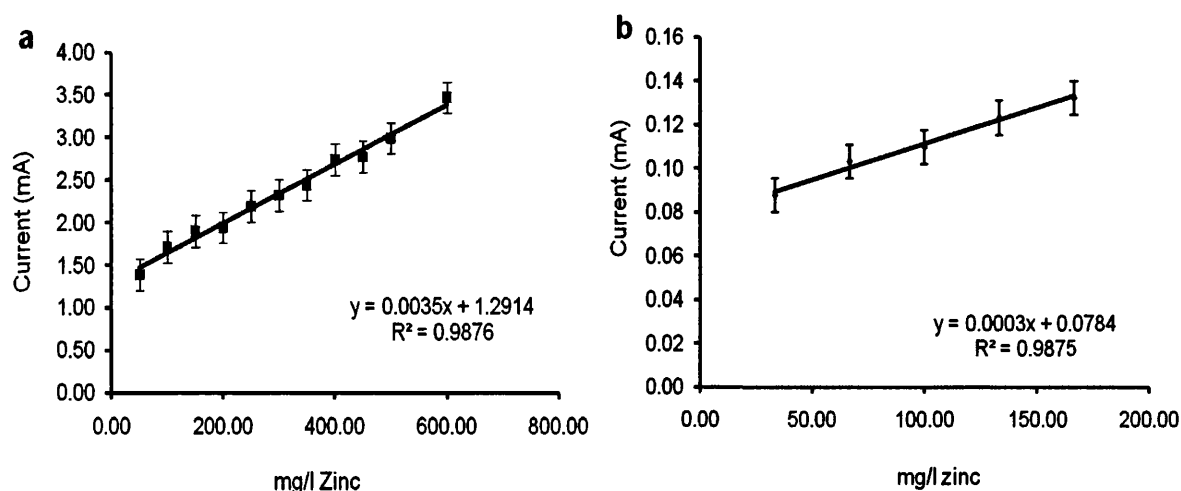
Figure 3-8: Zinc calibration curve cyclic voltammetry system with platinum auxallory electrode, Ag/AgCl standard and stainless steel working electrodes for a) acidic electrowinning and 0.1 mol/L acetic acid and b) alkaline electrowinning and 0.05 mol/L acetic acid.

3.3.2. The pH:

The pH level was measured with a combination pH electrode.

3.3.3. Calculations:

Calculations were carried using the Excel Spreadsheet Program. This was used for curve fitting, integration and other operations to provide data for graphs and diagrams. Current efficiency, (equation (5.2)) percent recovery, (equation (5.3)) and electrical energy, (equation (5.4)) are calculated using formulas presented in chapter 5. All constants, such as the electrochemical reaction constant and concentration/diafiltration constants were determined during this work. Details of the procedures undertaken are presented in chapters 4, 5 and 6 where appropriate. For stability analysis of data, three repetitions of the described experiments were performed and the arithmetic mean value reported with standard errors. The step of comparison of model predictions with experiments and determination of model

parameters are considered using best slop, best straight line and overall error for all points (Russell and Denn, 1972).

3.4. Modelling a Proposed Zinc Recovery Process:

The Zn recovery process proposed in this work is similar to that presented by Baticle et al. (2000), to recover nickel. As it can be seen in the diagram shown in figure 3-9, zinc effluent solution produced by the leaching unit is mixed with an aqueous solution of complexing polymer PEI at pH 5.5 in the reactor in the first step to form with the zinc ions present in the effluent. This process is countercurrent and the amount of zinc extracted depends on the type of zinc source and the equipment size. The complex solution obtained is filtered by an ultrafiltration membrane. The retentate obtained contains a Zn concentrate while the permeate is an effluent from which the metal has been removed and is recycled.

The retentate is then introduced in a second reactor under acidic conditions to de-complex zinc ions allowing separation and recycling the polymer in the retentate, while the permeate contains a concentrated Zn solution, the zinc solution is precipitated to form a Zn hydroxide this slurry that can then be introduced in the alkaline electrowinning cell to undergo electrochemical reduction. The main advantage of the alkaline electrowinning process is that only a small volume of solution needs to be treated by electrolysis, this solution having been obtained by the previous concentration of the initial volume from the membrane process.

Figure 3-9: Qualitative flow diagram for the recovery of the zinc metal

Experimental results of zinc PEUF and electrowinning were employed to construct models that predict the outcome of each unit when varying certain conditions. The models were also used to estimate each unit parameters optimum conditions as shown in chapters 4 and 5. From this point, an overall model was established for the zinc recovery process by establishing a mass balance around each unit and employing parameters from experiments and literature. The model is then used to perform a costs analysis of the system by varying extraction efficiency. The model is presented in chapter 6.

Chapter 4

4. BATCH MODE PEUF OF AQUEOUS SOLUTIONS OF ZINC

4.1. Introduction:

Membrane processes are considered to be one of the most important tools in the field of wastewater purification and reuse. This technology has several advantages in terms of low operative cost, conceptual simplicity, modularity and optimal quality of treated water. Furthermore, the ultrafiltration-complexation, (or polymer enhanced ultrafiltration, PEUF) has the ability to perform with high permeate flow-rate and high ion selectivity and economical feasibility for the separation of metal ions and complexes from solution (Molinari et al., 2004, Baticle et al., 2000, Geckeler, 2001).

The removal mechanism of metals via PEUF is based on the metal binding to the water-soluble polymer. Therefore, investigation of the complexation and decomplexation processes is necessary in order to understand the effect of varying process parameters on the retention of zinc metal. In this study it is assumed that the retention of a metal indicates the degree of complexation of metal by the polymer. However, this is a simplification and other mechanisms, such as the formation of metal oxide/hydroxide or the adsorption of metal onto the membrane, can interfere with the PEUF process (Juang and Liang, 1993a). This can happen if the pH is higher than 6.5 for most earth metals (Jones, 2005, Juang and Liang, 1993b). Metals could form insoluble hydroxides of sufficient size to be retained by the membrane, when the pH exceeds that value. Nevertheless, pH sensitivity of metal – polymer complexation can vary significantly between different metals. Based on the above, the control of pH is required to study the possibility of selectively binding metal ions (Jones, 2005, Baticle et al., 2000, Canizares et al., 2002, Juang and Liang, 1993a, Aliane et al., 2001, Trivunac and Stevanovic, 2006a, Trivunac and Stevanovic, 2006b). Consequently, experiments were performed to ascertain the retention characteristics of zinc metal during the ultrafiltration of aqueous zinc solution in the absence or presence of the polymer.

Two important factors to consider when selecting polymer type are: successful complexing and decomplexing of the metal ions and the ability to regenerate without excessive polymer damage. Poly(ethylenimine), PEI provides a good complexation

performance because it contains a high density of functional groups, good water-solubility, and metal selectivity (Jones, 2005). Based on this, PEI was chosen for the experimental work reported in this thesis.

The following section presents the results of varying pH and zinc content on metal retention within PEUF. Determination of binding constants and optimum conditions were also considered using metal retention data from batch mode experiments and the permeate produced from this stage will be a concentrated metal ion solution suitable for recovery of metal by electrowinning and/or other techniques with the consideration on technical and economical feasibility, (see chapter 6).

4.2. The Effect of pH on Metal Retention:

The effect of pH on the retention of characteristics in zinc solutions in the presence and absence of PEI was investigated in the Amicon filtration cell (Figure 3-2). The filtration experiment was run to allow a 10 ml sample of the permeate to be collected. This was then analysed for zinc content. The difference between the Zn added and that in the permeate was deemed to be retained by the membrane. The amount of zinc retained as function of pH is plotted in figure 4-1.
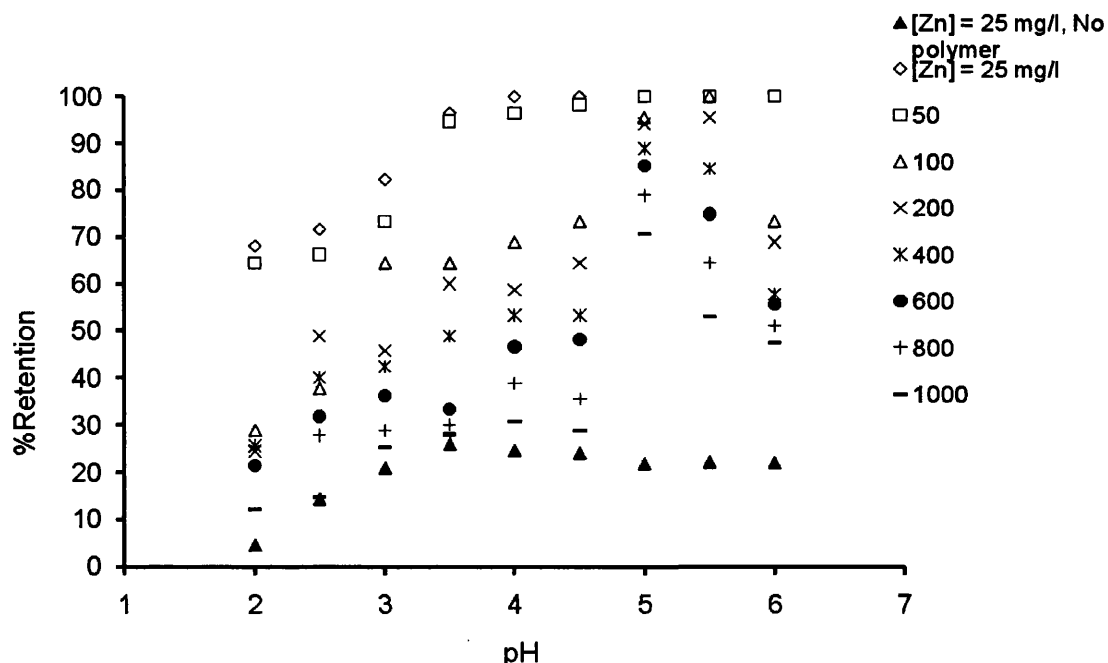
Figure 4-1: The effect of pH on zinc retention at different of zinc concentration. Experimental conditions were: 1 g/L PEI concentration, temperature = 25 °C, pressure = 30 psi and stirrer speed = 300 rpm.

In the absence of polymer there was some Zn retention observed, from 2 up to 25% depending on pH. This indicated that Zn^{2+} interacts with the membrane at low pH values. This membrane has an isoelectric point at a pH of 3.9 (Almutairi, 2008), and is negatively charged above this pH, clearly Zn is rejected at a pH above 4. Another factor concerning the adsorption of metal onto the membrane may take place due to the ionic strength of the solution.

Using PEI at 1 g/L, retention of the Zn^{2+} increases considerably over that in the absence of PEI, indeed at low concentrations (25 mg/L) it is retained at over 95% over a wide range of pH. Only at very low pH does the retention fall off to 60%. This is attributed to the binding of the Zn to the polymer. At higher concentrations of Zn the retention becomes more dependent on pH and optimal binding is seen at a pH between pH 5 and 5.5. This phenomenon can be explained firstly by the limited binding capacity of the PEI at very acid pH and that this increased considerably at higher pH. However, even this improved capacity is saturated at very high Zn additions. For example using 1000 mg/L results in only 65 % at pH 5 while at the same pH 100 mg/L is retained at 95%

It can also be concluded from this data that the presence of PEI had a maximum binding for Zn at pH 5.0-5.5. The capacity of the polymer to bind Zn is finite and becomes saturated at high Zn concentrations, so retention of Zn^{2+} decreases when increasing the concentration of zinc above these saturation levels. To increase the capacity of the system the polymer concentration would have to be increased.

4.3. Metal Absorption Characteristics:

Using the data generated in figure 4-1, the binding capacity of the system can be determined. Maximum capacity of the polymer for zinc ions, Q_{max} and the dissociation constant, K_L in Langmuir isotherm equation, (see equation (2.15)) is calculated using experimental data. The results obtained from the plot of the linearised form of the Langmuir isotherm for the batch mode data are presented in figure 4-2. All values of Q_{max} and K_L were calculated and tabulated in table 4-1. Most of the values of the coefficients resulted from a set of relationships with correlations, R^2, of above 0.9 for linear regression of data fitted to the Langmuir isotherm. The validity of the model was examined by plotting experimental and

calculated zinc bound using the Langmuir equation vs. mg of zinc per L of permeate solution and this provided good a match as shown in figure 4-3.
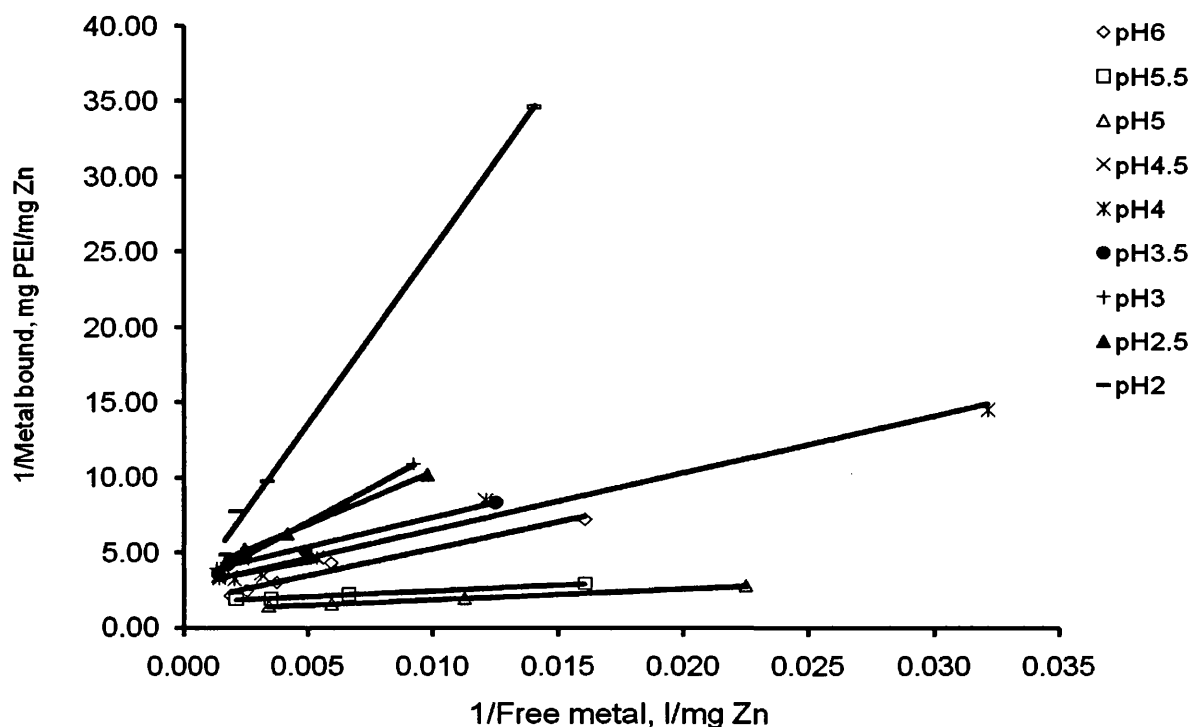
Figure 4-2: Langmuir isotherm analysis for zinc ultrafiltration at various pH values. The symbol represent practical data obtained while the line are the linear regression fits (table 4-1) presents the nuemrical data of these fits

From figure 4-3 and table 4-1 the binding capacity is pH dependent and in these simple systems the binding characteristics are determined by mixture of chelation and possible ionic interactions at acid pH. However, the binding constant is highest at pH 5.5 and lowest at pH 2.5. Above pH 5.5 the binding constant also increases. Above pH 7.0 precipitation of Zn hydroxides becomes significant (Jones, 2005). Therefore, this work was conducted by varying pH up to the maximum values of 6.

At very low pH the hydrogen ions out-compete Zn for the sites on PEI. This data provide the basis for describing Zn absorption and desorption on PEI and were used to relate the amount of metals binding as a function of polymer concentration and pH.

Table 4-1: Summary of data fits to binding isotherms to data acquired during batch mode polymer enhanced ultrafiltration experiment for solution of zinc metal, (see figure 4-3)

pH	Equation	R^2	Q_{max} , mg$_{Zn}$/mg$_{PEI}$	K_L, mg/L
2	$1/Q = 2328.9x \ 1/C_{iu} + 1.906$	0.997	0.424	987.24
2.5	$1/Q = 699.43x \ 1/C_{iu} + 3.383$	0.998	0.296	206.75
3	$1/Q = 433.28x \ 1/C_{iu} + 4.1095$	0.912	0.243	105.43
3.5	$1/Q = 430.02x \ 1/C_{iu} + 3.2816$	0.993	0.305	131.04
4	$1/Q = 374.13x \ 1/C_{iu} + 2.5063$	0.995	0.366	129.62
4.5	$1/Q = 308.58x \ 1/C_{iu} + 2.8622$	0.810	0.366	129.62
5	$1/Q = 73.45x \ 1/C_{iu} + 1.1511$	0.998	0.869	63.81
5.5	$1/Q = 28.908x \ 1/C_{iu} + 2.036$	0.962	0.491	14.20
6	$1/Q = 356.69x \ 1/C_{iu} + 1.6718$	0.978	0.598	213.36
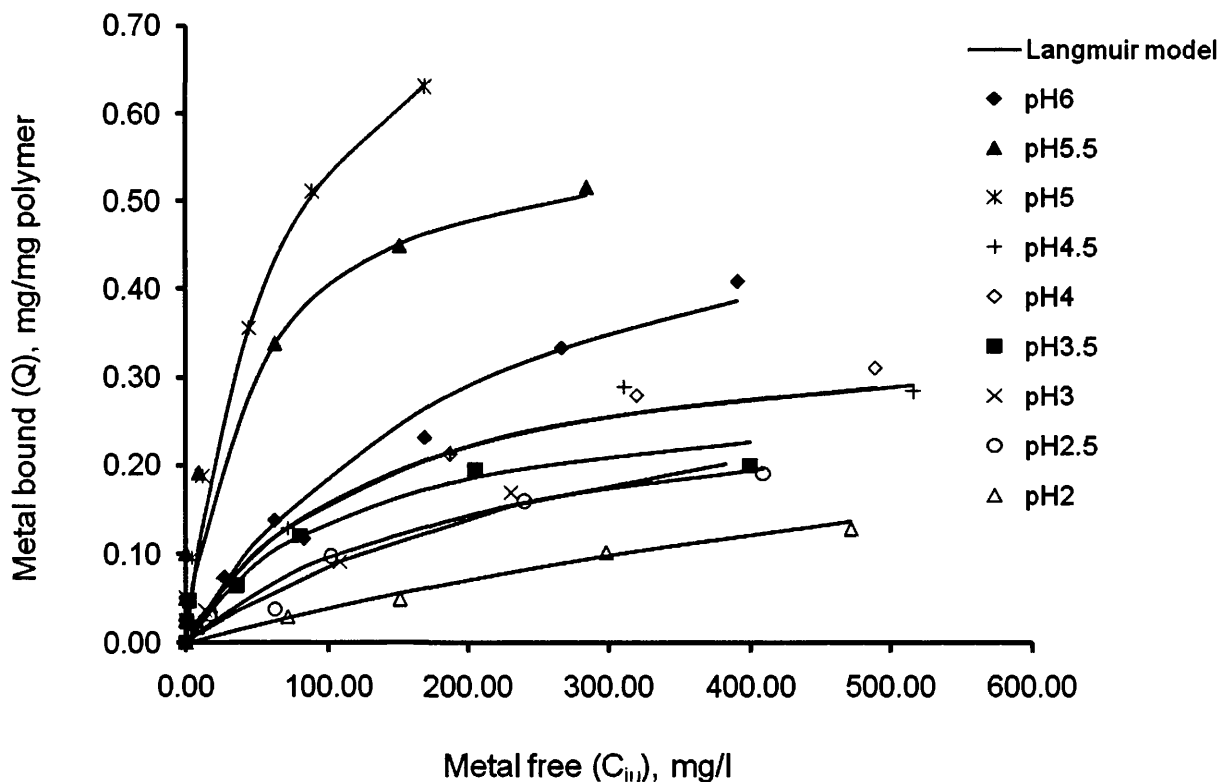
Figure 4-3: Experimental and calculated zinc binding isotherms as a function of pH using equation (2.17). The values of the Langmuir constant were as listed in table 4-1.

The coefficients employed in this work were obtained at relatively high zinc concentration intervals. This means most of the polymer active sites would be occupied by zinc ions in the complexation step. Therefore, the amount of zinc complexed during the filtration process could be determined in order to estimate the capacity of the polymer at that concentration level using the retention-pH relationship. Hence, the coefficient obtained at the high zinc concentration range provided a higher polymer capacity, when comparing it to one of lower concentration range (Jones, 2005, Almutairi, 2008). The data from samples at pH 5.5, (see figure 4-1) suggests a capacity of 0.1051 mg Zn^{2+}/mg PEI at pH 5.5.

4.4. Process Modeling:

The section above discusses the complexing ability of PEI with zinc ions and the rejection conditions of solution pH and zinc content of such a complex. However, it is required to optimize operation variables and suitable permeate flux that results in maximum membrane productivity. This section presents the modelling procedures to attain specified zinc concentrations and separation using mathematical models of a batch PEUF system.

4.4.1. Membrane Flux:

It is important to provide an equation, or set of equations, that allows the prediction from first principles of the membrane permeation rate and solute rejection for a given real separation. One of the objects in this chapter is to provide such a prediction for model systems, although the physical properties of real systems, both the membrane and the solute, are potentially complex. The general membrane equation is an attempt to state the factors which may be important in determining the membrane permeation rate for pressure driven processes. This can be written as following:

$$J = \frac{|\Delta P|}{\mu(R_m + R_c)}$$

(4.1)

where J is the membrane flux, expressed as volumetric rate per unit area, m^3/m^2.hr, $|\Delta P|$ is the pressure difference applied across the membrane, kg/m^2 (or atm), R_m is the resistance of the membrane, m^{-1}, and R_c is the resistance of layers deposited on the membrane or cake resistance, the filter cake and gel foulants, m^{-1}. If the

membrane is only exposed to pure solvent, for example water, then equation (4.1) reduces to:

$$J = \frac{|\Delta P|}{\mu(R_m)}$$

(4.2)

The resistance of the cake R_c, which if all filtered particles remains in the cake, may be written as:

$$R_c = \frac{rV_f C_b}{A}$$

(4.3)

where r is the specific resistance of the deposit, V_f is the total volume filtered, C_b represents the bulk concentration of particles in the feed (particle volume/feed volume) and A is the membrane area. Combining equations (4.1) and (4.3) gives:

$$J = \frac{1}{A}\frac{dV_f}{dt} = \frac{|\Delta P|}{(R_m + rV_f C_b / A)\mu}$$

(4.4)

The solution of the above equation for V_f at constant pressure gives:

$$\frac{t}{V_f} = \frac{R_m \mu}{|\Delta P|A} + \frac{C_b r \mu V_f}{2|\Delta P|A^2}$$

(4.4)

and yields a straight line on plotting t/V_f against V_f. The slope $(C_b r\mu /2|\Delta P|A^2)$ is the filtration resistance of the gel or cake and the intercept is a function of the membrane resistance.

Several pure water runs were performed at different pressures and the flux plotted against pressure as shown in figure 4-4. From this a membrane resistance was calculated using equation (4.2) and was found to be 1.8038×10^{12} m^{-1} under these experimental conditions. However, the membrane value supplied by the manufacturer was 4.00×10^{12} m^{-1}.

Several experiments were then set up over a range of pressure from 5 to 30 psi and polymer concentrations from 1 to 20 g/L at 25 $^\circ$C and 300 rpm. The permeate flux values were estimated by specifying the membrane surface area of 13.4 cm^2 and

measuring the permeate flow rate. Hence it was required to measure the volume collected as a function of time and calculate the cake resistances at different applied pressures. Values of the calculated cake resistances as a function polymer concentration are presented in table 4-2.
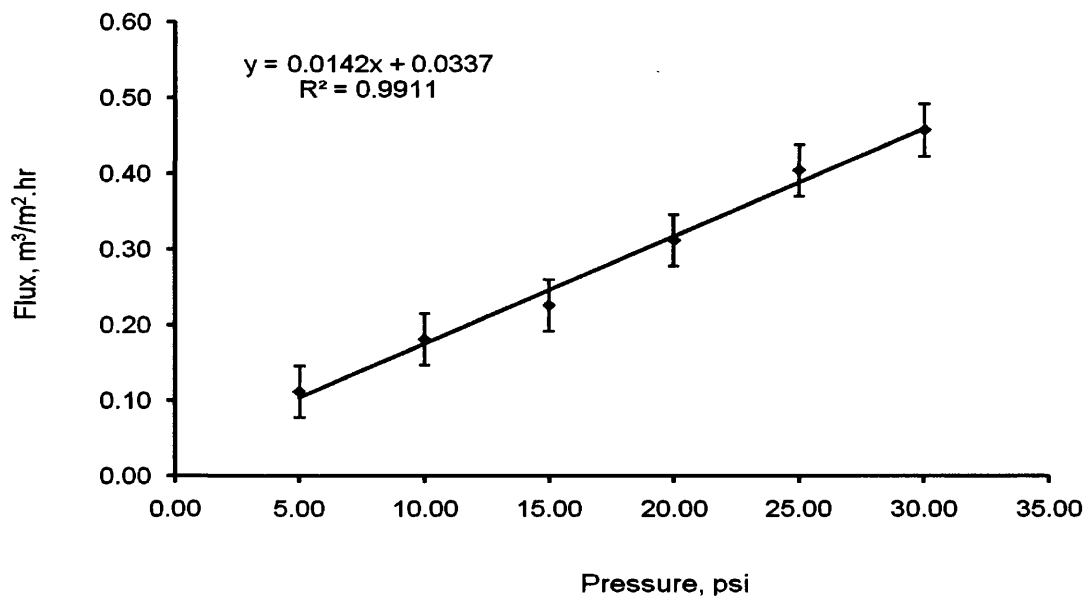
Figure 4-4: Flux behaviour as a function of operating pressure values for pure water at 25 °C, pH 5.5 and 300 rpm stirrer speed.

It can be seen from table 4-2 that cake resistance dramatically rises when increasing the applied pressure from 5 to 20 psi. However, the resistance was less affected, when increasing the pressure from 25 to 30 psi at higher PEI concentrations than 10 g/L. The resistance at PEI concentrations of 10, 15 and 20 g/L were not affected at higher pressure values than 5 psi. This is likely due to the concentration polarization becoming a controlling factor, as a cake layer develops.

Figure 4-5 presents the effect of applied pressure on the permeate flux rate. It is clear that the effect of pressure on flux is dominant at low polymer concentration. It was estimated that permeate flux reduces from 0.112 $m^3/hr.m^2$ for pure water to 0.091 $m^3/hr.m^2$ when polymer concentration was 1 g/L at an applied pressure 5 psi was reduced by a factor of 1.23. However, the flux increases with increasing pressure

from 0.091 $m^3/hr.m^2$ at 5 psi to 0.215 $m^3/hr.m^2$ at 30 psi, (by factor of 2.36), at PEI concentration of 1 g/L.

Table 4-2: Summary of cake resistance values as a function zinc-PEI concentration at 25 °C, pH 5.5 and polymer capacity of 0.1051 with various pressure drop values and [PEI] concentrations.

[PEI], g/L	Cake resistance $(R_c) \times 10^{+11}$, m^{-1}					
	ΔP = 5psi	ΔP = 10psi	ΔP = 15psi	ΔP = 20psi	ΔP = 25psi	ΔP = 30psi
1	0.57	1.89	5.59	7.49	9.45	11.34
2	0.75	3.78	8.52	14.99	18.70	22.50
4	1.88	7.57	15.68	22.63	28.38	33.61
6	2.82	11.30	19.87	26.48	37.85	45.48
10	9.39	37.53	56.46	75.65	94.44	113.28
15	18.83	37.58	56.37	75.27	94.29	113.73
20	18.78	37.53	56.40	75.45	95.29	112.42
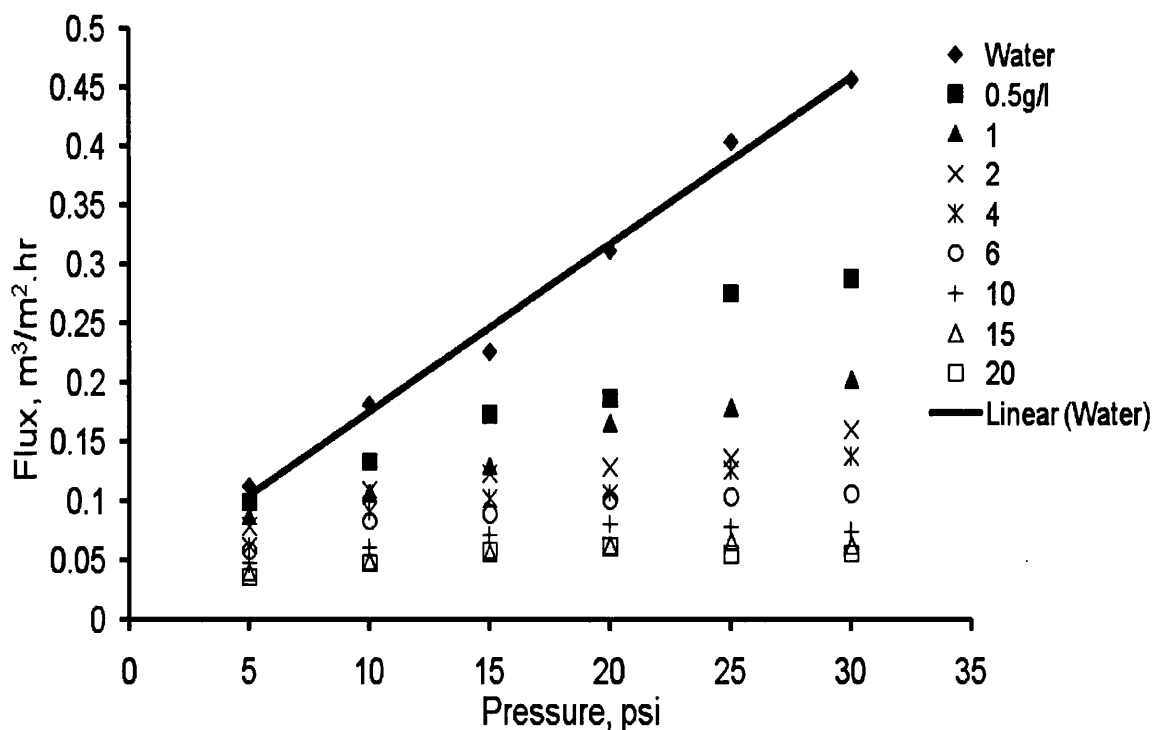
Figure 4-5: The effect of pressure on membrane flux at different polymer concentrations.

As the polymer concentration is increased the effect of pressure on flux is reduced and at high concentrations of polymer (>10 g/l) the flux is almost independent of pressure. This indicates the cake layer is now controlling the flux. This could be reduced by increasing the tangential velocity of fluid flow over the membranes surface i.e. stirrer rate.

Deviation from the linear flux-concentration relationship can be observed at higher pressure regardless of the other operating conditions. This is due to the consolidation of the cake layer of polymer. Therefore, the flux is independent of applied pressure and can clearly be observed when the feed concentration was above 6 g/L.

Using the data obtained, the flux can be calculated and plotted against the pressure. The resistance parameters were applied in equation (4.1) and the data from the model were plotted and compared with the experimental data, (see figure 4-6). From this figure, experimental and theoretical results gave a reasonably good fit for each case. Also, the flux was decreasing when increasing the PEI concentration due to increase in the cake thickness.
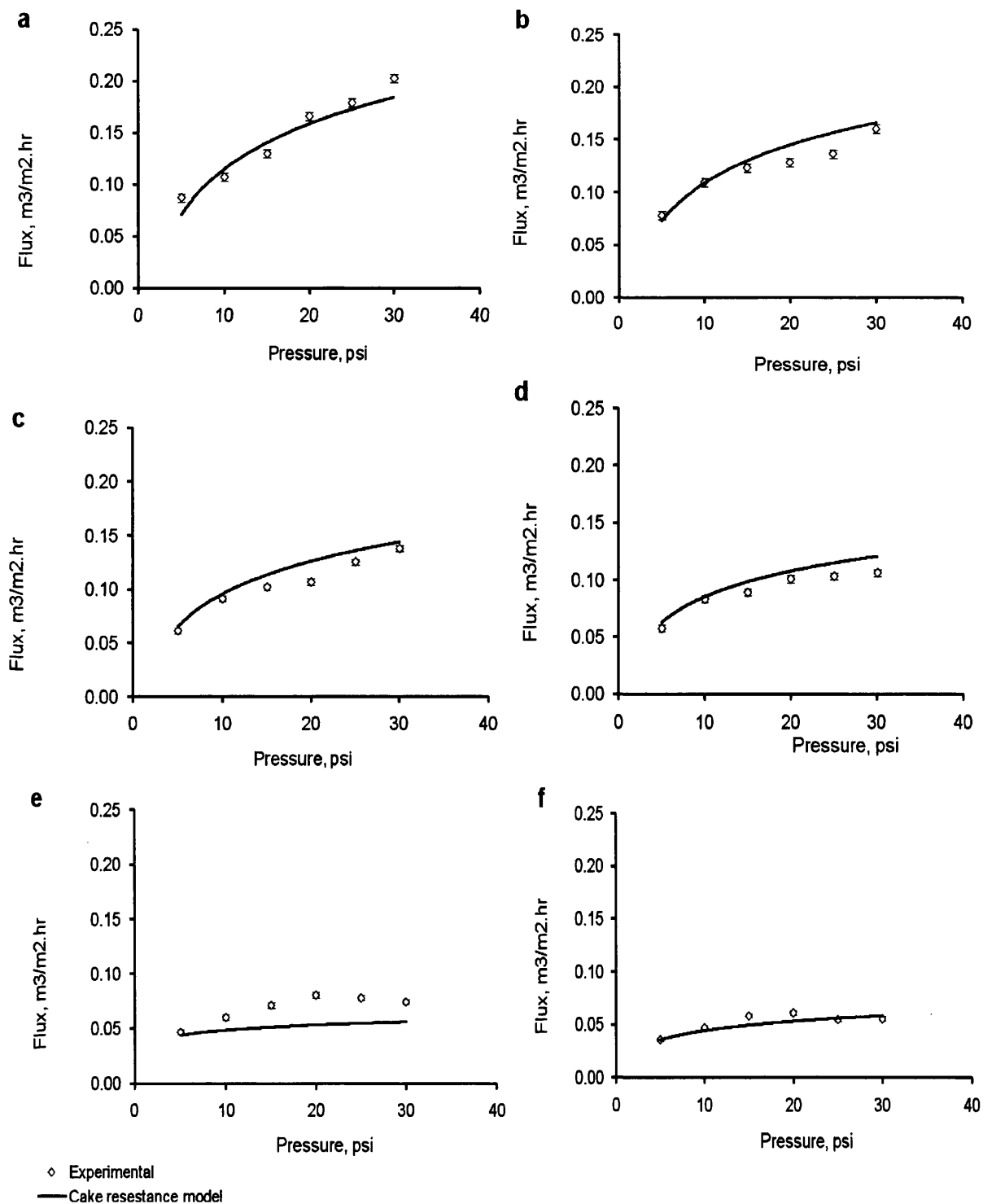
Figure 4-6: A comparison between experimental and calculated flux, (using equation.(4.1)) as a function of applied pressure at different PEI concentrations. Values of cake resistances were obtained from table 4-2. The analysis was performed at constant pH of 5.5, polymer capacity = 0.1051 mg Zn^{2+}/mg PEI, 25 ° C temperature and initial PEI concentrations of a) 1 g/L, b) 2 g/L, c) 4 g/L, d) 6 g/L, e) 10 g/L and f) 20 g/L.

4.4.2. Cake Resistance-Polymer Concentration Model:

Further elaboration of the flux model can be achieved by defining the relationship between cake resistance, polymer concentration and pressures. Therefore, several experiments were set up at different pressures (from 5 to 30 psi) and polymer concentrations (from 1 to 100 g/L), to estimate the permeate flux values. The results of cake resistance obtained were then plotted against polymer concentration values in figure 4-7. It can be seen from figure 4-7 that the relationship can be defined by a second order polynomial. Equations representing these relationships are listed in table 4-3 for different pressure.

From these results, it was possible to predict the membrane flux over a wide range of operating conditions where the model will be valid. This could be done by plotting calculated flux, using the cake-polymer concentration relationship combined with equation (4.1), and experimental flux versus applied pressure as shown in figure 4-8.
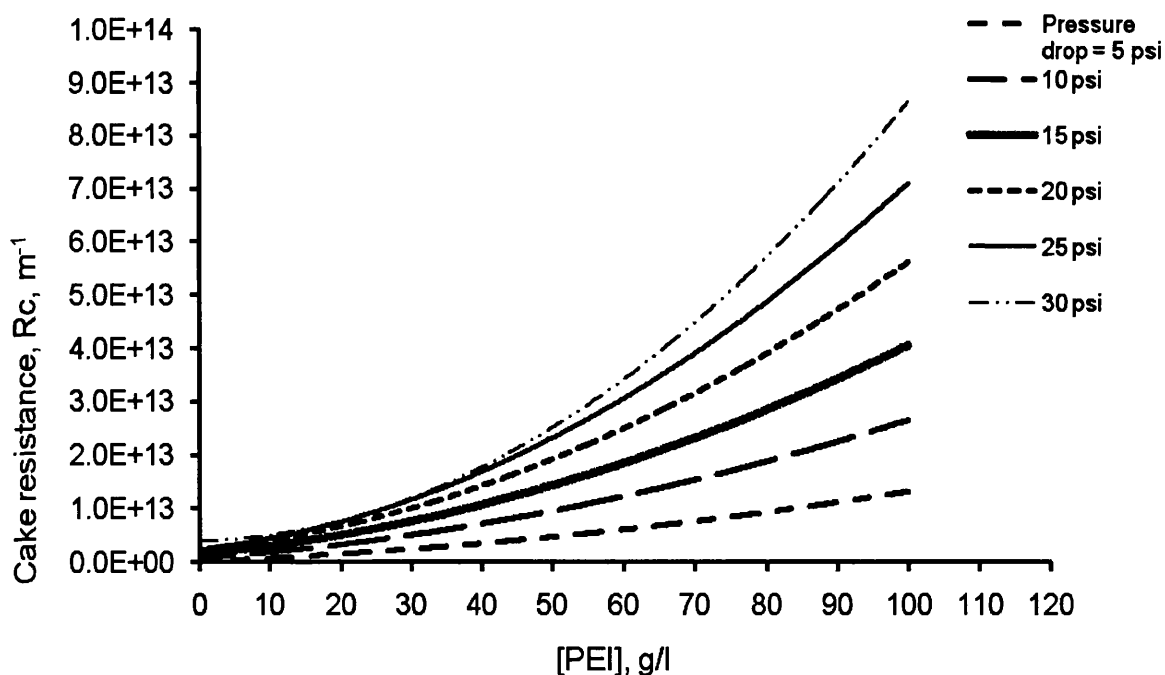
Figure 4-7: The effect of polymer concentration on cake resistance for various operating pressures at 20 o C and 300 rpm.

Table 4-3: Cake resistance-polymer concentration relationships obtained from figure 4-10 for various operating pressure.

Pressure, psi	R_c-[PEI] relationship	R^2	Equation order
5	$R_{c, 5} = 8E+08\text{x}[PEI]^2 + 5E+10\text{x}[PEI] + 2E+11$	0.986	2nd
10	$R_{c, 10} = 2E+09\text{x}[PEI]^2 + 1E+11\text{x}[PEI] + 7E+11$	0.982	2nd
15	$R_{c, 15} = 3E+09\text{x}[PEI]^2 + 1E+11\text{x}[PEI] + 1E+12$	0.981	2nd
20	$R_{c, 20} = 4E+09\text{x}[PEI]^2 + 1E+11\text{x}[PEI] + 2E+11$	0.982	2nd
25	$R_{c, 25} = 5E+09\text{x}[PEI]^2 + 2E+11\text{x}[PEI] + 3E+12$	0.980	2nd
30	$R_{c, 30} = 8E+09\text{x}[PEI]^2 + 2E+10\text{x}[PEI] + 4E+12$	0.961	2nd

It can be seen from figure 4-8 that the flux calculated using this approach improved the fitting to the experimental flux. Hence, the cake resistance-PEI concentration relationship was employed to study the effect of pressure drop and polymer initial concentration; on permeate flux, permeate volume and polymer concentration with respect to time within the conditions of pressure and polymer concentration.
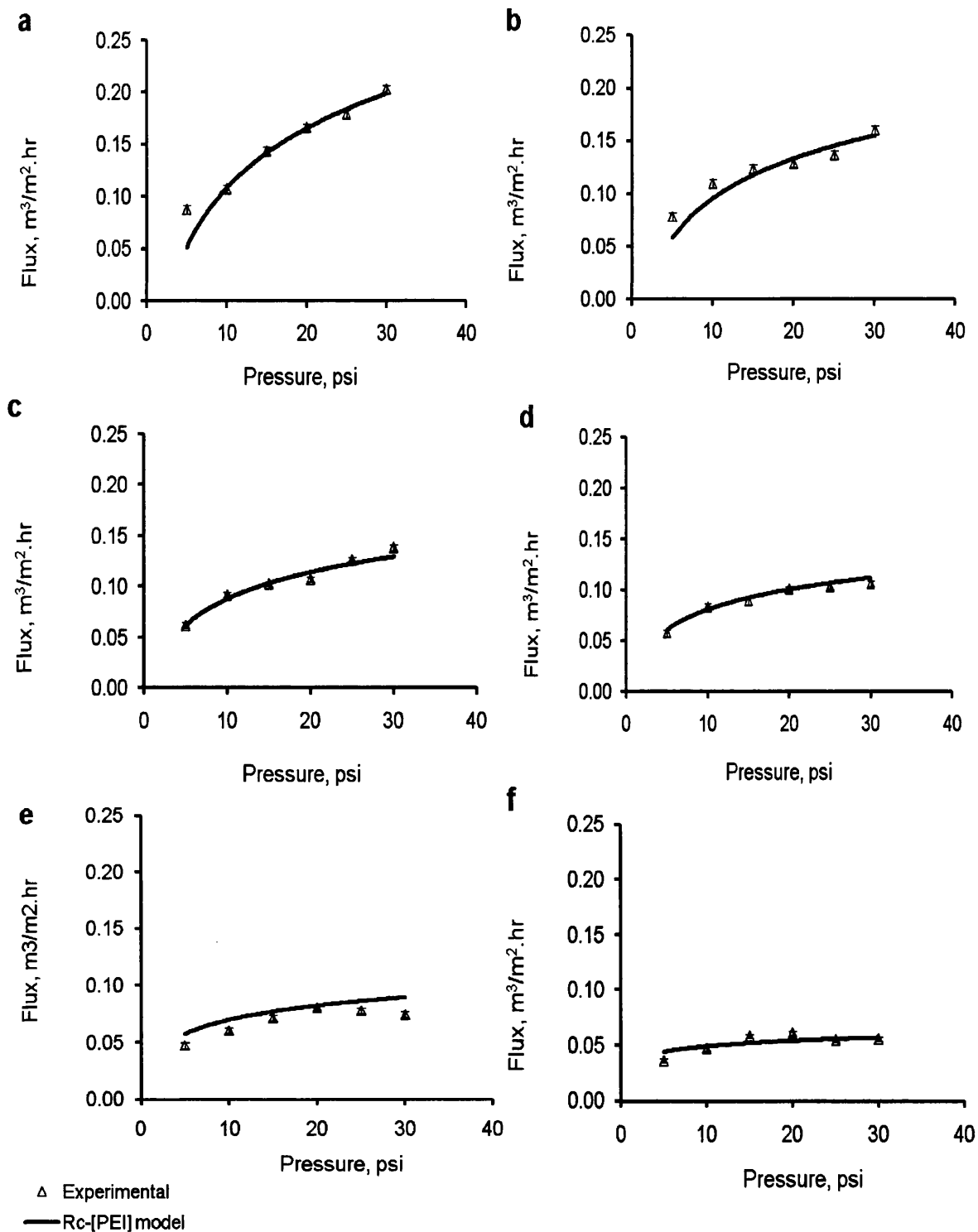
Figure 4-8: A comparison of the experimental and calculated flux, (using both cake resistance-polymer concentration relationship and equation.(4.1)) as a function of applied pressure and PEI concentration. Initial PEI concentrations of a) 1 g/L, b) 2 g/L, c) 4 g/L, d) 6 g/L, e) 10 g/L and f) 20 g/L. The analysis was performed at constant pH 5.5, polymer capacity = 0.10 mg Zn^{2+}/mg PEI and 25 °C temperature.

4.5. Diafiltration Process:

To concentrate and purify the absorbed materials a diafiltration process was investigated. This technique can be used to remove unabsorbed extraneous materials in a washing operation or to remove decomplexed ions in the regeneration of the polycheatogen. The process in this case consists of a concentration step followed by re-dilution with water and re-ultrafiltration in repetitive steps to bring about dilution and or purification as shown in figure 4-9.
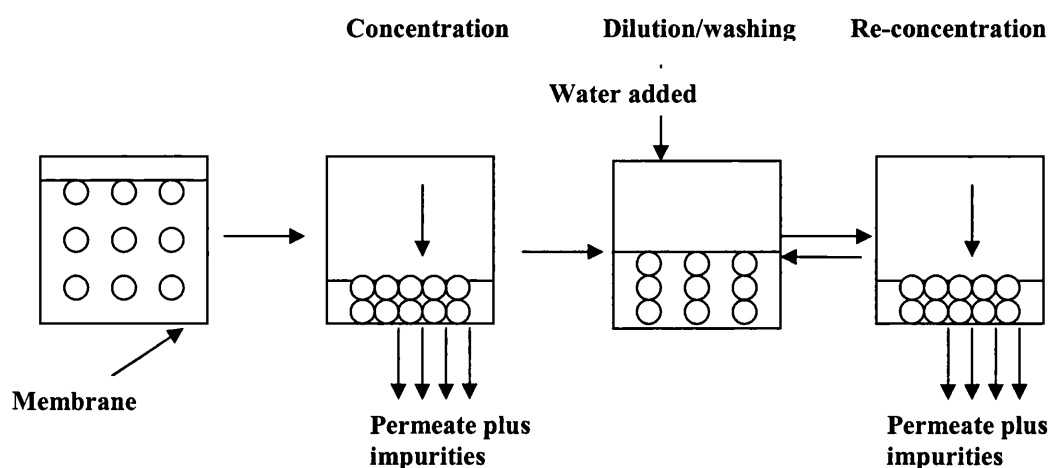
Figure 4-9: A summary of steps in a Diafiltration process.

The effect of design parameters of such a system was investigated in order to evaluate the optimum conditions. Two criteria were considered important; 1) to produce high recovery and purity of the metal and 2) to produce a high concentration of zinc in the permeate solution.

The calculation of the amount of free zinc concentration is equal to the amount of zinc flow out of the system divided by amount of water added to the system. Concentrations of zinc liberated from the polymer after complexation and decomplexation steps were calculated using Langmuir relationship and equation (2.16) can be rearranged to yield:

$$C_{iu} = \frac{QK_I}{Q_{max} - Q}$$

$$(4.6)$$

where C_{iu} is the amount of free zinc in solution, mg/L, K_I is dissociation constant, mg/mL, Q is the amount of metal complexed, mg metal/mg polymer and Q_{max} is the maximum capacity of polymer, mg metal/mg polymer.

Values of K_I and Q_{max} were obtained from table 4-1 at pH 5.5, for zinc complexation, and pH 2.5, for decomplexation. Therefore, the amount of HCl required to reduce the pH to 2.5 of 40 ml of 2 g PEI/L was 2.8 mL using figure 3-5 presented in Chapter 3.

The permeate flux was calculated using equation (4.1). Values of cake resistance were obtained using the R_c-[PEI] relationships listed in table 4-3 at different operating pressures. The effect of important design parameters: the operating pressure and the initial polymer concentration; were then investigated for the diafiltration process. Each step will be discussed individually in the following sections.

4.5.1. The Prediction of Filtration to Concentrate PEI-Zn Complex Solution:

After achieving the complexation of metal on the polymer, the effect of pressure, initial volume and initial polymer concentration was investigated with the filtration model. The permeate flux, permeate volume and polymer concentration were calculated as a function of time. All calculations of this model were performed using a MS Excel spreadsheet.

4.5.1.1. The Effect of Operating Pressure on the Filtration and Concentration of Zn-PEI Complex Solution:

The results of the effects of applied pressure on permeate flux, retentate volume and polymer concentration are shown in figures 4-10, 4-11 and 4-12.

In figure 4-10, the expected effect of applied pressure on retentate volume was observed. The volume decreased sharply with time for each pressure drop. However, it takes a longer time to filter the same amount of feed volume of 250 mL polymer-

zinc solution when at low pressure i.e. 210 min to filter 82%, (200 mL) of the solution at 5 psi and 43 min to filter similar amount at 25 psi.
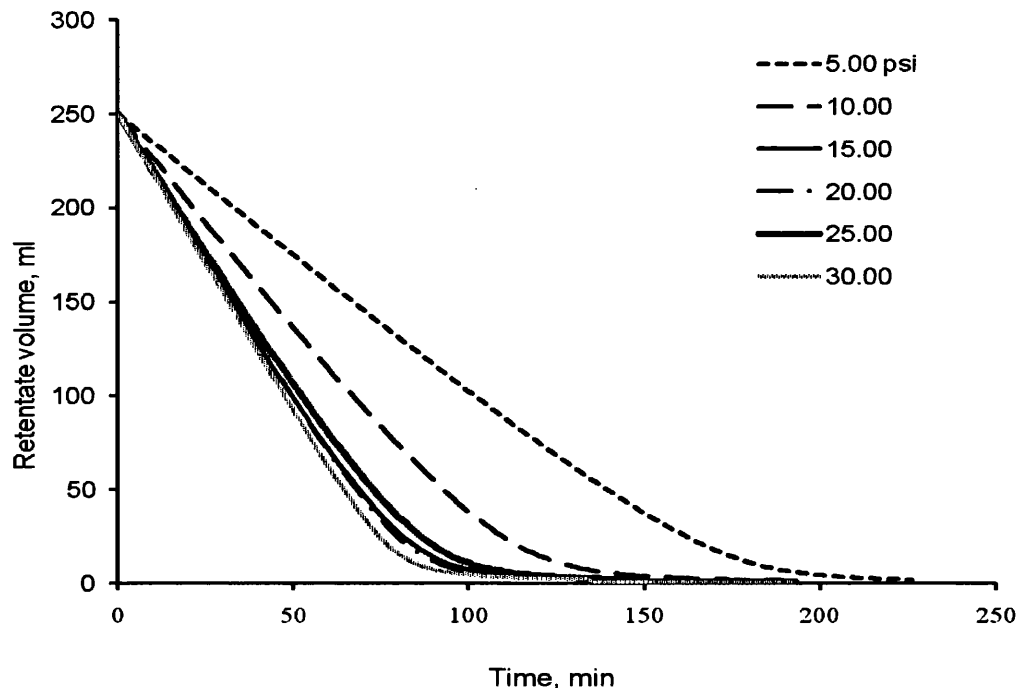
Figure 4-10: The effect of pressure on the retentate volume for the concentration of 2 g/L PEI initial concentration at pH5.5, polymer capacity = 0.1051 mg Zn^{2+}/mg PEI, 25 ° C, 300rpm. Initial feed volume = 250 mL and membrane area = 0.00134 m^2

Figure 4-11 plots the permeate flux as a function of time for different concentrations of PEI. The pattern of flux is that it remains fairly constant for an initial period followed by a rapid decline when the concentration of the polymer increases rapidly. At this point, permeate flux was thought be controlled by the cake layer of the polymer at the membrane surface. The time required before reaching the cake control zone becomes shorter with increasing applied pressure (and therefore increased flux). For example, the flux of permeate maintained at 0.095 m^3/m^2.h at the first 95 min and 0.192 m^3/m^2.h at 42 min at 10 and 20 psi respectively before the flux started to decline.

Figure 4-11 also shows that the permeate flux increased with increasing pressure but there were only slight increase above 15 psi as previously observed in the practical

experiments (figure 4-5). The amount of flux was estimated to be 0.048 m^3/m^2.h at 5 psi and 0.129 m^3/m^2.h at 20 psi.
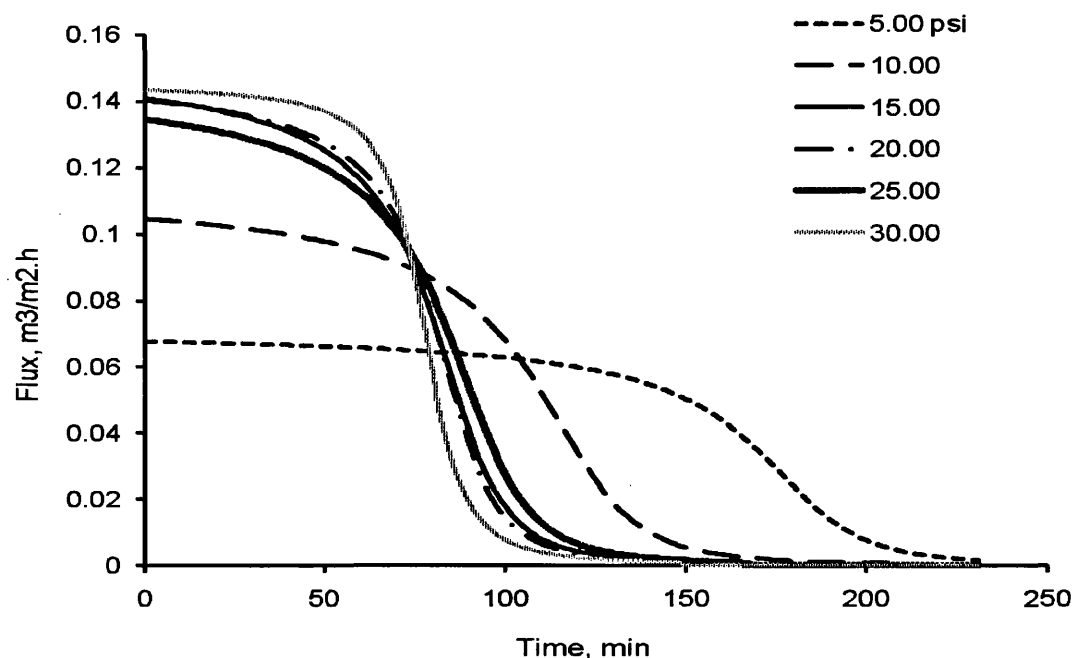
Figure 4-11: The effect of pressure on the permeate flux profile for a concentration of 2 g/L PEI at pH 5.5. The polymer capacity = 0.1051 mg Zn^{2+}/mg PEI at 25 ° C and 300 rpm. Initial feed volume = 250 mL and membrane area = 0.00134 m^2.

The polymer concentration was also calculated during the filtration and is presented in figure 4-12.

The polymer concentration initially increased slowly with time but then increased in an apparent linear fashion. This, however is not a simple relationship but is a combined function of the decreasing permeate flow rate and the increase in concentration of PEI

Results suggested running the unit as long as values of the flux for each pressure value remain constant. When flux starts declining, then concentration polarization controls the flux. It would seem that concentrations above 50 g/L are possible but 100 g/L are not feasible, (see table 4-4).
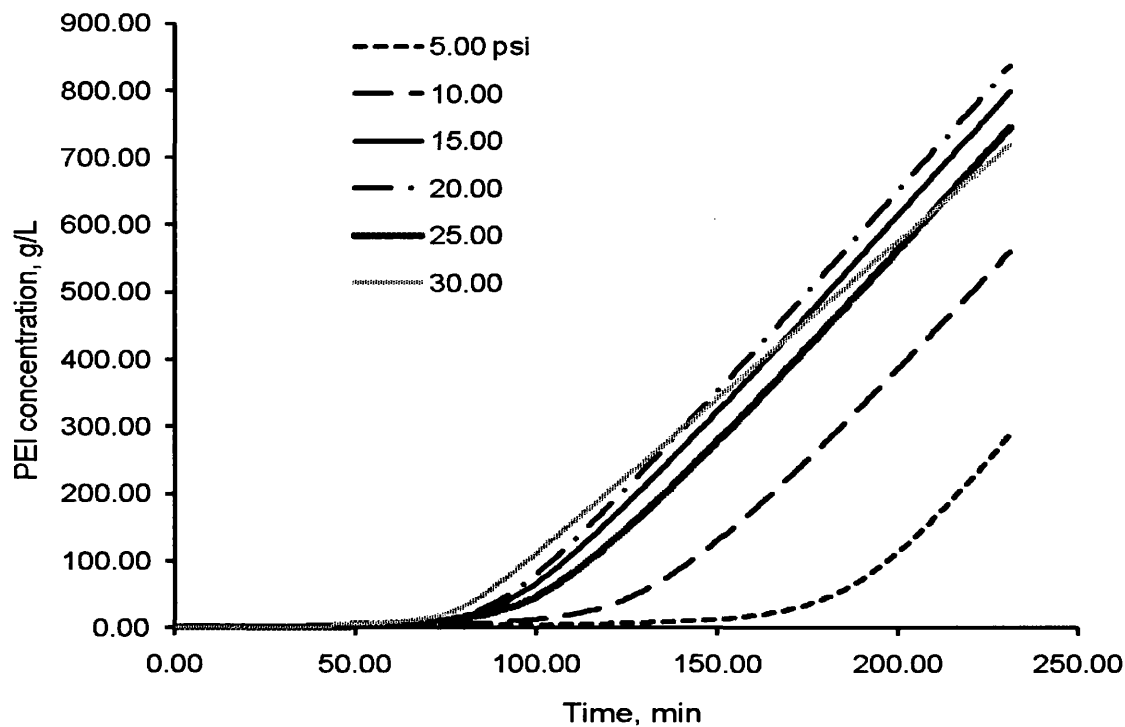
Figure 4-12: A simulation of the effect of operating pressure on concentration of PEI at pH5.5, polymer capacity = 0.1051 at 25 °C and 300 rpm. Initial feed concentration was 2 g/L, feed volume was 250 mL and membrane area = 0.00134 m^2

Table 4-4: The effect of pressure on estimated final polymer concentration before reaching cake limited flux. Initial concentration 2 g PEI/L at various operating pressure. Initial feed volume = 250 mL and membrane area = 0.00134 m^2.

Pressure, psi	Flux, m^3/m^2.h	Time required, min	Final PEI concentration, g/L
5	0.050	150	13.32
10	0.064	103	16.69
15	0.081	78	16.25
20	0.092	75	14.60
25	0.104	70	8.93
30	0.138	48	5.25

4.5.1.2. The Effect of Initial Concentration of Polymer on Filtration

The effect of initial polymer concentration on filtration performance was investigated further using the model response of flux, retentate volume and polymer concentration profiles. Based on the results discussed in the previous section, the effect of initial concentration was performed at 20 psi. Figure 4-13 shows the results of the simulation. The flux showed little change when an initial concentration of 1 and 2 g/L were used at the early stage of the process, (0.144, 0.140 $m^3/m^2.h$ up to 65 and 66 min respectively). However, the flux sharply declined as the polymer concentration increases towards the end of the concentration. At 2 and 4 g/L, the declined in flux increased with time and this might lead the process to operate under cake limitation control.
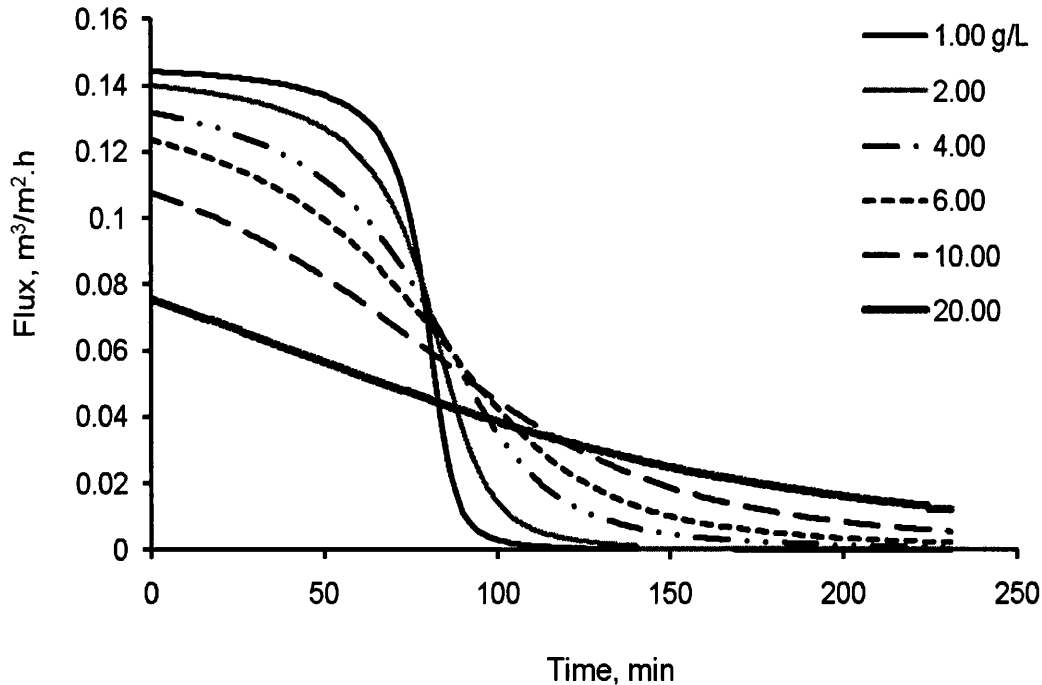
Figure 4-13: The effect of PEI concentration on permeate flux for concentration PEI at pH5.5, polymer capacity = 0.1051 mg Zn^{2+}/mg PEI, 20 psi pressure, 25 ° C and 300 rpm. Initial feed volume = 250 mL and membrane area = 0.00134 m^2.

The time required to reduce the volume of PEI solutions as a function of their initial concentration are presented in figure 4-14. Thus, the time to concentrate a volume of

the PEI solution by a factor of 10 increases with initial PEI concentration, for example, about 75 min for 1 g/L to >250 min for 20 g/L.
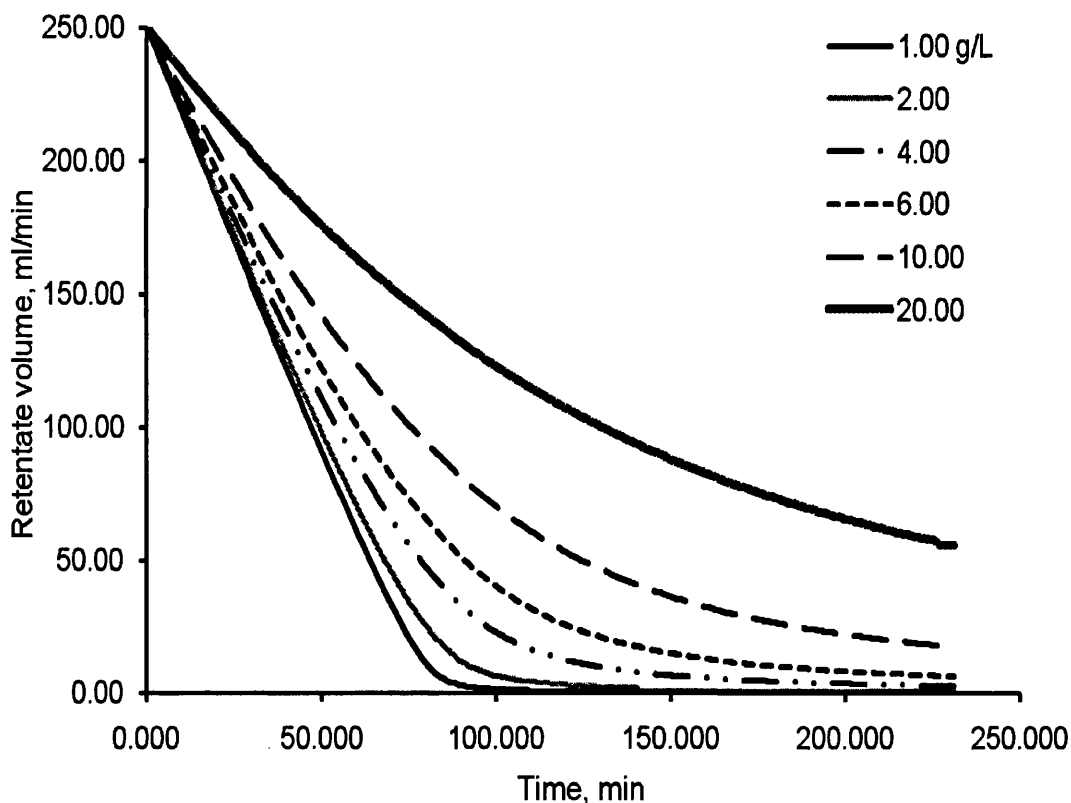
Figure 4-14: Permeate volume for concentration step of various PEI initial concentrations at pH 5.5, polymer capacity = 0.1051 mg Zn^{2+}/mg PEI, 20 psi pressures, 25 °C and 300 rpm. Initial feed volume = 250 mL and membrane area = 0.00134 m^2.

The effect of initial polymer concentration on the concentration profiles of PEI within the retentate as a function of time is shown in figure 4-15. Clearly the concentrations move to impossibly high concentrations at the end of these filtration processes. Clearly realistic concentrations should be in the 50 -100 g/L range above which filtrations would be relatively slow.
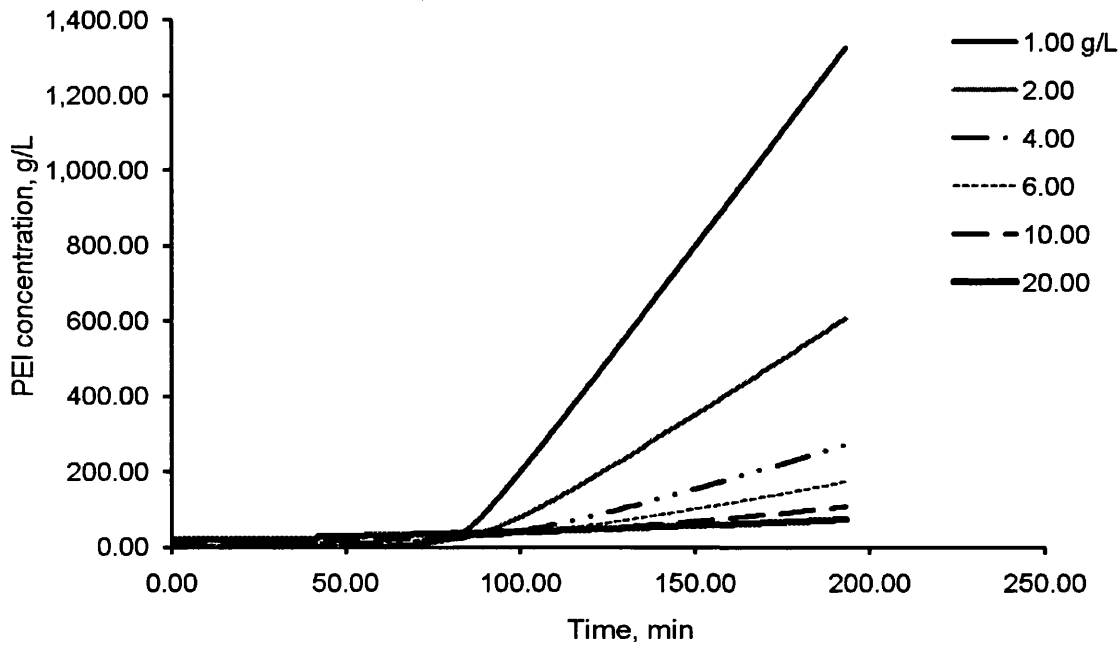
Figure 4-15: The effect of initial PEI concentration on the changes in polymer concentration filtration at pH 5.5, polymer capacity = 0.1051 mg Zn^{2+}/mg PEI, 20 psi pressures, 25 °C and 300rpm. Initial feed volume = 250 mL and membrane area = 0.00134 m^2.

The flux and filtration time are defined by the volume concentration factor or ratio, (VCF or VCR defined as the ratio of initial feed concentration and retentate volume (Baticle et al., 2000)) and this was considered in determining the best conditions. It is important to define VCR so that the amount of retentate solution can be used in the calculations of the decomplexation and washing stages. Figure 4-16 plots the flux as a function of the VCR. It seems that a VCR of around 10 at relatively low initial PEI concentrations provides a flux value that would give good productivity. This value was also recommended in the literature (Baticle et al., 2000). Beyond this value, the flux started to dramatically reduce and became very low at relatively low initial PEI concentrations.
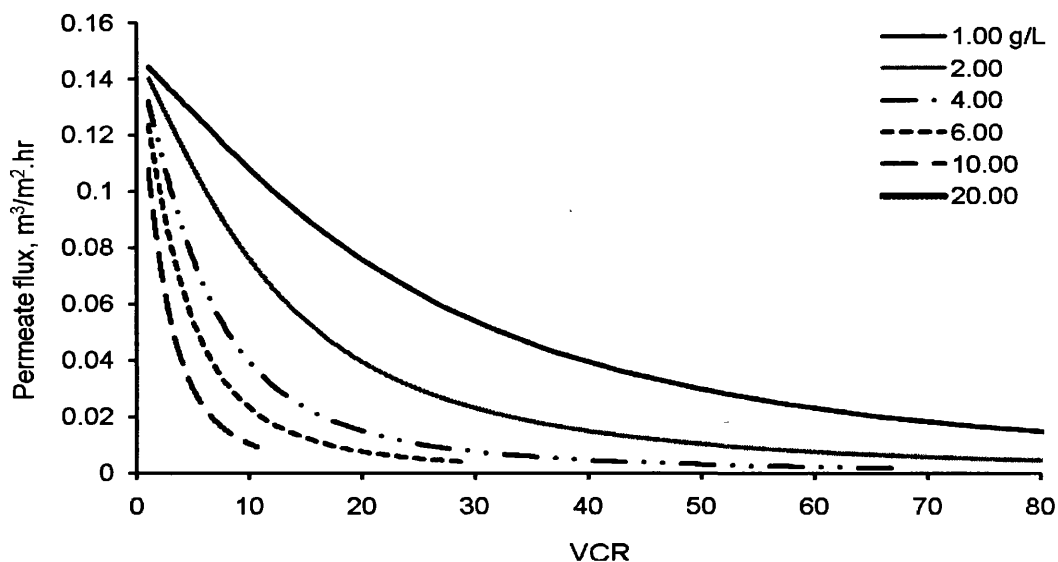
Figure 4-16: Permeate flow-rate as function of the volume concentration factor for concentration step of various PEI initial concentrations, pH 5.5, polymer capacity = 0.1051 mg Zn^{2+}/mg PEI, 20 psi pressures, 25 ° C, 300 rpm, initial feed volume = 250 mL and membrane area = 0.00134 m^2.

Values of concentrated PEI complexed with zinc were then estimated and listed in table 4-5 for each initial PEI concentration.

Table 4-5: Summary of zinc concentration in the complex solution after filtration at 20 psi , 25 ° C, 300 rpm, initial feed volume = 250 mL, membrane area = 0.00134 m^2 and pH5.5.

PEI concentration, g/L	Input Zn concentration, g/L	Zn concentration in complex, g/L	Zinc complexed %
0.5	0.051	0.40	82.80
1.0	0.1015	1.01	91.39
2.0	0.2	1.97	95.72
3.0	0.3	2.97	97.15
4.0	0.41	4.04	97.86
6.0	0.61	6.12	98.57
8.0	0.81	8.09	98.93
10.0	1.02	10.09	99.15

4.5.2. The Prediction of Decomplexed Concentrate Washing Using the Filtration Model:

The model was then used for prediction of washing stages and decomplexation. The function of the washing stages is to remove potential impurities by washing away the uncomplexed material leaving only the material that is complexed with PEI. Calculations of washing and decomplexation processes outputs were performed by assuming changing pH of concentrated solution obtained from the concentration stage, (in this study, it is desired to reduce the polymer pH from 5.5 to 2.5) by the addition of acidified water. Each washing time was assumed to filter almost all the added water so as to maintain as high a concentration as possible of complexed zinc after washing.

In this study the amount or proportions of acidified water added is varied by a washing factor, (washing feed/original volume of complexed material) of 1.5, 2.0 and 2.5. The volume of the combined acidified water and polymer were then concentrated to the original volume. This process would liberate a small amount of zinc from the polymer as it re-equilibrates with clean water. This was taken into account by determining the Zn released by using the Langmuir relationship, (equation (4.6)).

For the decomplexation step values of the Langmuir constants, K_l and Q_{max} at pH 2.5 where obtained from table 4-1. The flux was estimated using equation (4.1) where values of cake resistance where calculated using cake resistance-polymer concentration relationship at a 20 psi pressure drop, (see table 4-3).

Results of the concentration of zinc in the permeate and recovery percentages are presented in tables 4-6 and 4-7 respectively for five times washing and at different washing factors at initial polymer concentrations of 2 g/L. It can be noted from the tables that increasing the number of washing times led to a slight increase in zinc recovery but dramatic decrease in the outlet concentration at all washing factors employed. For example, an increase in washing times from 1 to 3 resulted in a reduction in the zinc outlet concentration from 2297.85 to 737.19 mg/L, but a slight increase from 58% to 62% was observed at washing factor of 1.5. Increasing number of washing times means increasing the amount of acidic water added and this in turn

could reduce the concentration of zinc released from the complex but slightly increase the mass transfer of zinc to the acidified water added at that level of washing factor.

Table 4-6: The effect of washing on final outlet concentration of zinc at different washing feed/retentate ratio of 1.5, 2.0 and 2.5. Initial polymer concentration was at 2 g/L.

Number of washings	final outlet zinc concentration, mg/L		
	Washing feed/retentate ratio = 1.5	2.0	2.5
1	2297.85	1531.90	1276.58
2	1095.62	770.77	594.79
3	737.19	516.45	386.81
4	581.53	388.75	285.65
5	481.83	311.63	223.21

Table 4-7: The effects of washing on zinc recovery at washing feed/retentate ratios of 1.5, 2.0 and 2.5. Initial polymer concentration was maintained at 2 g/L.

Number of washings	Accumulated outlet zinc recovery %		
	Washing feed/retentate ratio = 1.5	2.0	2.5
1	58.00	82.60	97.94
2	60.00	83.35	98.10
3	62.00	84.10	98.15
4	63.33	84.73	98.24
5	64.75	85.40	98.33

The outlet zinc concentration decreases from 1095.62 mg/L at a washing factor of 1.5 to 770.77 and 594.79 mg/L at washing factors of 2 and 2.5 respectively after two times washing. On the other hand, the recovery percentage increased from 60.00% at a washing factor of 1.5 to 83.35 and 98.10% at 2 and 2.5 respectively. This was due to the equilibrium between the free zinc ions and bound zinc ions at high concentrations of free zinc. With the increasing washing factor the free concentrations of Zn is lower so reducing the binding on the polymer and increasing the yield of Zn recovered in solution, (table 4-7).

4.6. Optimum Polymer Concentrations and Overall Membrane Productivity:

Generally, both efficient recovery, (at low washing factor), and high outlet zinc concentrations, (at high washing factor) are required for further processing. Therefore, it is required to determine the optimum polymer concentration that will produce reasonable recovery and high zinc concentration as possible, (for economical consideration) for the PEUF system. This could be characterised by introducing the concept of membrane productivity (Zn produce pure unit area of membrane) as a factor to optimise initial PEI concentration to produce as high a zinc concentration and zinc recovery as possible.

The two aims of producing high zinc concentration solution and high recovery percentages were examined by studying the effect of initial PEI concentration on membrane productivity and outlet zinc concentration after a two stage washing process. The results of the model are presented in figures 4-17 for membrane productivity and 4-18 for final Zn concentration using the Langmuir coefficients obtained in this work. Data of the effect of initial polymer concentration for each washing factor are presented in appendix 4.

It is shown in figure 4-17 that the maximum membrane productivity values were found to be equal to 0.083 kg Zn/m^2.hr, at initial PEI concentration of 3 g/L and at washing factors of 1.5; 0.089 kg Zn/m^2.hr at 4 g/L at 2 and 0.118 kg Zn/m^2.hr at 6 g/L and 2.5. At these optimum values of membrane productivity the concentration of zinc outlet was calculated to be 1753 mg/L at 1.5; 1546 mg/L at 2.0 and 1962 mg/L at 2.5, (obtained by cross referencing with polymer concentration the optimum membrane productivity figure 4-17 and polymer concentration in figure 4-18). It can also be seen from the figure 4-17 that membrane productivity was high and more sensitive to polymer concentration at a washing factor of 1.5 than it was at 2 and 2.5. However, the concentration of outlet zinc is an important factor since it is required to further generate $Zn(OH)_2$ using less NaOH in a smallest reactor volume for the integrated zinc recovery unit discussed in chapter 6.
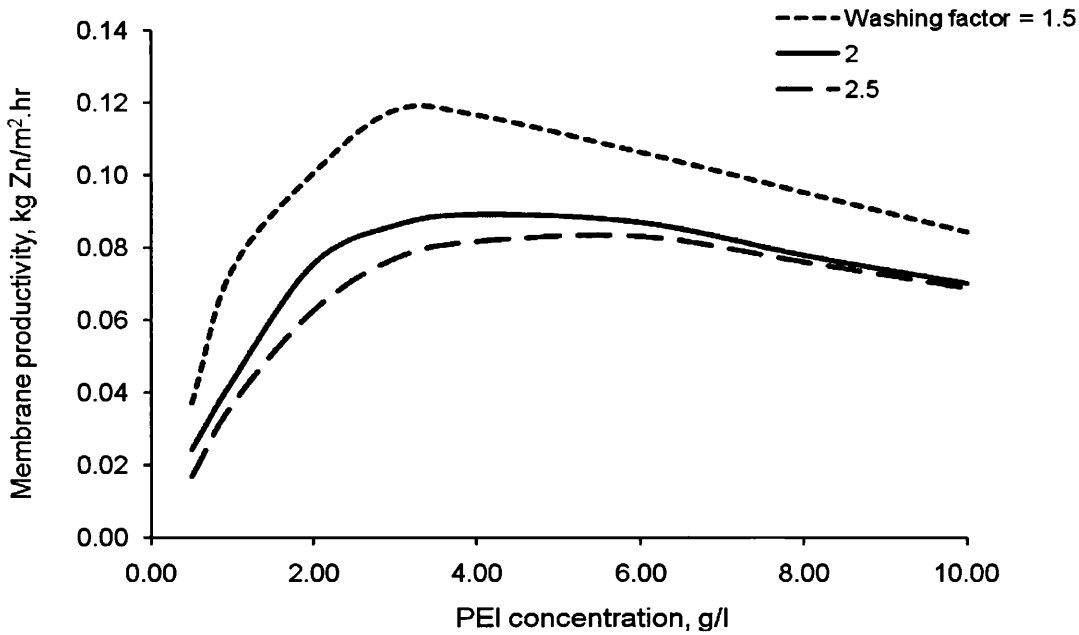
Figure 4-17: The effect of PEI concentration on membrane productivity for zinc production based on initial polymer concentration and washing ratio at pH 2.5 , 20 psi pressures, 25 ° C, 300 rpm, initial feed volume = 250 mL and membrane area = 0.00134 m^2.
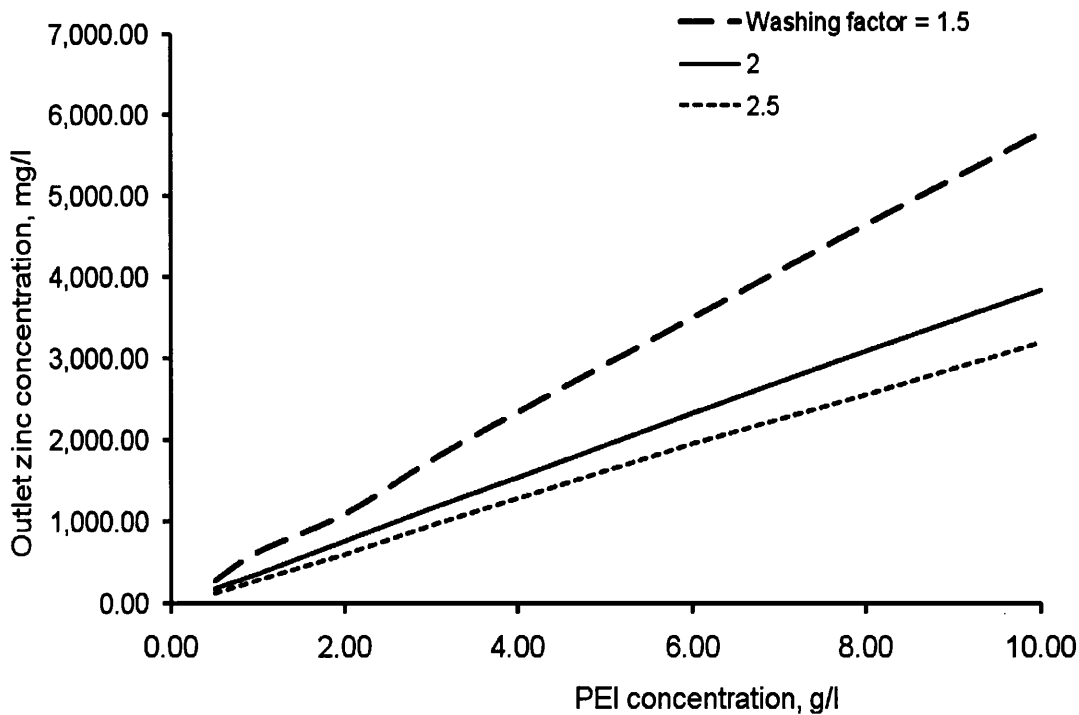
Figure 4-18 The effect of initial PEI concentration on outlet zinc concentration for various washing factors in a membrane system at 20 psi and a VCR of 10.

Further increases in initial PEI concentration led to a slight decrease in membrane productivity especially at washing factors of 2 and 2.5 and membrane productivity was shown to be less sensitive to washing factor beyond 6 g/L PEI concentration, (see figure 4-17) but outlet zinc concentration dramatically increased as shown in figure 4-18. Therefore, the concentration of polymer might be increased in order to further increase the outlet concentration with little reduction in membrane productivity at a washing factor of 2.

4.7. Conclusion:

The Polymer Enhanced Ultrafiltration (PEUF) model formulated and described in this chapter can be used to study the retention and flux of zinc ions in aqueous solutions in complex situations. The Cake resistance model was elaborated to give a good fit over the operational range of the process and be used to estimate the permeate flux while the Langmuir isotherm constants can be used to predict concentration of zinc to the adsorption, concentration, washing and decomplexing stages in the ultrafiltration system as a function of polymer concentrations and metal binding capacity.

Some zinc retention in the absence of PEI was found due most probably to metal-membrane interactions at acid pH where little or no insoluble zinc hydroxides are formed. Metal retention at low pH values is thought to be due to adsorption of metal ions onto the membrane surface where the negative membrane charge is partially masked by binding H^+ ions as previously indicated (Juang and Liang, 1993a, Almutairi, 2008). As pH increases, the availability of H^+ ions is reduced and zinc ions are bound by the membrane (Almutairi, 2008).

In the case of zinc aqueous solutions containing PEI, a significant increase in the retention of zinc occurs due to the binding efficiency between zinc ions and polymer molecules. Therefore, the formation of zinc-PEI complex is confirmed and the complex is subsequently retained by the membrane. At lower pH's, the concentration of H^+ ions increases, which leads to protonation of the metal binding sites on the polymer. This prevents the metal ions binding at those sites. However, increasing pH up to 6 results in a reduction in the protonation of the binding sites and this could increase the availability of metal binding sites. However, the data obtained in the

absence of PEI cannot be used to estimate operating conditions where the precipitation of zinc hydroxide will occur in the presence of PEI. This is because PEI has the ability of increasing zinc solubility and inhibiting the formation of zinc hydroxide (Jones, 2005).

As was found previously (Jones, 2005, Moreno-Villoslada and Rivas, 2002, Moreno-Villoslada and Rivas, 2003), and in this work, the Langmuir isotherms can be used to describe the complexation phenomena and fits well for most of the data obtained. Langmuir constants at each pH value are listed in table 4-1 and can be used when employing relatively high zinc contents in solution. For affective capture of the Zn ion the capacity of the polymer must not be exceeded as this will allow the Zn ion to pass through the membrane.

The ultrafiltration model formulated in this work can be implemented to predict the flux produced under various operation conditions of pressure drop, initial polymer concentration and pH 5.5, (for complexation step) and pH 2.5, (for decomplexation step). Consequently, the study has been conducted in order to find the suitable volume concentration factor required to operate the complexation and concentration stages with reasonable permeate flux (Baticle et al., 2000). This was done by first defining the best conditions of polymer initial concentration and pressure, by studying their effect on permeate flux, polymer concentration distribution and retentate volume with time. A VCR value of 10 can be selected for each stage at 20 psi.

The number of washing times was also considered in this study at a VCR of concentration after complexation of 10 for various washing factors. Washing times provide as high a zinc outlet concentration as possible and less concentration of zinc can be achieved as the washing times increased. Based on the results presented in tables 4-6 and 4-7, a two stage washing scenario achieves reasonable zinc productivity with relatively high concentrations, reducing process time and costs for pumping and reduced volumes downstream in the integrated recovery process.

According to the results of concentration and washing stage models, the membrane productivity becomes less affected by polymer concentration beyond optimum concentrations for all washing factors. It is also shown to be less influenced by a

washing factor above 2. Consequently, employing 6 g/L initial polymer concentration at 20 psi at the beginning of the whole ultrafiltration system process provides reasonable outlet zinc concentrations of 2329.0 mg/L with reasonable membrane productivity of 0.087 kg Zn/m^2.hr, zinc recovery of 77.77% and permeate flux of 0.037 m^3/m^2.hr at a washing factor of 2. The above data will be employed in chapter 6 for the integrated recovery unit. It should be noted that the undissociated Zn will be recycled with the PEI in the process rather than being lost as waste product.

Chapter 5

5. ZINC ELECTROWINNING STUDIES

Process parameters, such as electrolysis pH, initial concentration of metals, type of anode and cathode material and process kinetics, are important in the study of electrowinning units as they affect the efficiency of the unit, (see section 2.3.1.5 of literature review). Previously, the effect of solution pH, in acidic electrowinning, has been shown to have a major influence on current efficiency (Sharma et al., 2005, Blum and Hogaboom, 1949) and energy consumed in the passage of current (Fornari and Abbruzzese, 1999, Casas et al., 2000, St-Pierre et al., 1985b). The application of constant current, (or so called galvanostatic mode) is the most used strategy in industrial operations. Under galvanostatic operation, the current efficiency of zinc deposition is 77.3%, when charge transfer limits the process. When the system is diffusion limited it decreases to values as low as 0.1% (St-Pierre et al., 1996).

The aim of the work described in this chapter is to experimentally investigate the effect of electrowinning process parameters on the performance of the electrowinning process. This work included the development of a zinc electrowinning model using the metal deposition equation. The model was validated by comparing its performance with practical data of metal deposition efficiency at a variety of environmental conditions.

In order to evaluate the relative performance on various conditions it is necessary to assess the importance of the parameters in the optimisation of the process. Therefore, the work reports how the variables of initial zinc concentration, current density and NaOH concentration affect the process performance in terms of current efficiency, zinc deposition productivity and energy consumption.

The first stage of this work is to investigate polarographic analysis of zinc presence as a means of zinc concentration measurement followed by the zinc deposition via electrowinning. Current efficiency, concentration of NaOH and zinc initial concentration have been manipulated to optimise an electrochemical process in this work. An attempt to study acidic electrowinning was also addressed.

5.1. Measurement of Zinc Concentration by Electrochemical Method:

5.1.1. Polarographic Analysis of Zinc:

In conformity with normal voltammetric practice, cathodic (reduction) current are shown as positive and anodic (oxidation) current as negative. Figures 5-1, 5-2 and 5-3 show the results of cyclic voltammetry scans for various acetic acid concentrations from 0.1 to 0.0005 mol/L; the presence and absence of NaOH and zinc ions in solution mixture and various zinc concentrations in 0.1 mL of 0.05 mol/L of acetic acid respectively. The scan was carried out at scan rate of 100 mV/sec over a range of -700 to +1500 mV at 25°C in anaerobic conditions. The highest peak was observed from figure 5-1 when the acetic acid concentration exceeds 0.08 mol/L. However, below this value small peaks of the solution current resulted.
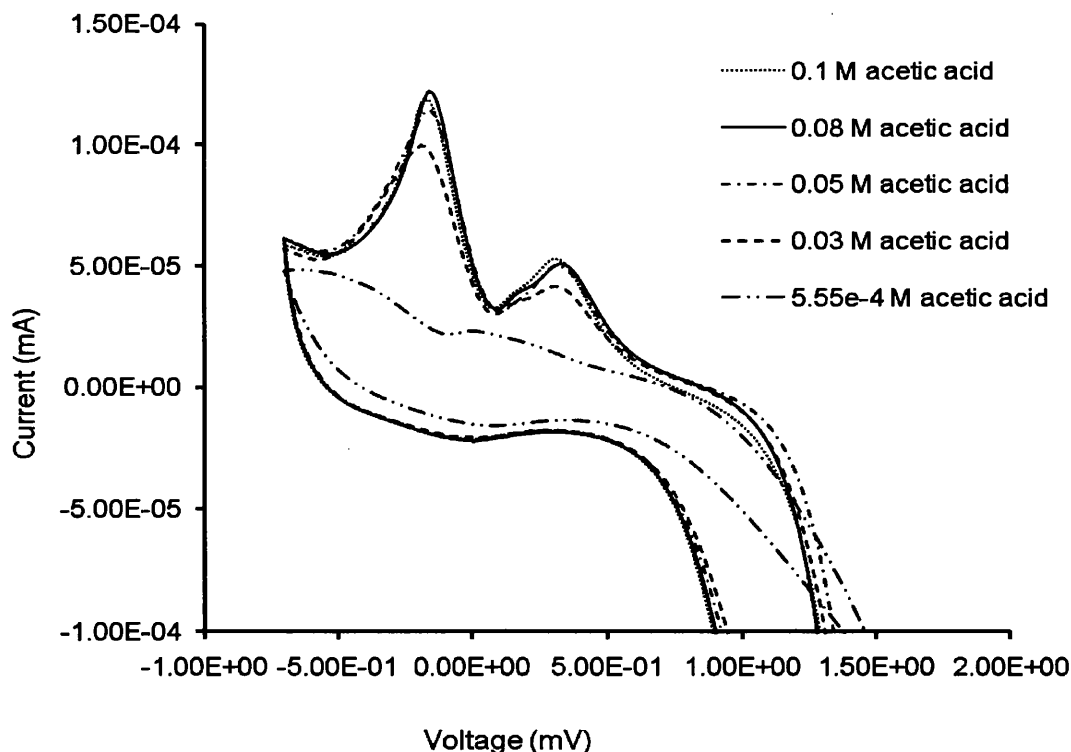
Figure 5-1: The effect of varying acetic acid concentrations in the absence of zinc on cyclic voltamograms with a stainless working electrode, platinum auxillory, Ag/AgCl standard cell.

The presence of acetic acid, zinc ions and NaOH showed the highest peak level. This confirmed the conditions required to determine zinc ions from alkaline solutions. However, this combination may not be suitable for measuring the zinc ions that resulted from the acidic electrowinning processes as indicated in figure 5-2. The effect of varying zinc concentration in a solution containing 0.1 mL of 0.1 mol/L acetic acid was detected and plotted in figure 5-3. Concentrations from 50 to 400 mg/L could show clear current peaks. This helps identifying the possible range of zinc concentration in order to obtain the calibration curves presented in figure 3-7.
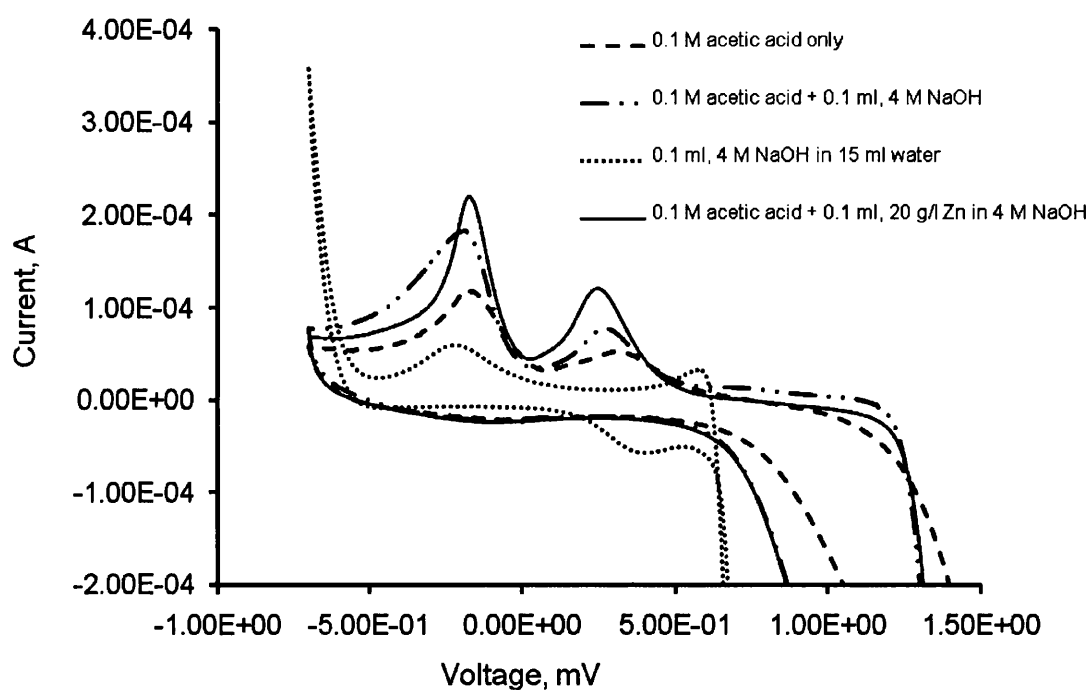
Figure 5-2: The effect of changing solution components on cyclic voltammetry performance, using stainless steel working electrode, a platinum auxillary electrode, Ag/AgCl standards electrode.
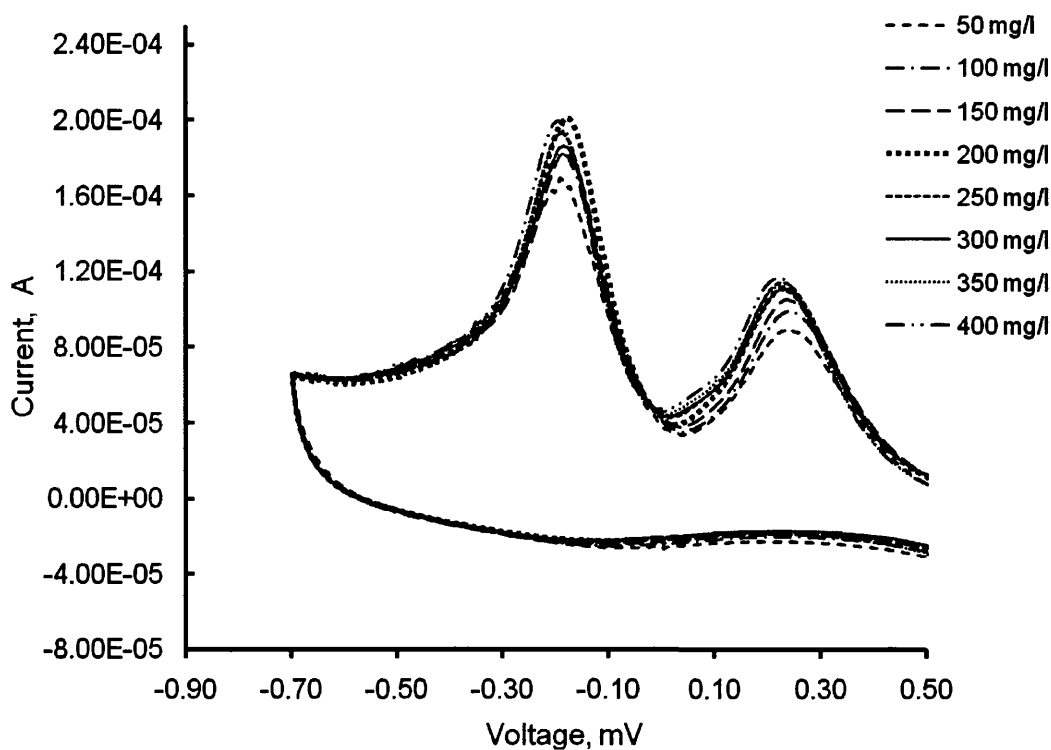
Figure 5-3: The effect of different zinc concentrations on cyclic voltammetry performance, using a stainless steel working electrode, platinum auxellory and Ag/AgCl standard.

5.2. Experimental Results:

Two schemes have been employed to recover zinc in order to improve the performance of the system (Freitas and de Pietre, 2004, Youcai and Stanforth, 2000, St-Pierre et al., 1985a, Fratesi et al., 1997, Ramachandran et al., 2004, St-Pierre and Piron, 1990). These are discussed in the following sections.

5.2.1. Zinc Electrowinning from Acidic Chloride Solutions:

Preliminary studies on acid electrowinning of zinc were carried out, however these were abandoned due to the poor performance and efficiency of Zn recovery. Zinc chloride solution was the preferred medium in acidic electrowinning due to the high solution conductivity (Fratesi et al., 1997). However, the process produces protons that require the careful addition of an alkali to main the optimal solution pH.

The use of an insoluble anode of RuO_2/Ti could increase the capabilities of the cell to deposit the desired purity and recovery of zinc for further applications (Sharma et al., 2005, Fornari and Abbruzzese, 1999, Fratesi et al., 1997, St-Pierre and Piron, 1990). This type of anode is capable of resisting chlorine and oxygen attacks on the anode during acidic electrolysis of the process (Sharma et al., 2005, Fornari and Abbruzzese, 1999, Fratesi et al., 1997, St-Pierre and Piron, 1990). However, preparing such an anode can be costly when employed in the zinc recovery process industry nowadays.

The measure of the efficiency of deposition is the current efficiency which is defined as:

$$Current\ efficiency\ =\ \frac{actual\ amount\ of\ metal\ deposited \times 100}{amount\ of\ metal\ deposited\ according\ to\ Faradays\ Law} \tag{5.1}$$

which in mathematical terms can be written as:

$$\eta_I\ =\ \frac{m\,n\,F}{M\int I\,dt} \tag{5.2}$$

where η_I is the current efficiency, m is the mass of metal deposited in grams, n is the charge of deposited ions, F is the number of Faradays per mole of consumed ions, M is the molar mass of the deposited metal, I is the total current and t is the deposition time. The percentage of zinc deposited can be defined as following:

$$recovery(\%) = \frac{wt_{Znd}}{wt_{Zn0}} \tag{5.3}$$

where wt_{Zn0} is the initial weight of zinc in solution and wt_{Znd} is the amount of zinc deposited on the cathode in grams. The electrical energy consumed, W, during each experiment was calculated using the following formula:

$$W\ =\ \frac{m\,n\,F\,V}{\eta_I\,M} \tag{5.4}$$

where V is the operating cell voltage.

Under normal electrowinning conditions at acid pH, there is a net production of protons. The first experiment therefore was to investigate the effect of adding alkaline hydroxides of Zn or Na to maintain the pH. This was achieved by using a titrator to maintain a constant pH during the experiment. The current efficiency, the recovery of zinc and specific energy usage were then determined at a series of set pH values. The performance of acidic electrowinning of zinc in terms of recovery of zinc from zinc chloride solution was relatively low < 50%. Hence, the maximum zinc recovery and current efficiency required utilization of a large amounts of energy for the Zn recovered. This rules out the suitability of the process on a large scale integrated unit, since optimization estimation of the process depends on the economic aspects (energy consumption) associated with the operation (St-Pierre and Piron, 1990).

The above observed results are due to the evolution of hydrogen on the cathode surface associated with zinc electrowinning. Zinc reduction has a high sensitivity to the presence of hydrogen ions in the electrolyte. This reduces the current efficiency and metal recovery and increases operating cost via electrical energy used. It also has a significant effect on the nature of deposits. Hence, several works have been conducted to reduce hydrogen ions by adding buffers (Yin and Lin, 1996) or by adding alkaline solution to control the pH (Gurmen and Emre, 2003). These suggestions showed little improvement in the performance of the acidic electrowinning studied in this work.

5.2.2. Alkaline Zinc Electrowinning Performance:

Zinc metal deposited from an alkali electrolyte solution onto a conductive surface in an electrowinning process can yield a high current efficiency and productivity, and minimize energy consumption (Gurmen and Emre, 2003, St-Pierre and Piron, 1986). This is because adsorbed hydrogen catalyses the zinc electrodepositing particularly on a steel cathode (Freitas and de Pietre, 2004). Moreover, electrical energy can be further reduced by passing nitrogen gas to reduce oxygen evolution since this has high overpotential, which makes up approximately 0.8 V or 20–25% of the total cell voltage (Schmachtel et al., 2009).

A number of experiments were performed on zinc oxide powder dissolved in sodium hydroxide solution to give sodium zincate:

$$ZnO + 2NaOH + H_2O \rightarrow Na_2Zn(OH)_4 \qquad (5.5)$$
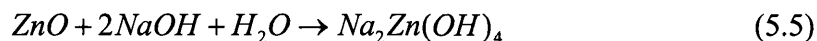
The electrochemical mechanism of zinc deposition at the cathode occurs as follows:

$$Zn(OH)^{2-} + 2e^- \rightarrow Zn + 4OH^- \qquad (5.6)$$

and at the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (5.7a)$$

$$2O_2 + 4H^+ + 4e^- \rightarrow 4OH^- \qquad (5.7b)$$
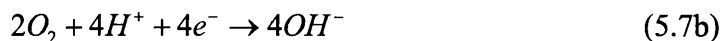
Therefore, zinc deposition electrochemical reaction takes place and hydrogen evolution only appears at potentials higher than those necessary to obtain zinc at the zinc concentrations. Consequently, in this system the effect of electrowinning parameters were studied since hydrogen evolution would reduce the efficiency of the systems (Freitas and de Pietre, 2004, St-Pierre and Piron, 1992). It is also possible to manipulate the structure and the size of electrodes by increasing the surface area at a specified current density (St-Pierre and Piron, 1990).

Consequently, this type of electrowinning was preferred in the design of an integrated selective zinc recovery unit in order to increase the productivity and economic viability. Other factors, such as system temperature and the addition of tetra-alkyl ammonium hydroxide, (up to a certain amount depends on operating cost), to improve the efficiency of the cell (Afifi et al., 1991). Parameters of initial zinc concentration, NaOH concentration and current density were varied in order to study the behaviour of the electrochemical batch reactor in this work. These data would then be used to develop a numerical model of the process.

5.2.2.1. Effect of Zinc Initial Concentration:

The effect of concentration on the deposition efficiency was investigated. Initial concentrations of Zincate solutions from 2.5 g/L to 30 g/L of Zn were run in the electrowinning cell and the zinc deposition determined. The plot of current efficiency as a function of initial Zn concentration is shown figure 5-4. This indicates that the optimum initial concentration of above 20 g/L gave current efficiencies of over 99%.
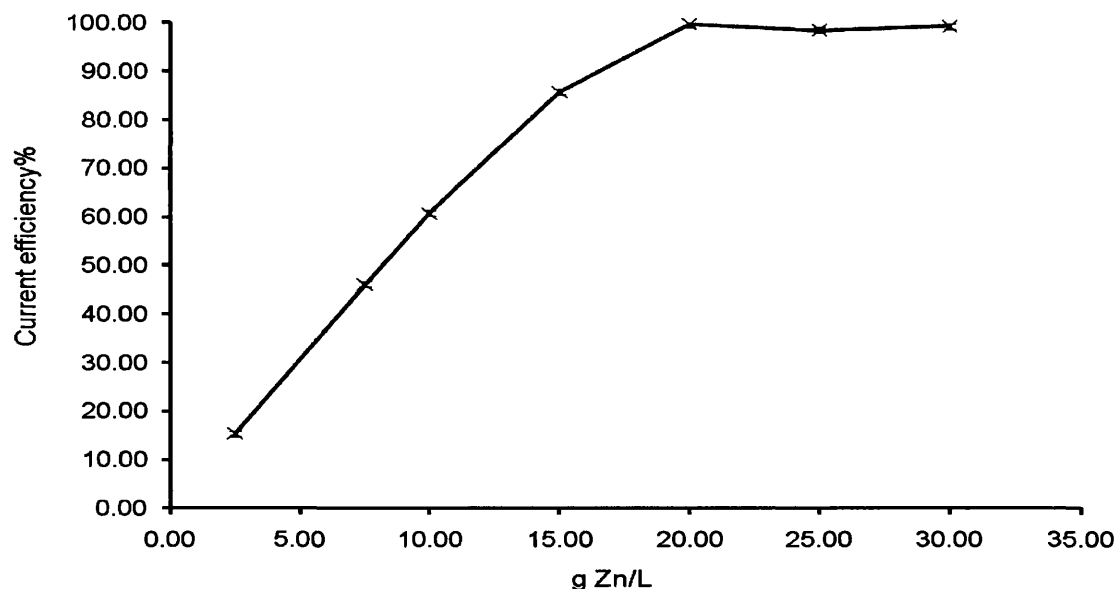
Figure 5-4: The effect of zinc initial concentration on current efficiency. All data were obtained and calculated at a fixed current density of 2000 A/m^2 and NaOH concentration of 4 mol/L and 25^{0}C.

In figure 5-5 the effect of initial concentration on the zinc recovery is shown. It can be seen from the figure that the amount of zinc recovered can reach a maximum of 98% when the initial concentration was 10 g/L. However, at this value of concentration, the cell performed with a low current efficiency of 50%. After 10 g/L the recovery of zinc starts to dramatically reduce and the system gives a poor recovery beyond 20 g/L.

The electrical energy usage showed little change with the initial concentration, (figure 5-6). Overall, a slight variation between 0.8 and 0.9 kWh/kg was obtained when Zn^{2+} concentration was between 7.5 and 30 g/L. However, at a value of [Zn^{+2}] of 20 g/L, the response of the cell produced a consumption of electricity of 0.941 kWh/kg zinc.
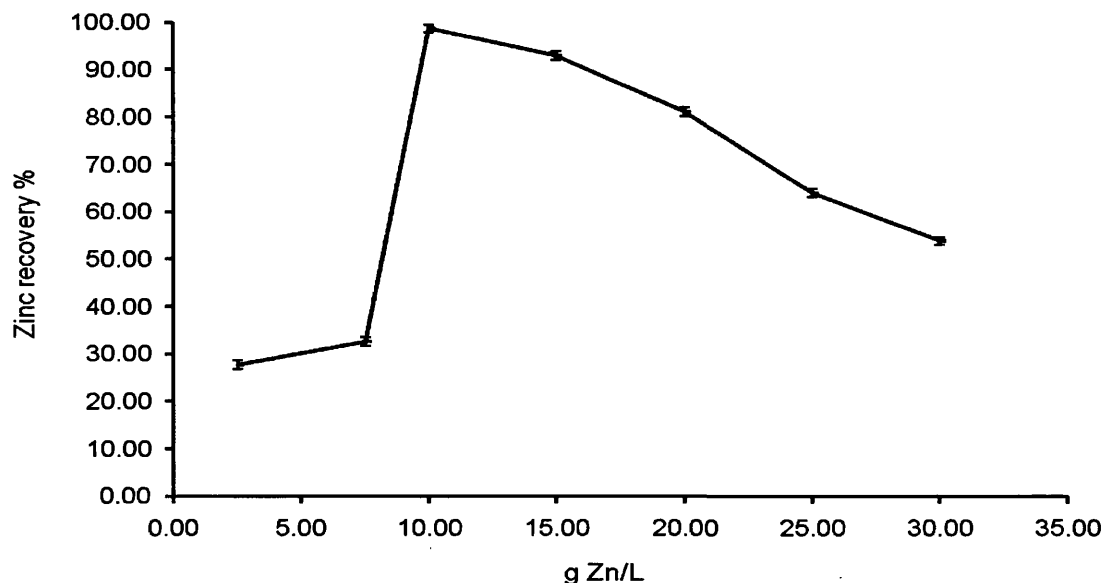
Figure 5-5: The effect of initial concentration on the recovery percentage. All data were obtained and calculated at a fixed current density of 2000 A/m^2 and NaOH concentration of 4 mol/L and 25^{0}C.
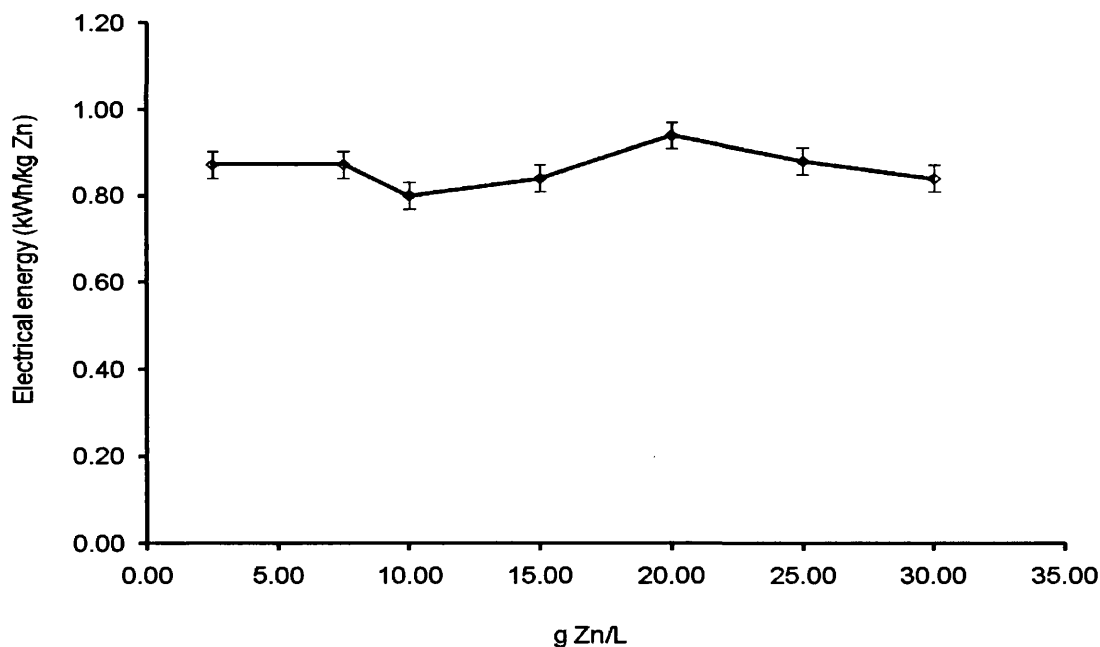
Figure 5-6: The effect of initial concentration as a function of energy usage. All data were obtained and calculated at a fixed current density of 2000 A/m^2 and NaOH concentration of 4 mol/L and 25^{0}C.

The zinc concentration profile in the electrowinning cell was also studied in order to obtain the electrochemical rate constant of zinc deposition as a function initial Zn profile. Figure 5-7 shows the concentration profiles as a function of time at several starting concentrations of Zn. The results show that the amount of zinc in solution decreases with time as it deposited on the cathode. This value was found to be dependent on the initial concentration. An equilibrium was reached after about 45 min when initial concentration is 20 g/L and after about 20 min for example when the initial concentration is 7.5 g/L.
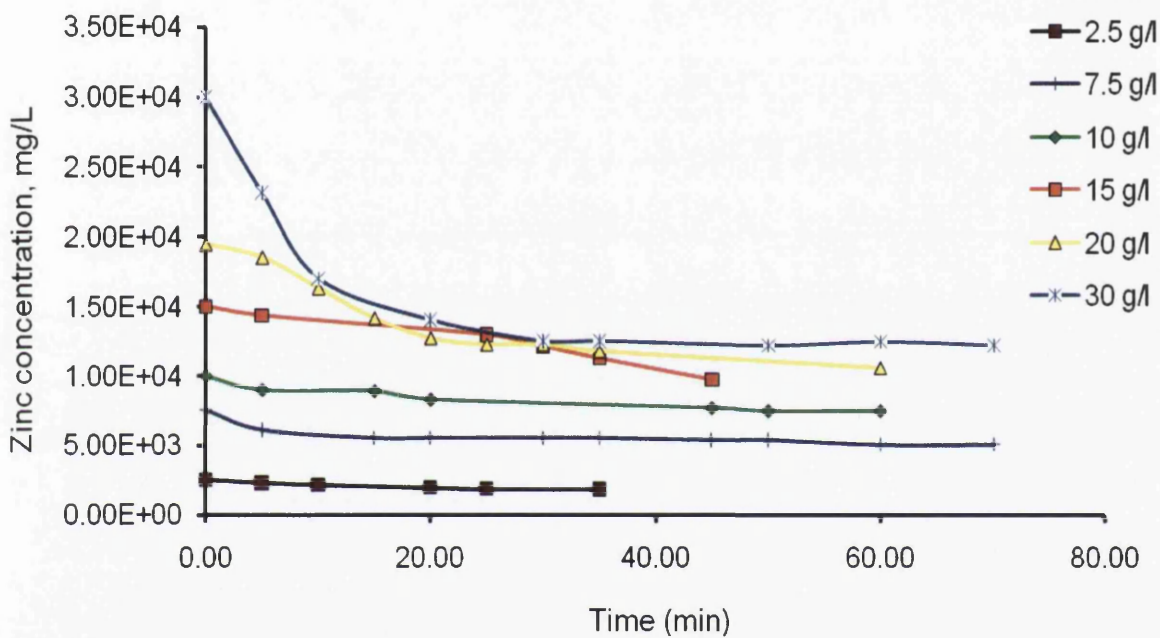
Figure 5-7: The effect of initial zinc concentration on zinc concentration remaining. All data were obtained at a fixed current density of 2000 A/m^2 and NaOH concentration of 4 mol/L. Concentrations were calculated using the calibration curve, (figure 3-7).

It can be seen from the above results that the influence of initial zinc concentration used on the quantity of zinc deposition is a critical factor. Above 10 g/L, the process would be efficient in an integrated Zn recovery system.

5.2.2.2. Effect of Current Density:

The current density can be defined as follows:

$$CD = \frac{I}{A_c}$$

(5.8)

where A_c is the electrode area, m^2.

Thus the effect of current density was investigated by changing the current passing thought the electrowinning cell while maintaining a constant electrode area and a fixed concentration of Zn and NaOH. This was done by recording the deposited weight and the remaining zinc in solution.

The results of the effect of current density on current efficiency are presented in figure 5-8. The current efficiency curve rises steadily towards the maximum value of 98% at current density of 2000 A/m^2. However, the efficiency drops sharply when the current density exceeds this value. The effect of the applied current density on the recovery of zinc is more substantial (see figure 5-9) with a considerable increase from 19% at 500 A/m^2 up to 85% at 2250 A/m^2.
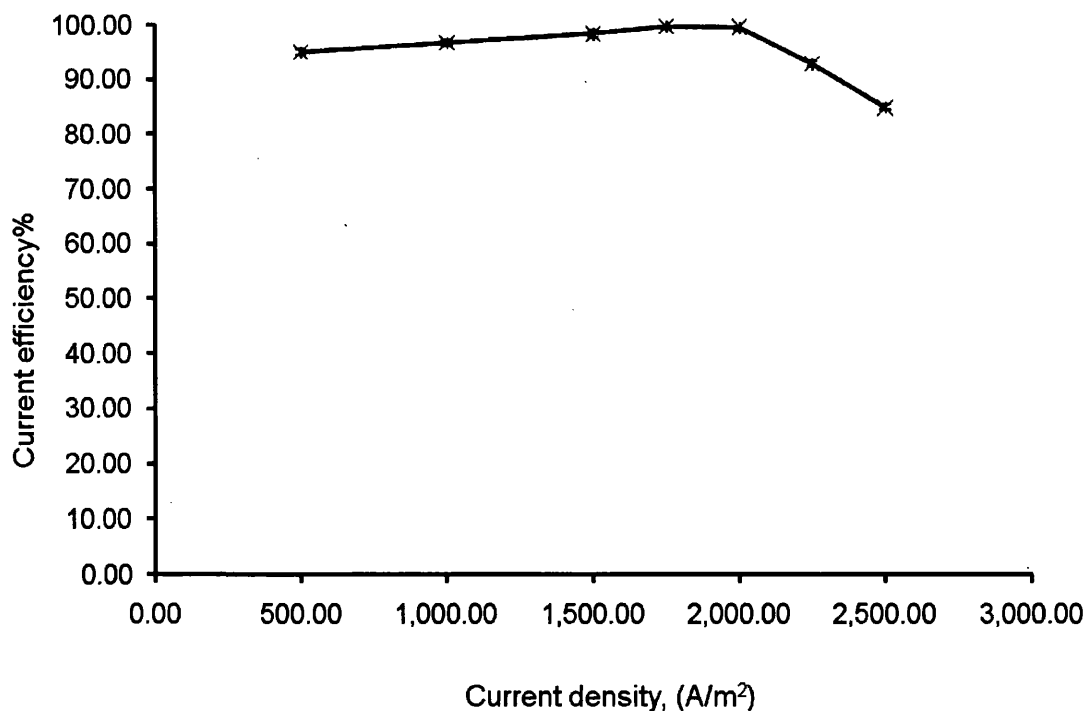
Figure 5-8: The effect of current density on the system current efficiency for electrowinning of Zn. All data were obtained and calculated at a fixed initial concentration of 20 g/L and NaOH concentration of 4 mol/L.

Zinc recovery was less affected when the value of current density applied exceeds 2250 A/m^2. This is due to the limited surface area of the cathode. The effect of current density on the amount of electrical energy used is presented in figure 5-10. The curve shows a slight increase with increasing current.

The zinc concentration in the electrowinning cell decreases with time (see figure 5-11). The results show that the zinc concentration decreases with an increase of the amount of applied current. However, beyond 2250 A/m^2, the efficiency of the zinc recovery is reduced. The figure also shows that the time required to perform maximum zinc recovery under these conditions should not exceed 30 minutes.
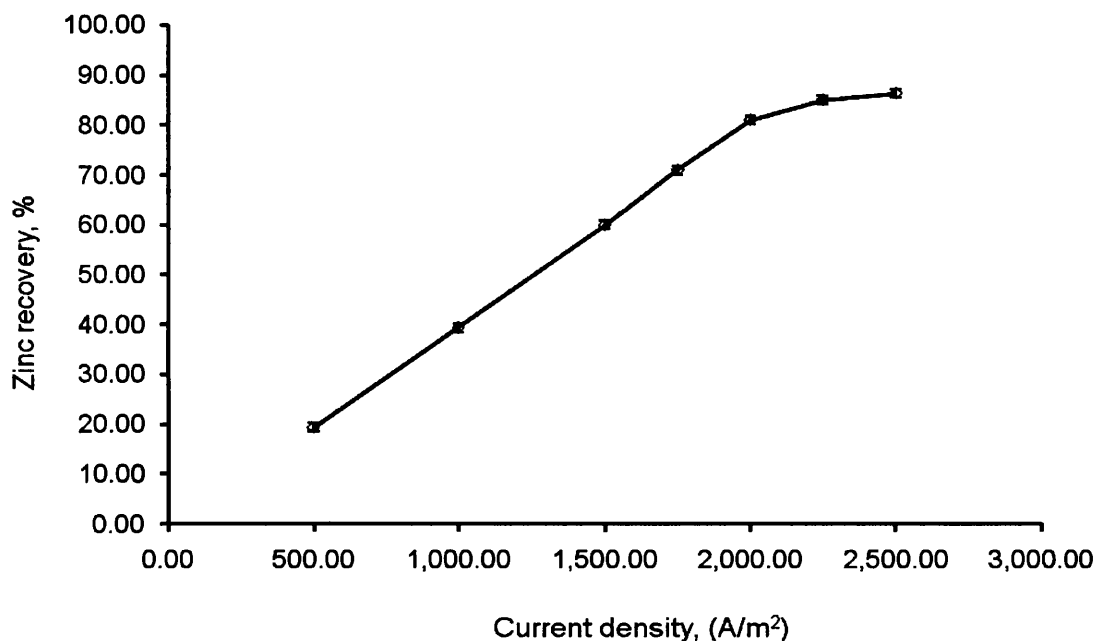
Figure 5-9: The effect of current density on the zinc recovery in electrowinning. All data were obtained and calculated at a fixed initial concentration of 20 g/L and NaOH concentration of 4 mol/L.
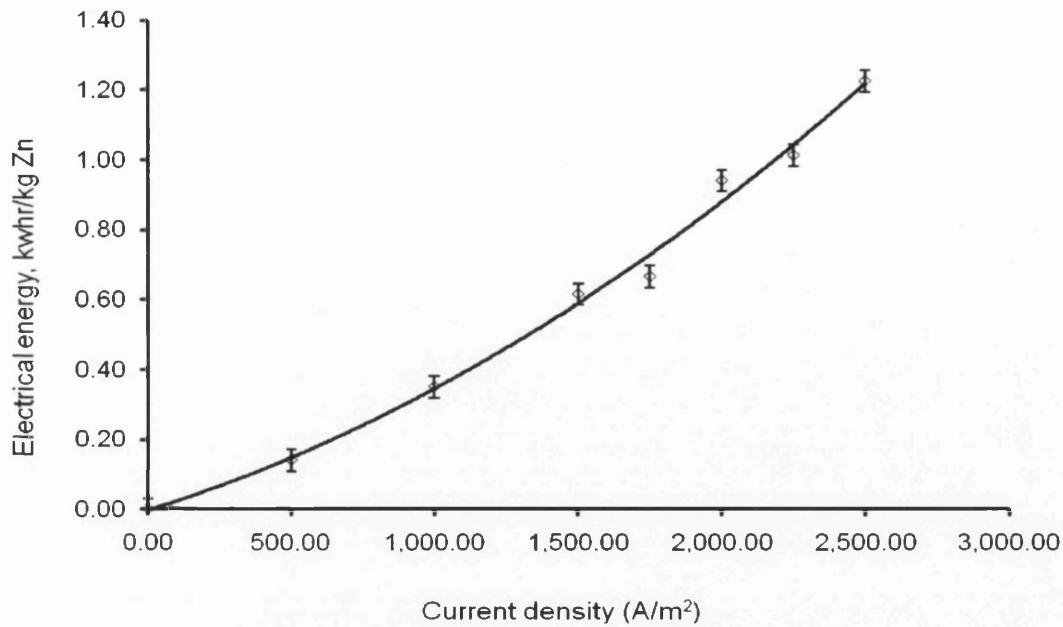
Figure 5-10: The effect of applied current density on the electrical energy used during zinc electrowinning. All data were obtained and calculated at a fixed initial concentration of 20 g/L and NaOH concentration of 4 mol/L.
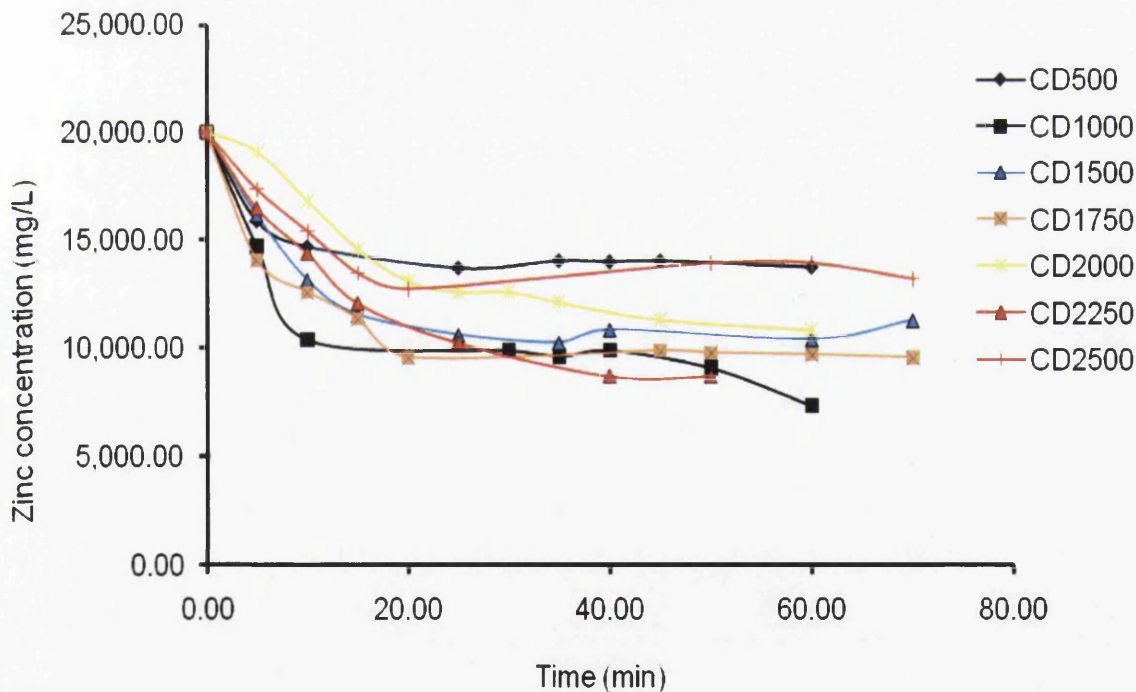
Figure 5-11: The effect of current density on concentration of zinc remains. All data were obtained at a fixed initial concentration of 20 g/L and NaOH concentration of 4 mol/L. Concentrations were calculated using the calibration curve, (figure 3-7).

From the results shown in figures 5-8, 5-9 and 5-10 the optimum value of current density for this particular system lies between 1750 and 2000 A/m^2.

5.2.2.3. Effect of NaOH Concentration on Electrowinning of Zinc:

Previous work carried out with zinc (St Pierre and Wragg, 1994) has shown that NaOH concentration can influence the performance of the electrowinning cell. Thus a series of experiments were carried out to investigate the effect of NaOH concentration in the electrowinning cell while maintaining the current density and initial zinc concentrations. Samples were taken periodically to measure the dissolved zinc concentration during the electrowinning process. The total deposited zinc on the electrode was measured by weight. The results of varying the concentration of NaOH used to dissolve zinc oxide at fixed current density and zinc initial concentration are shown in figures 5-12, 5-13, 5-14 and 5-15.

Figure 5-12 shows that a good efficiency > 90% was recorded between 3 and 6 mol/L. However, at 4 mol/L, the current efficiency was at its maximum of 99.6%. A further increase in NaOH concentration value leads to a slight reduction in efficiency.
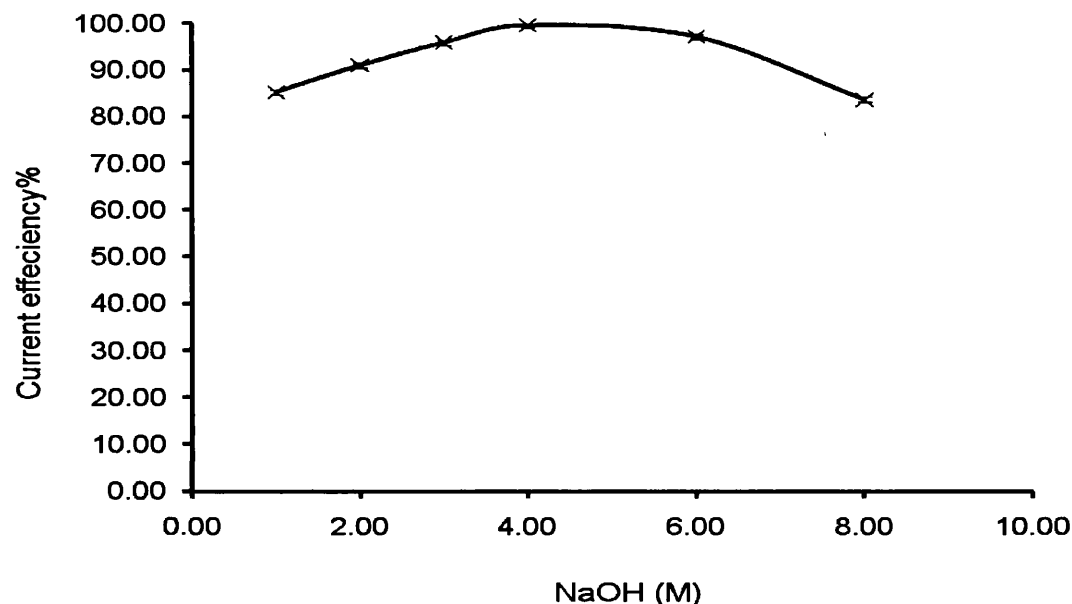
Figure 5-12: The effect of NaOH concentration on the system current efficiency. All data were obtained and calculated at a fixed initial concentration of 20 g/L and an applied current density of 2000 A/m^2.

Similar behaviour was observed when the Zn recovery was measured as shown in figure 5-13. The recovery of zinc reaches the maximum percentage of 81% when the concentration of NaOH was 4 mol/L.

The amount of electrical energy used to produce a kg zinc metal is highest at a NaOH concentration of 3 mol/L, (0.96 kWh/kg) and then becomes more efficient as the NaOH concentration increases (e.g. 0.85 kWh/kg metal deposited).

When the zinc concentration remaining in solution was measured with time over a range of NaOH concentrations, it could be seen that 2 to 6 mol/L gave the best decrease in concentration and that an equilibrium was reached after almost the same time of 30 minutes.
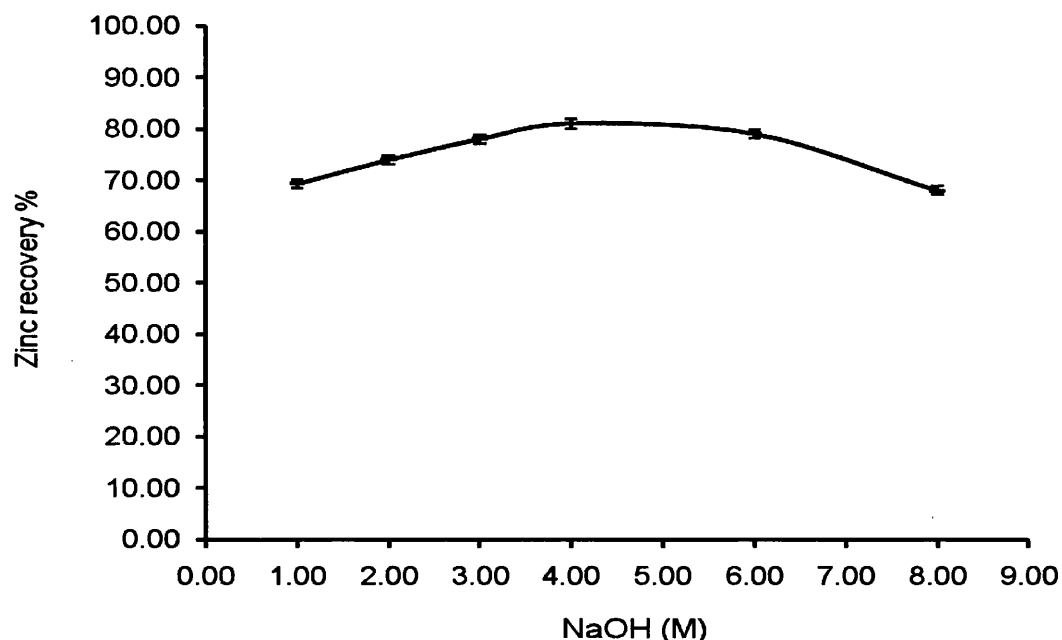
Figure 5-13: The effect of NaOH concentration on zinc recovery performance. All data were obtained and calculated at an initial concentration of 20 g/L and an applied current density of 2000 A/m^2.

All these data show that the best conditions are at least 20 g/L zinc initial concentration, 2000 A/m^2 current density and 4 mol/L NaOH solution at 25°C. Also, it was seen that by contrast that the percent recovery of zinc dramatically increased when the current density value was varied to a higher value (see figure 5-15).
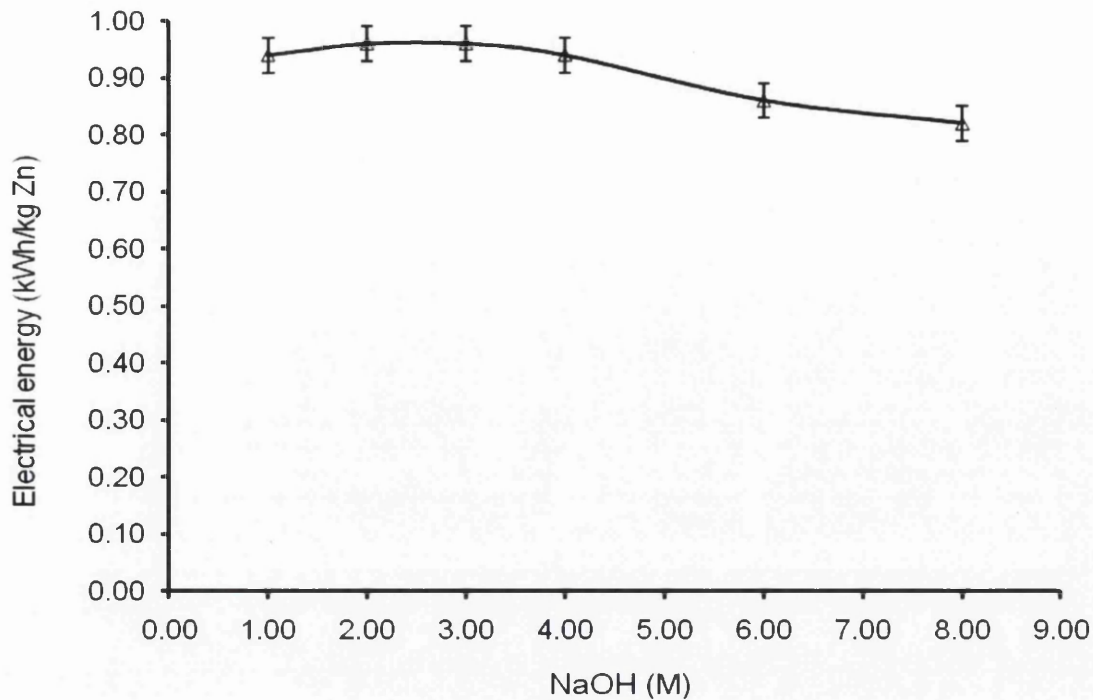
Figure 5-14: The effect of NaOH concentration on zinc electrical energy consumption. All data were obtained and calculated at a fixed initial concentration of 20 g/L and an applied current density of 2000 A/m^2.
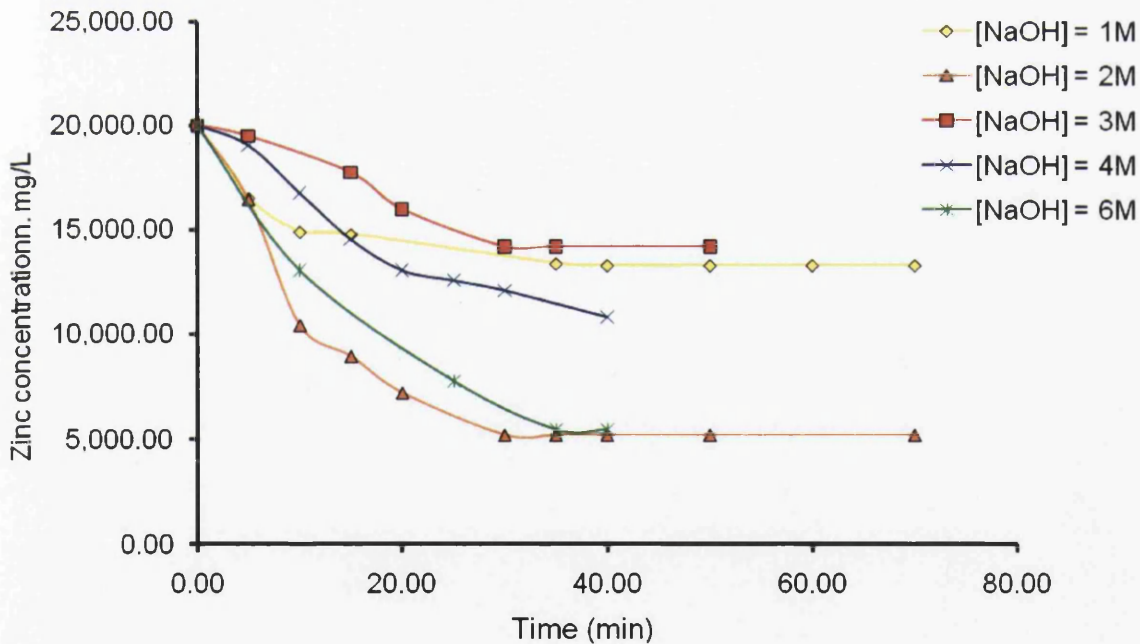
Figure 5-15: The effect of NaOH concentration on concentration of Zinc in solution. All data were obtained at a fixed initial concentration of 20 g/L and a current density of 2000 A/m^2. Concentrations were estimated using the calibration curve, (figure 3-7).

These conclusions are consistent with those of St-Pierre and Piron (1990) and St-Pierre and Piron (1986). However, the recovery percentage becomes less affected beyond a certain value of current density.

Of particular interest are the observations concerning the electrical energy usage and the recovery efficiency of the electrowinning cell. St-Pierre et al. (1985a) used energy consumption criteria as a means of obtaining their cell parameters. Their experiments were successful in that the amount of energy used was lower, 2.14 kWh/kg, at their optimised conditions of 60 g/L zinc concentration, 7 mol/L NaOH and lower current density of 500 A/m^2 at 40^0 C.

St-Pierre and Piron (1990) suggested that using an excess of hydroxide is required to dissolve the zinc oxide. However, excessive NaOH to dissolve fixed zinc concentration is wasteful. St-Pierre and Piron (1990) based their electrolyte compositions obtained from previous pilot plant studies and actual operating plant data for the zinc alkaline electrowinning process at an initial Zn concentration of 60 g/l in 7.5 mol/L NaOH and 1000 A/m^2 current density. Those data were obtained based on the solubility of zinc oxide in sodium hydroxide. However, the results of NaOH concentration variation in this study showed only a marginal influence even though the electrical energy required was reduced by increasing the concentration of NaOH. In addition, the formation of hydroxyl ions by the cathodic reaction could cause the dissolution of zinc metal deposited on the cathode and produce insoluble ZnO and a carbonate complex ($3Zn(OH)_2$. $2ZnCO_3$) at an early stage of the process (Ogle et al., 2000). Therefore, anaerobic electrowinning (no oxygen or carbon dioxide) is performed in order to reduce the negative effect of hydroxide and carbonate ions. This showed an increase in metal deposition percentage and improved morphology of deposited metal in this work.

Youcai and Stanforth (2000) and Frenay et al. (1986), mentioned that the cost-effectiveness of zinc electrolysis from alkaline media would be decreased. Their researches were based on previous work reported in the literature (St-Pierre and Piron, 1986) and (St-Pierre and Piron, 1990). It can be seen from the above results that NaOH concentration variation might only have an economical impact. Consequently, the selection of optimum values should be between 3 and 4 mol/L NaOH concentration. This might depend on the effect of the NaOH price on the

economy and in turn the amount of NaOH used by the whole recovery system, (see chapter 6).

Overall, alkaline electrowinning provided dramatic improvements in zinc deposition compared with acidic electrowinning. St-Pierre and Piron (1992) stated that hydrogen has, relatively, a very high overpotential compared to the zinc overpotential on zinc cathodes. This favours the zinc deposition reaction and allows hydrogen to evolve at more negative potentials than those required to obtain the zinc limited current density. This has been supported by Wijenberg et al. (1998). The above could explain the high current efficiency achieved by St-Pierre and Piron (1986), (who employed a magnesium cathode), St-Pierre and Piron (1990) and this work with a stainless steal cathode. However, the system current efficiency should not be the only electrochemical characteristic to represent the performance since it is not significantly influenced by current density and the NaOH concentration, (see figures 5-11 and 5-15), as originally suggested made by St-Pierre and Piron (1990).

5.3. Alkaline Zinc Electrowinning Modeling:

The development of a mathematical model for zinc electrowinning is important to the understanding of the behaviour of the system. Modelling can help improve the design of the system and recognise the role of the process variables involved in the efficiency of the process. Electrochemical kinetics deals with the factors that directly affect the rate of reactions at the electrode surface, which is related to the productivity of the cell. Key variables include initial metal concentration and current density, $A.m^{-1}$. Kinetic constants can be determined using experimental data from the batch electrowinning system. A kinetic analysis can lead to a model for electrowinning of zinc from solution and, conversely, the principle of zinc electrowinning kinetics can be used to describe a model for an industrial scale electrowinning cell.

Several publications have considered the mathematical modelling of electrolyte zinc deposition including theoretical analysis of galvanostatic and potentiostatic systems. Theoretical models have been developed to describe the flow behaviour of conducting particles in a fluidized bed electrode for electrowinning of metal ions present in the dilute solution for potential, current distributions and mass transfer

rates (Thilakavathi et al., 2009). A simulation of electrical field, current density distribution and fluid flow in a conventional batch reactor for aluminium electrowinning in ionic liquid electrolyte has also been investigated (Zhang and Reddy, 2007). The deposition of zinc in a packed bed based on material balances was also proposed (El-Shakre et al., 1994). However, the derivation of this model was mass transfer based with little detail on reaction kinetic. Attempts have also involved a modified Butler-Volmer equation for metal deposition and Tafel equation to govern the hydrogen evolution (Saleh et al., 1995). However, in this system some constants were measured at zero-current potential, which may not be the appropriate equilibrium potential (Pickett, 1979). In addition, the above models describe the process of electrowinning as a first order reaction. This might be true in the specific time periods of the process but systems typically reach an equilibrium where first order kinetics cannot apply e.g. limitation of cathode surface area. Numerical modelling of the variation in 2-ethylicolinate on a lead cathode in sulphuric acid solutions under galvanostatic conditions were presented by Romulus et al.(2006). This was based on the combination of reaction rate and mass transfer equations. Other work has been focused on the development of electrochemical processes to involve potentiostatic and galvanostatic control (Scott, 1993).

The electrowinning of zinc on a stainless steel cathode is a surface reaction (Segel, 1993, Fogler, 1992). Both involve a single substrate, or reactant going to a single product. The metal deposition equation gives the instantaneous or initial reaction rate relative to the maximum velocity at a given zinc concentration. The reaction sequence can be written as:

$$Zn^{+2} + 2e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Zn_{metal}$$

(5.9)
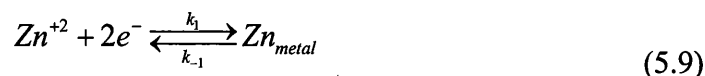
It can be assumed that mass transport limitations are negligible when employing a constant current mode for general order kinetics (Scott, 1993). Also, the rate of the zinc metal formation is rapid compared to the rate at which zinc metal dissociates back to the zinc ion, and zinc metal and zinc ions will not be in equilibrium in the initial stages of the process. Therefore, the cathode surface area in the system affects the time to reach steady state. Hence, as a starting point in this study the zinc

deposition was considered as the irreversible type. The equation that describes the metal deposition forward reaction is:

$$\frac{r}{r_{\max_f}} = \frac{[Zn^{2+}]}{k_{d_f} + [Zn^{2+}]}$$

(5.10)

where $r = -\dfrac{d[Zn^{2+}]}{dt}$, is the reaction speed, $[Zn^{2+}]$ is the concentration of zinc ions

at time t, $k_{d_f} = \dfrac{k_{-1}}{k_1}$ represents the deposition constant for forward reaction, (a

dynamic or pseudo-equilibrium constant expressing the relationship between the actual steady state concentrations), and $r_{\max_f}$ is the maximum velocity of the forward reaction.

The concentration of zinc ions were recorded as function of time for different initial zinc concentration and current density, (see sections 3.2.1.1 and 3.2.1.2 above). These data were used to determine the first order electrochemical reaction rate constant. Two assumptions are considered in the analysis of the data and modelling. These are described in the following individual sections.

5.3.1. First Order Reaction Assumption:

If the reaction is considered to be first order then the effect of limited cathode surface area is negligible. Therefore, the linear relationship between reaction rate and zinc concentration in solution when $[Zn^{2+}] \square \ k_{d_f}$ can be derived from equation (5.10) where $[Zn^{2+}]$ in the denominator may be ignored:

$$r_{d_f} = k_1[Zn^{2+}]$$

(5.11a)

where $k_1 = \dfrac{r_{\max_f}}{k_{d_f}}$. The equation describes the reversible reaction when

$[Zn_{metal}]_{eq} \square \ k_{d_r}$ is:

$$r_{d_r} = k_2[Zn_{metal}]$$

(5.11b)

where $k_2 = \dfrac{r_{max,r}}{k_{d_r}}$. The net reaction rate can be written as:

$$\frac{d[Zn^{2+}]}{dt} = k_1 \left[\frac{1}{K_{eq}}[Zn^{2+}]_0 - [Zn^{2+}] \right] \qquad (5.12)$$

where $K_{eq} = \dfrac{[Zn_{metal}]_{eq}}{[Zn^{2+}]_{eq}} = \dfrac{k_1}{k_2}$, equilibrium constant. Equation (5.12) is an ordinary

differential equation which can be solved (Mařík and Tihlaříková, 2008):

$$[Zn^{2+}] = e^{-k_1 t} + (1 - \frac{1}{K_{eq}})[Zn^{2+}]_0 \qquad (5.13)$$

The linearised form of the above equation is:

$$\ln[Zn^{2+}] = \ln\{(1 - \frac{1}{K_{eq}})[Zn^{2+}]_0\} - k_1 t \qquad (5.14)$$

Value of $-k_2$ presented in table 5-1 can be calculated by plotting $\ln\left[Zn^{+2}\right]$ verses time, t which results is straight line with slope equal to $-k_1$. As shown in figure 5-16.

Table 5-1: The effect of Zn concentration on the reaction rate constant for different at constant current density of 2000 A/m² in 4M NaOH. Values estimated from the slop of the linear relationships shown in figure 5-16.

Zinc initial conc., g/L	$-k_1$ (min^{-1})	$-k_2$ (min^{-1})	K_{eq}
2.5	0.0077	0.020	0.382
7.5	0.0051	0.011	0.482
10	0.0055	0.011	0.517
15	0.0086	0.017	0.509
20	0.008	0.017	0.466
30	0.020	0.014	1.465
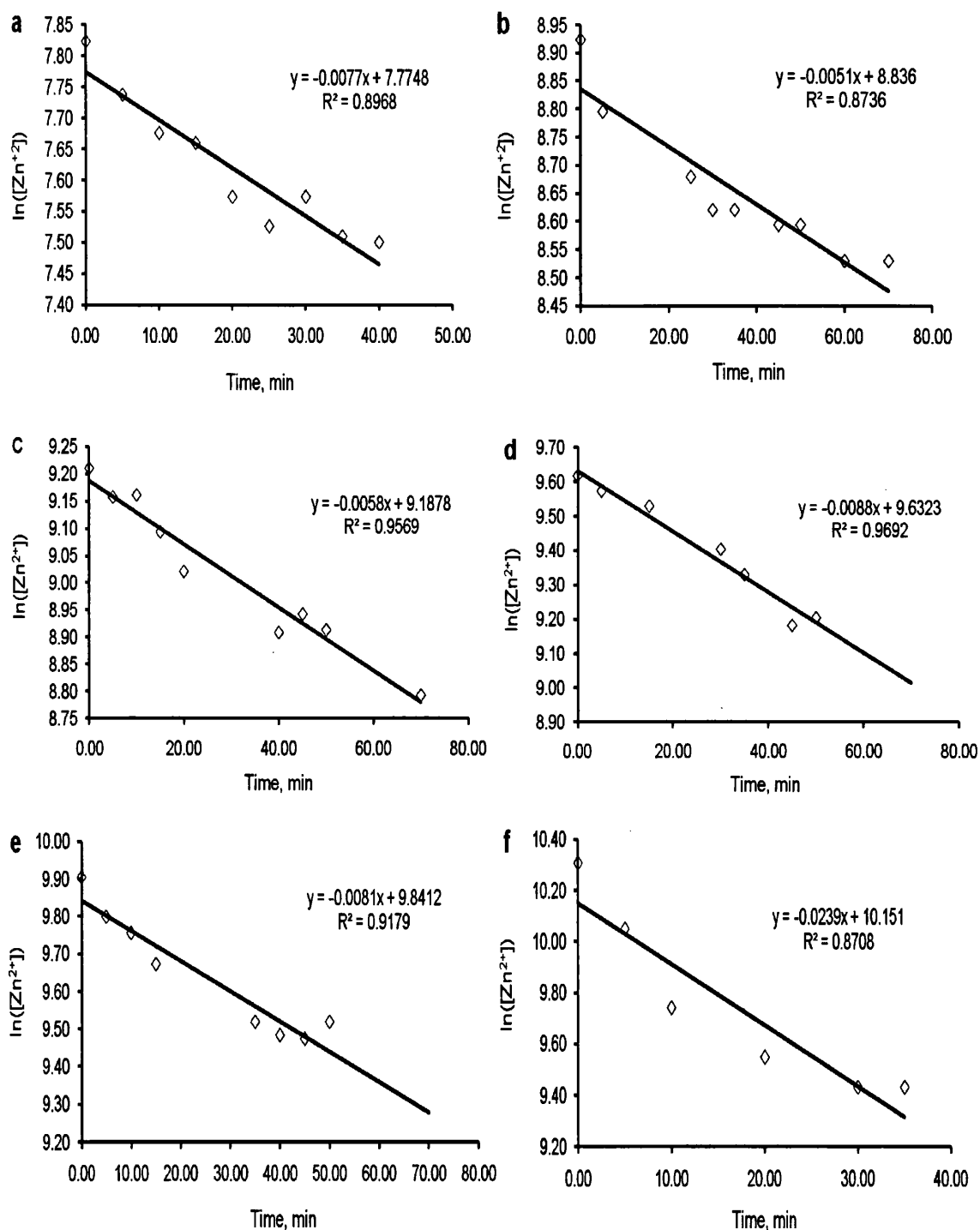
Figure 5-16: Integral method analysis for first order reaction at a constant NaOH concentration of 4 mol/L and a current density of 2000 A/m² and an initial zinc concentration of a) 2.5 g/L, b) 10 g/L, c) 15 g/L, d) 20 g/L, e) 25 g/L, and f) 30 g/L. No inhibition is assumed in this model. (experimental data are derived from the work in section 3.2.1.1).

The results of model fitting of the data were not good either at low or high zinc concentrations as indicated by the residual values of the linear fitting. Therefore further modifications to the model were considered as the assumption of first order kinetics did not predict the rates of electrodeposition.

5.3.2. Limited Surface Area Assumption:

The calculations of metal deposition constants can be performed by first evaluating the forward reaction constants assuming that no reverse reaction occurs at the beginning of the deposition process (Segel, 1993). These values are then employed in the full equation in order to determine the reverse reaction constants. Each step will be discussed individually in the following two sections.

5.3.2.1. Irreversible Formation of Zinc Metal:

It can be assumed that no reversible reaction occurs at the beginning of the process because effectively there is no back reaction. Therefore, zinc metal and zinc ions present in the system will not be in equilibrium. Hence, electrowinning of zinc of forward reaction rate constants can be determined by rearranging equation (5.8) and inverting as follows:

$$r_{\max_f} dt = -\frac{k_{d_f} + [Zn^{2+}]}{[Zn^{2+}]} d[Zn^{2+}] \qquad (5.15)$$

Integrating between zero-time, t_0, and any other time, t and corresponding two zinc ions concentrations, $[Zn^{2+}]$ and $[Zn^{2+}]_0$ yields:

$$r_{\max_f} \int_{t_0}^{t} dt = -\int_{[Zn^{2+}]_0}^{[Zn^{2+}]} \frac{k_{d_f} + [Zn^{2+}]}{[Zn^{2+}]} d[Zn^{2+}] \qquad (5.16)$$

Separating the terms in the right hand expression and integrating:

$$r_{\max_f} \int_{t_0}^{t} dt = -k_{d_f} \int_{[Zn^{2+}]_0}^{[Zn^{2+}]} \frac{d[Zn^{2+}]}{[Zn^{2+}]} - \int_{[Zn^{2+}]_0}^{[Zn^{2+}]} d[Zn^{2+}] \qquad (5.17)$$

$$r_{\max_f} t = 2.3 k_{d_f} \log \frac{[Zn^{2+}]_0}{[Zn^{2+}]} + ([Zn^{2+}]_0 - [Zn^{2+}]) \qquad (5.18)$$

Therefore, values of k_{d_f} and r_{max_f} is determined by using the integral form of the above equation since values of $[Zn^{2+}]$ and $[Zn^{2+}]_0$ with respect to time are determined experimentally. Rearranging equation (5.18) to a linear form using logs yields:

$$\frac{2.3}{t} \log \frac{[Zn^{2+}]_0}{[Zn^{2+}]} = -\frac{1}{tk_{d_f}}([Zn^{2+}]_0 - [Zn^{2+}]) + \frac{r_{max_f}}{k_{d_f}} \qquad (5.19)$$

The plot of $\dfrac{2.3}{t} \log \dfrac{[Zn^{2+}]_0}{[Zn^{2+}]}$ versus $\dfrac{([Zn^{2+}]_0 - [Zn^{2+}])}{t}$ is a linear relationship with

slop equal to $-\dfrac{1}{k_{d_f}}$ and intercept of $\dfrac{r_{max_f}}{k_{d_f}}$ as shown in figure 5.17. Generally this

relationship was a good fit to the experimental data.

5.3.2.2. Reversible Deposition of Zinc Metal:

At equilibrium, the rate of the consumption of zinc ions is assumed to be equal to the rate of the formation of zinc metal. Also, the formation and dissolution of zinc metal can occur at the electrode surface. Based on the assumption that a decrease in zinc deposition rate with time results from saturation of the electrode surface and zinc metal product inhibition or the approach of equilibrium, the net rate can be expressed as:

$$r_{net} = \frac{r_{max_f}[Zn^{2+}]}{k_{d_f}(1 + \frac{[Zn_{metal}]}{k_{d_r}}) + [Zn^{2+}]} - \frac{r_{max_r}[Zn_{metal}]}{k_{d_r}(1 + \frac{[Zn^{2+}]}{k_{d_f}}) + [Zn_{metal}]} \qquad (5.20)$$

where $[Zn_{metal}]$ is the concentration of zinc metal produced at time t, k_{d_r} represents the deposition constant for back reaction and r_{max_r} is the maximum velocity of the reversible reaction.

The net reaction rate is equal zero at equilibrium. Therefore, the relationship between equilibrium constant, K_{eq} and reaction constants can be defined as:
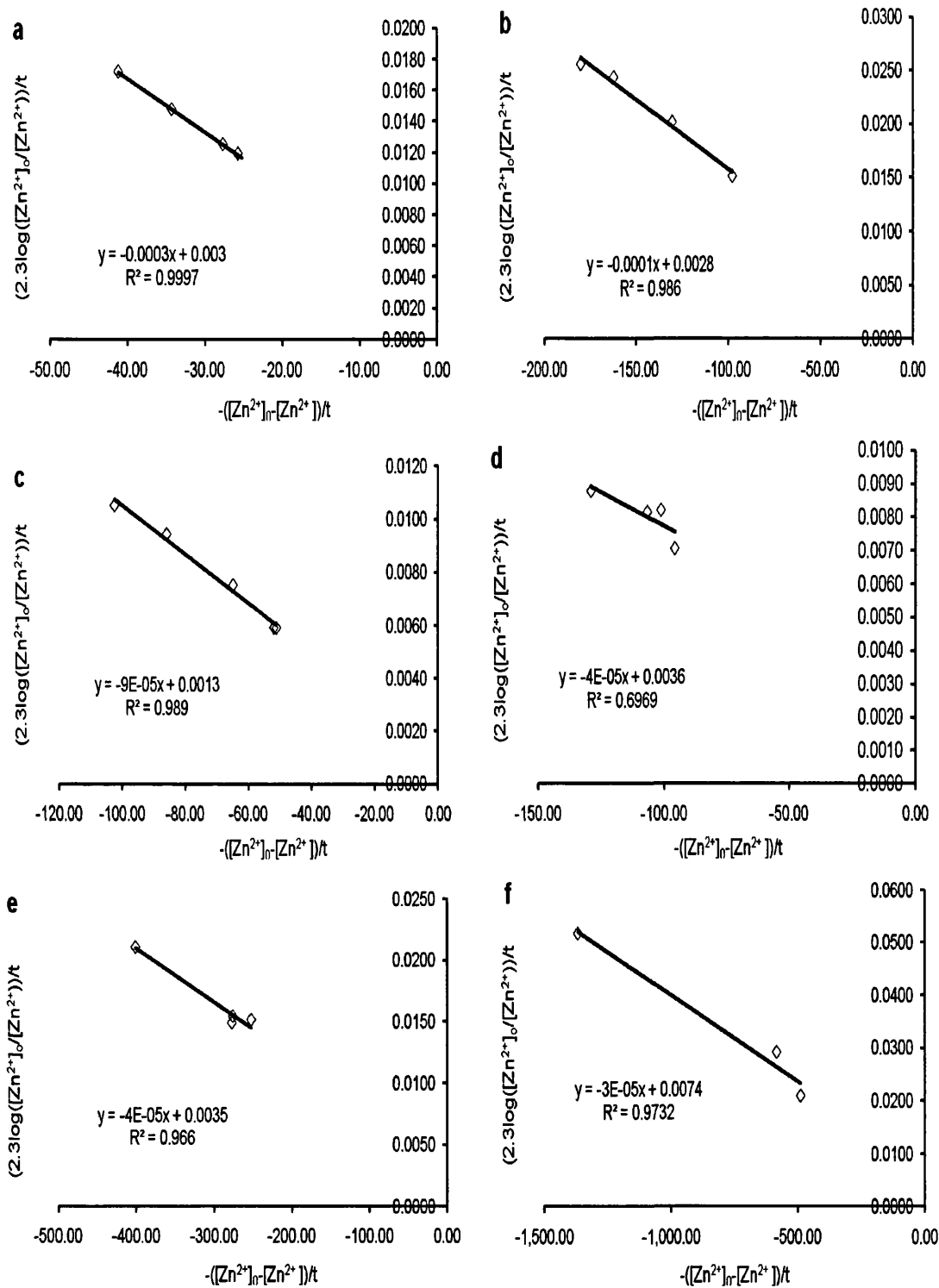
Figure 5-17: The effect of Zn concentration on the analysis of the zinc electrowinning reaction during the early stage of electrowinning at a constant NaOH concentration of 4 mol/L and a current density of 2000 A/m^2 . a) 2.5 g/L, b) 7.5 g/L, c) 10 g/L, d) 15 g/L, e) 20 g/L and f) 30 g/L using equation (5.19).

$$K_{eq} = \frac{[Zn_{metal}]_{eq}}{[Zn^{2+}]_{eq}} = \frac{r_{max_f} k_{d_r}}{r_{max_r} k_{d_f}} \tag{5.21}$$

where $[Zn_{metal}]_{eq}$ and $[Zn^{2+}]_{eq}$ are the concentration of zinc metal and zinc ions at equilibrium.

The complete integrated form of equation (5.20) can be represented as:

$$\left(\frac{r_{max_f}}{k_{d_f}} + \frac{r_{max_r}}{k_{d_r}} \right) t = \left(\frac{1}{k_{d_f}} - \frac{1}{k_{d_r}} \right) [Zn_{metal}] - 2.3 \log \left(1 - \frac{[Zn_{metal}]}{[Zn_{metal}]_{eq}} \right)$$

$$\left(1 + \frac{[Zn^{2+}]_0}{k_{d_r}} + \frac{\left(\frac{1}{k_{d_f}} - \frac{1}{k_{d_r}} \right)}{\left(\frac{r_{max_f}}{k_{d_f}} + \frac{r_{max_r}}{k_{d_r}} \right)} \frac{r_{max_r}}{k_{d_r}} [Zn^{2+}]_0 \right) \tag{5.22}$$

From equation (5.21), substituting for r_{max_r} in equation (5.22) and rearranging to a linear form yields:

$$\frac{2.3}{t} \log \left(1 - \frac{[Zn_{metal}]}{[Zn_{metal}]_{eq}} \right) = \left(\frac{\left(k_{d_r} - k_{r_f} \right)(1 + K_{eq})}{k_{d_r} k_{r_f}(1 + K_{eq}) + (k_{r_r} + k_{r_f} K_{eq})[Zn^{2+}]_0} \right) \frac{[Zn_{metal}]}{t}$$

$$- \frac{r_{max_f} \left(1 + \frac{1}{K_{eq}} \right)}{k_{d_f} + (\frac{k_{d_f} K_{eq} + k_{r_r}}{k_{r_r}(1 + K_{eq})})[Zn^{2+}]_0} \tag{5.23}$$

The value of k_{d_r} can be estimated by plotting $\frac{2.3}{t} \log \left(1 - \frac{[Zn_{metal}]}{[Zn_{metal}]_{eq}} \right)$ vs $\frac{[Zn_{metal}]}{t}$,

(see figure 5-18) and r_{max_r} is determined using equation (5.21).

Values of k_{d_f}, k_{d_r}, r_{max_f}, r_{max_r} and K_{eq} are presented in tables 5-2 and 5-3 for various zinc initial concentrations and current density values respectively. The constant values in table 5-3 were estimated from figures 5-17 and 5-18.
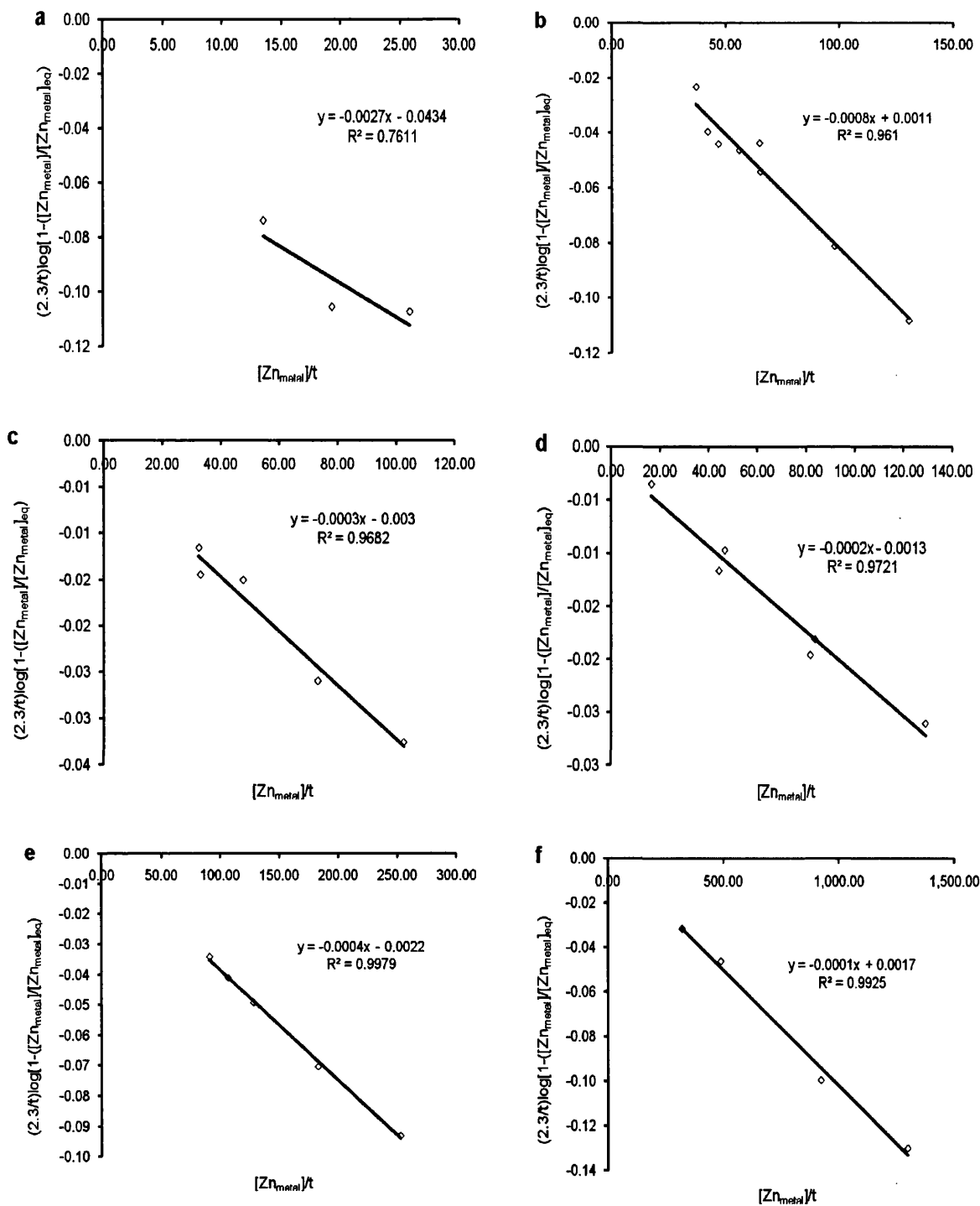
Figure 5-18: The analysis for zinc electrowinning reaction as reversible reaction considering limited cathode surface area at a constant NaOH concentration of 4 mol/L and a current density of 2000 A/m² and an initial zinc concentration of a) 2.5 g/L, b) 7.5 g/L, c) 10 g/L, d) 20 g/L, e) 25 g/L and f) 30 g/L using equation (5.23).

Table 5-2: The effect of Zn concentration on Values of k_{df}, k_{dr}, r_{maxf}, r_{maxr} and K_{eq} at constant current density of 2000 A/m² and NaOH concentration of 4 mol/L.

[Zn^{+2}]$_0$, g/L	k_{d_f}, mg/L	r_{max_f}, mg.L^{-1}.min^{-1}	k_{d_r}, mg/L	r_{max_r}, mg.L^{-1}.min^{-1}	K_{eq}
2.5	3333.33	10	2041.30	16.01	0.38
7.5	10000.00	28.00	6978.21	40.52	0.48
10	11111.10	14.44	10321.20	26.00	0.52
15	25000.00	90	9552.85	63.40	0.54
20	25000.00	87.50	15093.99	98.25	0.54
30	33333.33	216.67	30926.38	137.22	0.66

Table 5-3: The effect current density on the values of k_{df}, k_{dr}, r_{maxf}, r_{maxr} and K_{eq} constant zinc concentration of 20 g/L and NaOH concentration of 4 mol/L.

C.D., A.m^{-1}	k_{d_f}, mg/L	r_{max_f}, mg.L^{-1}.min^{-1}	k_{d_r}, mg/L	r_{max_r}, mg.L^{-1}.min^{-1}	K_{eq}
500	20833.33	35.00	19127.83	75.64	0.43
1000	25000.00	462.5	20177.72	310.31	1.20
1500	25000.00	255.00	17314.82	191.39	0.92
2000	25000.00	87.50	15093.99	98.25	0.55
2250	25000.00	230.00	17574.26	218.75	0.74
2500	33333.33	353.33	13073.50	315.49	0.44

5.3.3. Model Implementation:

5.3.3.1. Reaction Rate versus Zinc Ions Concentration Curves:

The effect of initial Zn concentration on relative reaction rate and unreacted zinc ion concentration is presented in figure 5-19. By examining the figure, each curve can be divided into three regions. At very low concentrations, the curve is linear where the rate is directly proportional to the concentration of zinc ions, (first order kinetics). At very high zinc ion concentration, the velocity becomes more independent of the

concentration indicating zero order kinetics. Between that, the relationship follows neither first order nor zero order kinetics. This confirms the applicability of equation (5.22) and the assumption of production inhibition due to the limited electrode surface area and the reversible reaction.
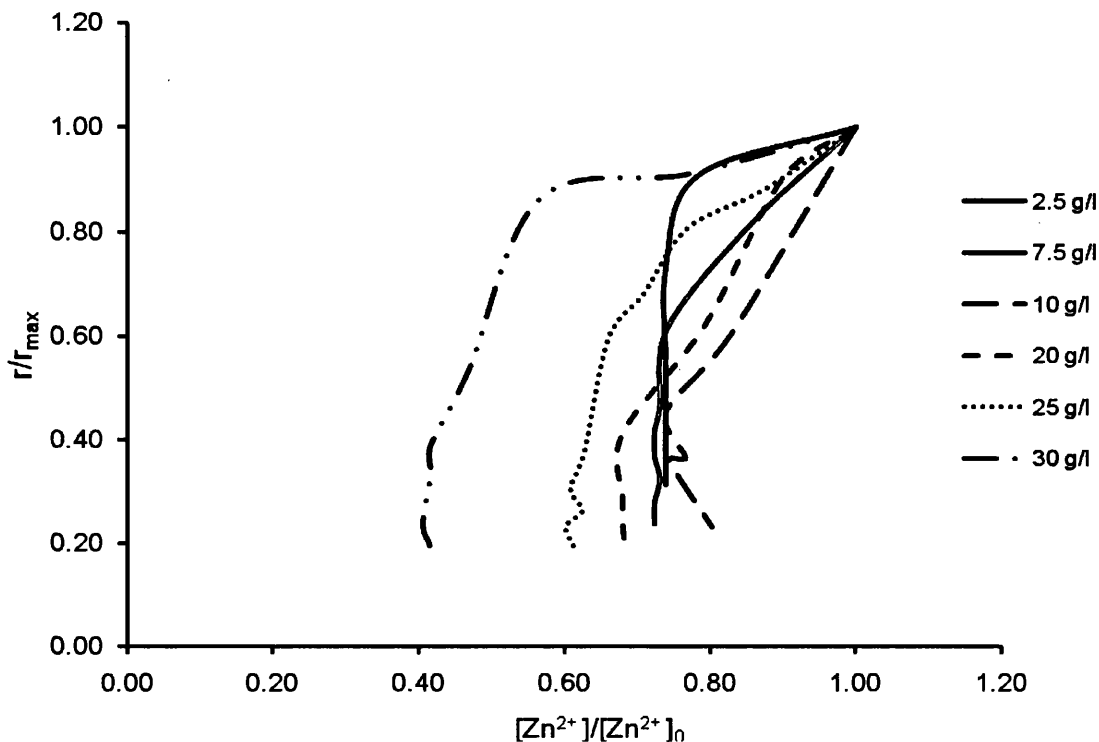
Figure 5-19: The effect of unreacted zinc fraction on relative reaction rate (r/rmax) at a various initial zinc concentrations.

5.3.3.2. Experimental and Model Data Fitting:

Based on the data presented in table 5-1 and 5-2, equations (5.12) and (5.20) can be employed to calculate the concentration distribution of zinc ions theoretically. The calculated concentration was plotted against time and the graph obtained was compared with the data obtained from the experiment, (see figure 5-20). Both the first order model (equation (5.11)) and the limited surface model are compared with experimental data. Both models gave good fits with the experimental data at times of less than 30 min but as the reactions proceed the first order model predicts concentrations much lower than the experimental data and the validity of the model

becomes uncertain. This becomes clearer when increasing initial zinc concentrations. Therefore, the concentration of zinc becomes strongly dependent on the solution volume after 30 min running time. This can be clear for most of the initial zinc concentration values. However, using the limited surface model and the calculation of metal absorption constants, and maximum rate values gave good agreement with experiments at all operating times especially at high initial zinc concentrations. For example, at initial concentrations of 10 and 30 g/L, the error associated with the first order model calculations is up to an average of 11.2 and 25.0% whereas the error in the case of metal limited surface area is recorded to be less by an average of 2.0 and 2.3% respectively.

Similar behaviour was obtained when varying the current density as shown in figure 5-21. However, zinc concentration seems to be less influenced with time by varying current density. This can be demonstrated by comparing the average error obtained, (i.e. from 15.1 and 14.8% with first order assumptions down to 3.6 and 3.7% with limited cathode surface area model for 500 and 2000 A.m^{-1} respectively).

The above results indicate that electrowinning of zinc does not follow first order kinetics after an initial depletion period. Therefore, the influence of limited surface area should be used particularly when high initial zinc concentration solutions were subjected to alkaline electrowinning.
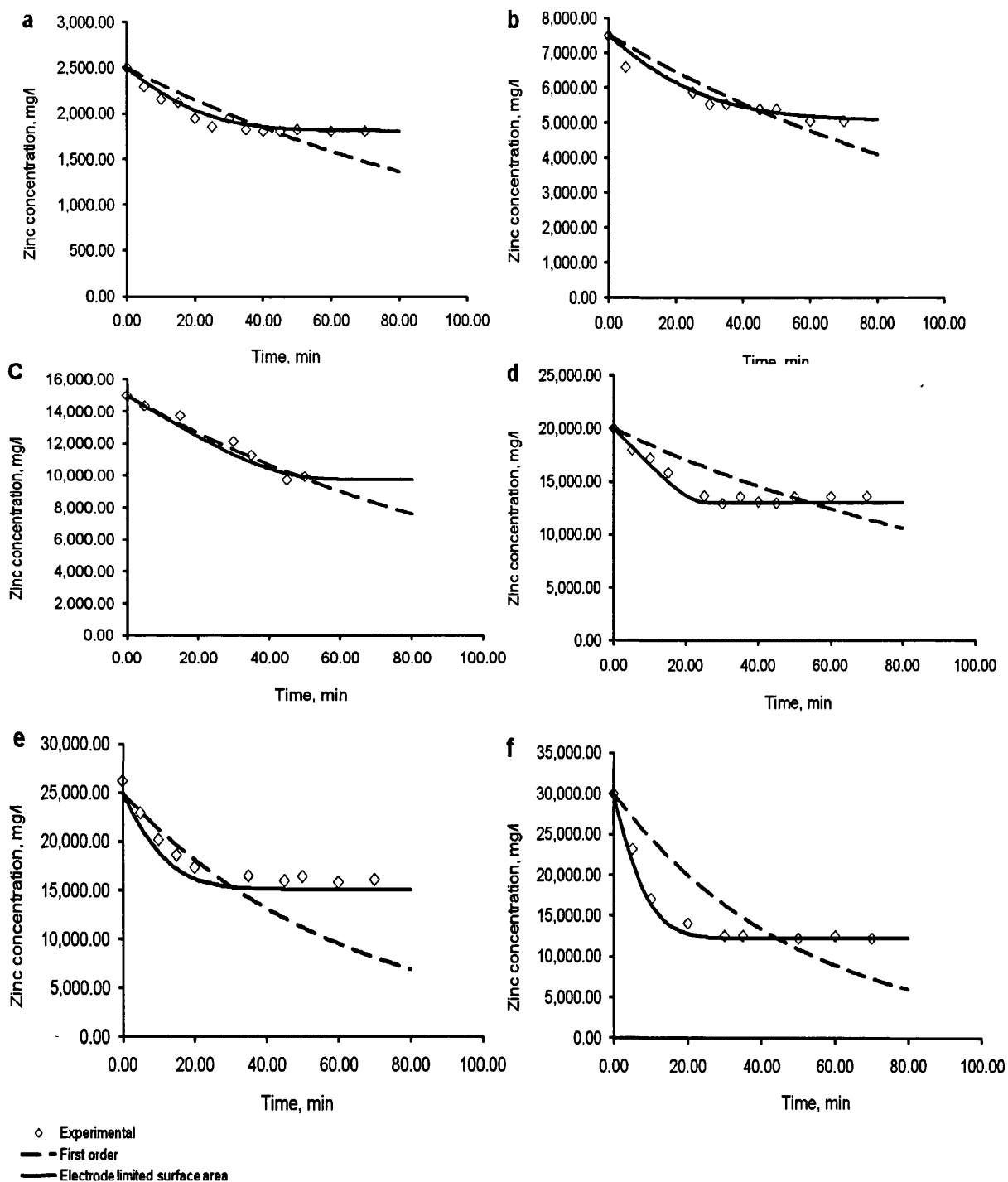
Figure 5-20: Experimental and calculated zinc concentration profile using first order and limited electrode surface area kinetics models. The analysis was performed at a constant NaOH concentration of 4 mol/L and a current density of 2000 A/m² and an initial zinc concentration of a) 2.5 g/L, b) 7.5 g/L, c) 10 g/L, d) 15 g/L, e) 20 g/L, and f) 30 g/L.
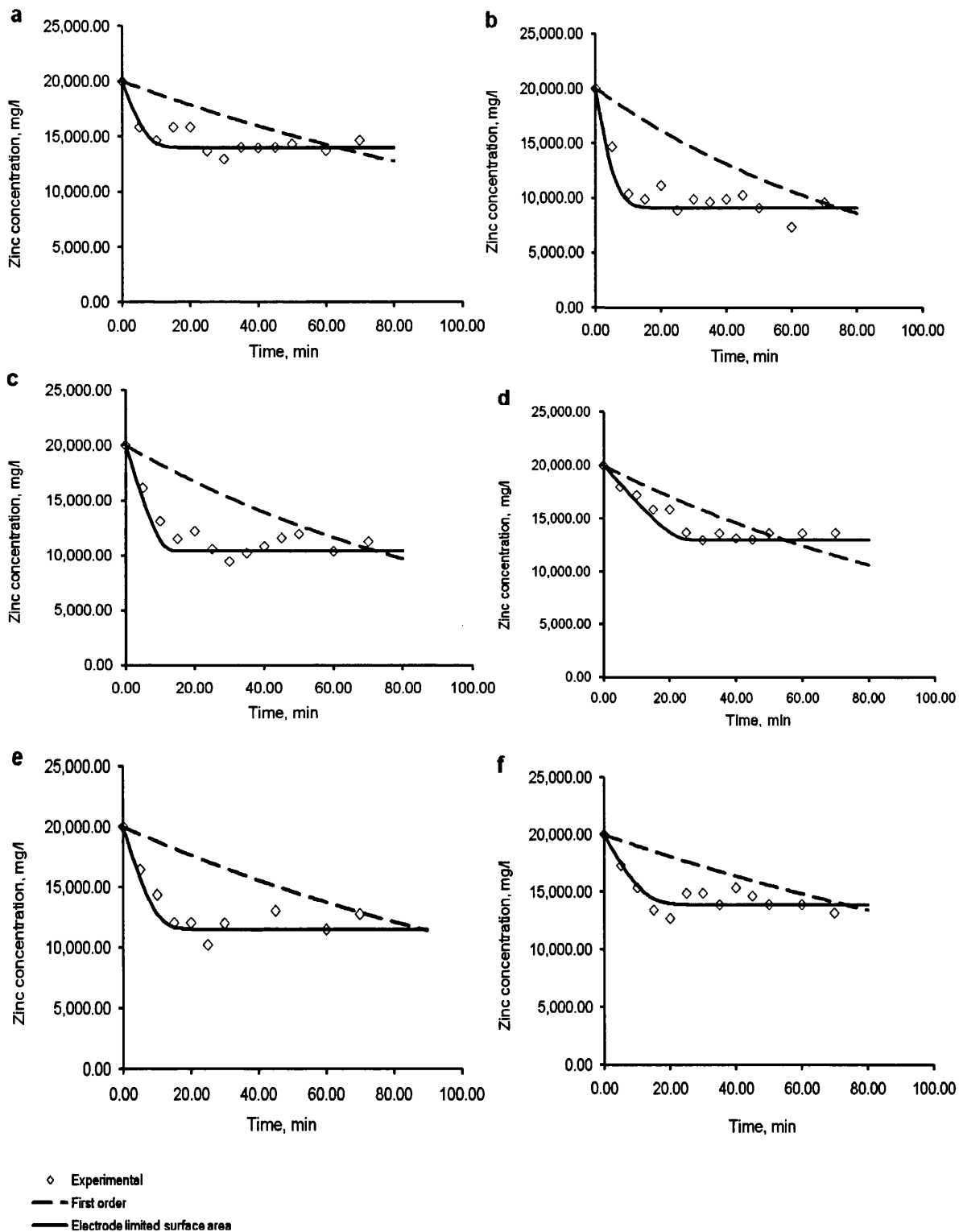
Figure 5-21: Experimental and calculated zinc concentration profile using first order and limited electrode surface area kinetics models. The analysis was performed at a constant NaOH concentration of 4 mol/L, an initial zinc concentration of 20 g/L and a current density of a) 500 A/m^2, b) 1500 A/m^2, c) 2000 A/m^2, d) 2250 A/m^2, and e) 2500 A/m^2.

5.3.4. Anaerobic Alkaline Zinc Electrowinning:

The formation of hydroxyl ions by the cathodic reaction could cause the dissolution of zinc based metal from the cathode and produce precipitate as ZnO and $3Zn(OH)_2$. $2ZnCO_3$ at early stages of the process (Ogle et al., 2000). Therefore, the behaviour of zinc electrowinning was examined by passing nitrogen gas, none-gassed or air gassed streams during electrowinning. The limited cathode surface area model is applied in order to confirm the validity of the model for the development of an electrowinning cell.

It can be noticed from figure 5-22 that the amount of zinc deposited was increased from 7,921 mg/L to 15,510 mg/L for anaerobic process, (about 52% deposition increase). On the other hand, the results of passing an air stream though the solution showed poorer recovery of zinc of 2,757 mg/L. Also, the value of reaction constants have been obtained using the integrated method employed in section 5.2.3. An increase in reaction constants was recorded when a nitrogen gas stream was passed with the highest recovery of 88.55%. This obviously improved the efficiency of the unit and in conclusion, reduced the effect of hydroxide ions on the cathodic reaction.
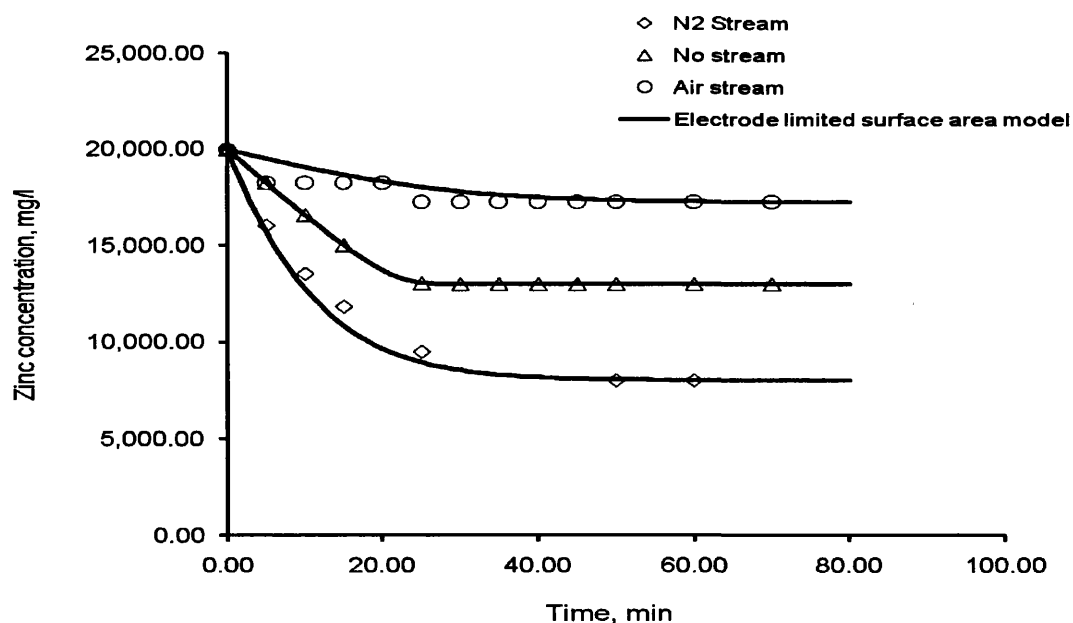
Figure 5-22: The effect of gassing on the disolved zinc concentration during electrowinning using an initial zinc concentration of 20 g/L at 4 mol/L NaOH and a current density of 2000 A/m^2.

Table 5-4: Values of k_{df}, k_{dr}, r_{maxf}, r_{maxr} and K_{eq} for different zinc electrowinning development schemes at initial zinc concentration of 20 g/L, current density of 2000 A.m^{-1} and NaOH concentration of 4 mol/L.

Gas stream	k_{d_f}, mg/L	r_{max_f}, mg.L^{-1}.min^{-1}	k_{d_r}, mg/L	r_{max_r}, mg.L^{-1}.min^{-1}	K_{eq}
Air	20408.0	2.04	18684.23	11.69	0.16
None	25000.0	87.50	15094.00	98.25	0.47
N$_2$	25000.0	242.50	22516.30	145.77	1.50

The calculations of kinetic constants were performed using steps explained in section 5.4.2. Experimental and calculated amounts of zinc remaining in solution during electrowinning were shown to be in good agreement with the model. This supports the validity of the limited surface area model for any further development of zinc electrowinning systems. It can be seen from table 5-4 that value of forward and backward maximum rate and deposition constant values are dramatically increased when passing nitrogen gas through the system. Also, values of the equilibrium constant were increased indicating that more zinc is deposited before the system reaches equilibrium. Also, it was found that the cell current efficiency is slightly increased but the energy used is reduced from 0.94 kWh/kg to 0.767 kWh/kg with a nitrogen stream. The morphology of zinc deposition was improved and a thicker deposition resulted when passing a nitrogen gas stream through the system as can be seen in figure 5-23.
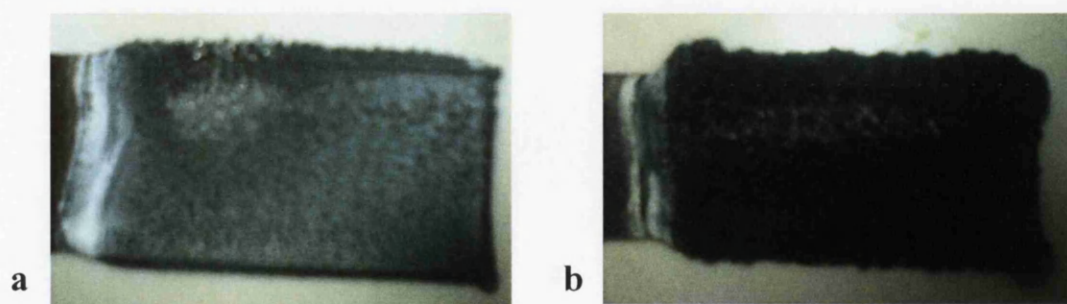
Figure 5-23: Photograph of zinc deposited obtained at a) normal electrowinning and b) anaerobic electrowinning.

5.4. Conclusion:

There are numerous publications concerned with the effects of design and operation on the economic performance of an electrochemical batch reactor. However, there appears to be little published which provides formal procedures for the selection of a specific or 'best' condition from an economical point of view.

The acidic zinc electrowinning using sodium hydroxide, NaOH and zinc hydroxide, $Zn(OH)_2$ to maintain pH and RuO_2/Ti anode still provides a poor performance. This means hydrogen gas as a result of the reduction of hydrogen ions generated during electrolysis has a strong influence on the electrowinning process.

Alkaline electrowinning has been described by many authors (St-Pierre and Piron, 1986, St-Pierre and Piron, 1990, Wijenberg et al., 1998, St-Pierre et al., 1985a) for various metals including zinc. It was quickly found for zinc, that alkaline electrowinning was potentially a more efficient process than the acidic electrowinning. In this chapter, the effects of operating parameters for the electrowinning cell are discussed. In order to evaluate the relative performance of the various conditions it is necessary to assess the importance of changing key parameters. These were the effects of initial zinc concentration and current density on current efficiency. Only small changes in current efficiency were observed when changes to NaOH were made. Generally, current efficiency was high, (between 86% and 99% at 15 and 30 g/L respectively). This is due to the fact that a small part of the current applied was consumed in the formation of hydrogen gas at the cathode. Hydrogen ion concentrations are substantially lower than at high pH of the alkaline (around pH 13) bath compared to that in the acid bath (around pH 4).

The results of the experiments in this project for alkaline zinc electrowinning show that an increase in the current density for a fixed value of initial zinc and NaOH concentration increase the zinc recovery percentage and electrical energy used by the system. The process worked well above 10 g/L but even then the reaction comes to equilibrium and so a high concentration of zinc is required for an efficient electrowinning process. Therefore addition of Zn concentrate would be required to give efficient recovery.

The metal deposition kinetics followed a first order reaction at low concentration however when the systems approached equilibrium, a model based on limited cathode surface area gave better prediction of performance and fitted the experimental data very well.

Therefore, the limited cathode surface area model can describe the process over wide range of Zn concentrations. This confirms the importance of considering the reverse reaction and cathode limited deposited area in the alkaline electrowinning of zinc. Using this approach, the prediction of the process can be improved, since most of the previous models derived in the literature only consider a first order kinetics (Thilakavathi et al., 2009, El-Shakre et al., 1994, Saleh et al., 1995).

The limited cathode surface area model can be employed in several alkaline zinc electrowinning applications in order to improve the prediction of these systems and provide more accurate results for overall process evaluation and economics. This was demonstrated by an attempt to increase the productivity when passing the nitrogen stream through the system. The data of the experiments of electrowinning cell results performed under optimum conditions presented in table 5-5 will be employed in the design of industrial scale zinc recovery units, which will be covered in chapter 6.

Table 5-5: Optimum Anaerobic alkaline galvanostatic electrowinning parameters and results.

Term	Value
Initial zinc concentration, g/L	20
NaOH concentration, mol/L	4
Electrodes	Stainless steel
Current density, A/m^2	2000
Specific energy consumption, kWh/kgZn	0.767
Current efficiency%	98
Percentage recovery	88.55
Run time, min	70

Chapter 6

6. ASSESSMENT OF AN INTEGRATED ZINC RECOVERY PROCESS

This chapter discusses the final stage of the project aim concerning modelling of the design and operation of a zinc recovery unit. Although not all of the stages of these processes have been studied in detail, the two major steps in Zn capture based on PEUF (see chapter 4) and purification by electrowinning (see chapter 5) have been the subject of the preceding two chapters of experimental work. In this part of the work the data generated was used in a process model based on leaching a mining tailings waste. Several successive steps are involved; leaching and complexation of the metal by means of polymeric ligands; ultrafiltration of the complex, which produces a purified recyclable effluent together with a concentrated metal complex solution; this is decomplexed by acidification; ultrafiltration of the concentrate after acidification allows the recycling of the complexing agent; and the free metal solution is then precipitated using sodium hydroxide to form a Zn hydroxide solid, and finally after dissolution in an alkaline environment to form a concentrated zinc solution, the metal in a pure form is recovered by electrolysis. At the same time, the regeneration of HCl, NaOH and distilled water required was considered using an electrodialysis unit.

The results of the model were assessed in terms of the profit analysis in relation to the feed rate and this in turn provides the relationship between zinc production rate, (i.e. zinc demanded) and the overall net profit.

The model was constructed using a MS excel worksheet based on material balances performed for each unit individually and the second, final economic evaluation of the whole process as functions of zinc extraction efficiency and the amount solid feed in order to validate the study. Data employed in this work, (see appendix A1) were obtained from the literature and laboratory work for the ultrafiltration experiments presented in chapter 4 and zincate electrolysis described in chapter 5.

6.1. Unit Operations Description and Material Balance:

The quantitative flow diagram for the integrated process is shown in figure 6-1. The following sections describe the mathematical model for each unit individually.

Basis: One operating day
Unit designed to extract 50% of zinc from 1000 t of solids containing
2% by weight zinc per day

Material input

Processing

Products

Solids
980 t inerts
20.00 t Zn

Leaching & complexation unit
19739.47 t Water
9.86 t Zn
48.51 t PEI
29.56 t NaCl

Solids output
980.00 t inerts
12.93 t Zn
0.05 t PEI
0.03 t NaCl
19.79 t Water
0.115 t HCl

Polymer solution
48.56 t PEI
2.79 t Zn
19759.23 t water
115.28 t HCl
20.23 t NaOH

Concentration unit
9.86 t Zn
48.51 t PEI
1924.37 t Water

Permeate
17815.10 t water
29.56 t NaCl

Acidic water
7.89 t HCl
3975.29 t water

Decomplexation and washing unit
7.1 t Zn free
14.74 t ZnCl$_2$
3975.29 t water

Retentate
48.51 t PEI
2.8 t Zn

NaOH solution
8.65 t NaOH solids
45.40 t water

Zn(OH)$_2$ sedimentation
10.74 t Zn(OH)$_2$

NaCl solution
12.65 t NaCl
4020.70 t water

Zincate formation
19.39 t zincate
352.52 t water

Electrowinning cell
99.99% Zinc metal
6.26 t Zn

2.22 t zincate
8.65 t NaOH solids
352.52 t water

NaCl input
21835.78 t water
42.21 t NaCl

Electrodialysis
25.61 t Cl$_2$

13.17 t HCl
28.86 t NaOH solids
21822.80 t water

Figure 6-1: Quantitative flow diagram for the production of zinc using PEUF and electrowinning for zinc purification and recovery.

Calculations of the operating conditions were based on a feed flow-rate of solids containing 2% by weight zinc with 0.1% losses in the polymer employed for leaching.

6.1.1. Continuous Leaching and Complexation Processes:

6.1.1.1. Introduction:

The sources of the leaching materials can come directly from mining tailings which are to be reworked for Zn recovery. Alternatively they may be generated directly from virgin ore. The tailings are preferable as these will already be in the form for leaching so avoiding the costs of crushing and grinding. The fine solids are thus passed through the leaching unit where a leach solution of PEI was directly in contact with particles so that zinc could be progressively and selectively be removed from the ore leaving a depleted inert materials and a complexed PEI-Zn stream to be refined.

The leaching process typically proceeds in three parts: first the phase change as the metal dissolves and is absorbed onto the polymer (the precise nature of this is unknown in this case); secondly it passes through the solvent in the pores of the solid to the outside of the particle by diffusion, and thirdly the transfer of the solute from the solution in contact with the particles to the main bulk of the solution, typically this also controlled by diffusive and convective mass transfer. Any one of these three processes may be responsible for limiting the extraction rate. However, the first process is believed to usually occur so rapidly that it has a negligible effect on the overall rate. If the diffusion of the solute through the porous structure of the residual solids is the controlling factor, the material should be of small size so that the distance the solute has to travel is small. On the other hand, if diffusion of the solute from the surface of the particles to the bulk of the solution is the controlling factor, a high degree of agitation of the fluid would be required.

The leach reagents need to be at about pH 5.5 (as discussed in chapter 4), to make sure the absorption reaction and capacity of the PEI is at its maximum forming a good metal complex. Therefore, adjustment of the pH of the solution is necessary so that metal ions can be recovered. Therefore, additions of HCl and/or NaOH solutions are made in order to obtain suitable pH. The precise amounts will be

dependent on the nature of the mineral ore which may be composed of carbonates, for example.

6.1.1.2. Material Balance:

The feed solid passes through a series of washers arranged to provide countercurrent flow of the solids and solvent. The washing solvent of polymer solution at certain concentration could also be passed through in a countercurrent scenario to perform complexation and washing at the same time (see figure 6-2). This should enable zinc ions to be continuously absorbed by PEI up to the polymer capacity of 0.1051 mg Zn/mg PEI, (see section 4.3).

If, for example, it is required to leach 1,000 t of solids per day containing, 2% zinc (20 t zinc/day), a particular percentage of the metal will be recovered via complexation with 6.0 g/L PEI solution as an optimum concentration, (see chapter 4). The precise extraction rate will affect the size of the unit, the more efficient extraction the less material that will be required to be processed. Generally the extraction and its process conditions will be dependent on the nature of the ore/tailings (i.e. chemistry of the inert materials, particles size and type of the zinc mineral, the study of which are beyond the scope of the current project). To address this problem within the modelling process calculations four different extraction efficiencies have been used (see section 6.2), and its impact on the economy of the process can be assessed.

The results of the leaching material balance model are listed in table A5-1. Based on the data provided in appendix A1, the amount of the solution produced from a three stage leaching unit can be estimated by applying the overall, PEI and zinc metal material balance on the system shown in figure 6-2 as the following:

overall material balance:

$$F_L + F_{PEI} = W_S + W_P \tag{6.1}$$

where F_L is the total amount of solids fed to the unit, (input stream 1), t/day, F_{PEI} is the total amount of polymer solution fed to the unit, (input stream 2), t/day, W_S is

the amount of solids output as inert, (product stream 2), t/day, W_P is the amount of complex solution output, (product stream 1), t/day.

Input 1:
t solid/day
t Zn/day

Input 2:
t PEI/day
t Zn/day
t NaOH/day
t water/day

$F_{PEI} X_2$ $F_{PEI} X_3$

Product 1:
t PEI/day
t Zn/day
t water/day
t HCl/day
t NaCl/day

Stage 1   Stage 2   Stage 3

W_1 W_2 W_3

First thickener   **First washing thickener**   **Second washing thickener**

Product 2:
t non Zn
t solid/day
t Zn/day
t PEI/day
t NaCL/day
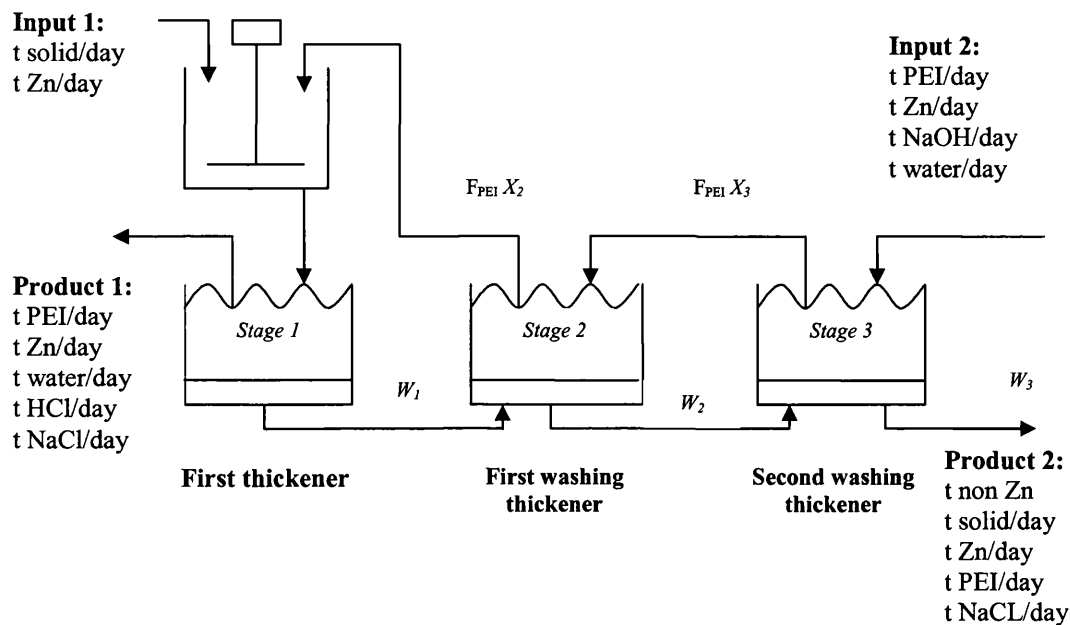
Figure 6-2: Agitator and washing system. Liquid is referred to as the overflow and a mixture of insoluble residue and solution is referred to as the underflow.

For the zinc material balance:

$$f_{L,Zn} + f_{PEI,Zn} = w_{S,Zn} + w_{P,Zn} \qquad (6.2)$$

where $f_{L,Zn}$ is the amount of zinc in the solid feed stream, t/day, $f_{PEI,Zn}$ is the amount of zinc in the polymer solution stream input, t/day, $w_{S,Zn}$ is the amount of zinc in the solid inert stream, t/day, $w_{P,Zn}$ is the amount of zinc in the liquid product stream, t/day.

For the PEI material balance:

$$f_{L,PEI} + f_{PEI,PEI} = w_{S,PEI} + w_{P,PEI} \qquad (6.3)$$

where $f_{L,PEI}$ is the amount of PEI in the solid feed stream, t/day, $f_{PEI,PEI}$ is the amount of PEI in the polymer stream input, t/day, $w_{S,PEI}$ is the amount of PEI in the solid inert stream, t/day, $w_{P,PEI}$ is the amount of PEI in the liquid product stream, t/day

For the solid inert balance:

$$f_{L,solid} + f_{PEI,solid} = w_{S,solid} + w_{P,solid} \qquad (6.4)$$

where $f_{L,solid}$ is the amount of non zinc solid in the solid feed stream, t/day, $f_{PEI,solid}$ is the amount of none zinc solid in the polymer stream input, t/day, $w_{P,solid}$ is the amount of none zinc solids in the liquid product stream, t/day and $w_{S,solid}$ is the amount of none zinc solid in the inert stream.

The amount of zinc leaving with liquid products at the beginning of the process, which is function the amount of zinc complexed with PEI and nature of feed input to the system was estimated using:

$$w_{P,Zn} = f_{L,Zn} \times \frac{X_{complexation}}{100} \times \frac{X_{Extraction}}{100} \qquad (6.5)$$

where $X_{complexation}$ represents the fraction of zinc complexed with PEI, obtained from table 4-5 for initial polymer concentration of 6.0 g/L and $X_{Extraction}$ is the extraction efficiency which depends on the type and nature of the feed input. The amount of polymer required, $f_{PEI,PEI}$ to recover $w_{P,Zn}$ t/day can be calculated as:

$$f_{PEI,PEI} = L \times w_{P,Zn} \qquad (6.6)$$

where L is the polymer capacity obtained as indicated in section 4.1.

The amount of PEI solution losses during the leaching operation was assumed to be relatively small and could be neglected. Therefore, the overall PEI losses, $f_{Loss,PEI}$ occur due to the other operations. $f_{Loss,PEI}$ was evaluated as:

$$f_{Loss,PEI} = (X_{PEI,losses} / 100) \times w_{P,PEI} \qquad (6.7)$$

where $X_{PEI,losses}$ is the fraction of polymer solution losses during the recovery operation.

The amount of NaOH, HCl and water losses were calculated using equation (6.7) for each substance amount input. Therefore, amount of each species output from the unit was obtained from the difference between initial material amount and losses. Water required for preparing 6.0 g/L PEI solution was estimated by subtracting the amount of PEI solution from 50% PEI solvent before the operation started. Knowing both the concentrations of zinc remaining and polymer after the washing stage, (see section 4.18); $C_{Zn,w}$ and $C_{PEI,w}$ in g/L, the total amount of polymer solution, R_w after washing and before dilution was then calculated as:

$$R_w = \frac{f_{PEI,PEI} \times 1000.00}{C_{PEI,w}}$$
(6.8)

and the amount of zinc input in polymer stream, $f_{PEI,Zn}$ could be determine as:

$$f_{PEI,Zn} = \frac{C_{Zn,w} \times R_w}{1000.00}$$
(6.9)

The total PEI solution entering the leaching system was determined using the dilution formula as:

$$F_{PEI} = \frac{R_w \times C_{PEI,w}}{C_{PEI,F}}$$
(6.10)

where $C_{PEI,F}$ is the concentration of polymer required to perform the complexation step, (6.0 g/L). Therefore, the zinc output with solid inert is calculated by rearranging equation (6.2) as:

$$w_{S,Zn} = f_{L,Zn} + f_{PEI,Zn} - w_{P,Zn}$$
(6.11)

All the non zinc solids leaves via the W_S stream. Therefore, values of $f_{L,solid}$ and $w_{S,solid}$ were calculated as:

$$f_{L,solid} = w_{S,solid} = F_L - f_{L,Zn}$$
(6.12)

Therefore,

$$W_S = w_{S,solid} + w_{S,Zn} \qquad (6.13)$$

and from equation (6.1):

$$W_P = F_L + F_{PEI} - W_S \qquad (6.14)$$

Before the whole integrated process starts running, it was required to drop the polymer solution pH from pH 10 to pH 5.5 by the addition of 0.5 mol/L HCl and provide an initial PEI concentration of 6.0 g/L. The amount of HCl solution was estimated by multiplying the amount of PEI solution required at the beginning of the process by HCl-polymer volume ratio obtained from figure 3-5. Therefore, the amount of 37% HCl could be estimated via:

$$f_{HCl} = \frac{F_{HCl} \times Mwt_{HCl} \times C_{HCl}}{1000.00 \times 0.37 \times \rho_{HCl}} \qquad (6.15)$$

where F_{HCl} is the amount of 0.5 mol/L HCl, t/day, Mwt_{HCl} is the molecular weight of HCl, C_{HCl} is the concentration of the solution in mol/L and ρ_{HCl} is the specific gravity of 0.37% concentrated HCl = 1.18.

The amount of 0.5 mol/L NaOH required changing PEI solution pH, (from pH 2.5 to pH 5.5), F_{NaOH}, t/day was estimated using figure 3-5 since 1.0 mole of HCl is equivalent to 1.0 mole NaOH. Hence, the amount of NaOH solids required to prepare a solution of 0.5 mol/L, f_{NaOH} is calculated as:

$$f_{NaOH} = \frac{F_{NaOH} \times Mwt_{NaOH} \times C_{NaOH,Leaching}}{1000.00} \qquad (6.16)$$

where Mwt_{NaOH} is the molecular weight of NaOH and $C_{NaOH,Leaching}$ is the concentration of the solution in mol/L. Water required for preparing 0.5 mol/L NaOH and 0.5 mol/L HCl solutions was estimated by subtracting the amount of each solution from NaOH solids or 37% HCl at the beginning of the operation.

6.1.2. Continuous Concentration/Ultrafiltration Process:

After complexation during the leaching stage calculations, the liquid stream produced, W_p, was used as feed into the continuous ultrafiltration unit in order to concentrate the polymer-metal ions complex. The unit can also be used to perform decomplexation of the polymer-metal complex by acidification and then washing stages after concentration. The sequence of operating the system to perform the above three stages will be discussed in section 6.1.9. The mathematical modelling for the continuous feed PEUF process was developed from the fundamental principle of mass balance alongside the application of the Langmuir isotherms data obtained from section 4.1.2. All the results of the concentration ultrafiltration material and energy balance are presented in table A5-2.

From chapter 4, the behaviour of ultrafiltration concentration performed in a batch system was studied. However, this section deals with the system as a continuous case. The system suggested in this case is shown in figure 6-3, where feed enters the system at mass rate W_P and permeate and retentate leave the system at P_C and R_C respectively. The addition of NaOH to the PEI solution before leaching took place should result in the formation of NaCl, since the polymer releases Cl^- ions attached to the polymer structure (Kobayashi et al., 1987, Canizares et al., 2005, Jones, 2005, Jaung and Shiau, 2000). All the NaCl is assumed to leave via the permeate stream and passed through the electrodialysis system for the generation of NaOH, HCl and re-produce distilled water.

For the design purposes, the material balance around the system described in figure 6-3 can be performed as follows:

Overall material balance:

$$W_P = R_C + P_C \tag{6.17}$$

For the zinc balance:

$$W_P C_{Zn,W_P} = P_C C_{Zn,P_C} + R_C C_{Zn,R_C} \tag{6.18}$$

where: $C_{Zn,Wp}$ = Zinc concentration in feed, g/L, $C_{Zn,Rc}$ = Zinc concentration in retentate, g/L, $C_{Zn,Pc}$ = Zinc concentration in permeate, g/L.

Feed stream:
t Zn/day
t PEI/day
t water/day
t HCl/day
t NaCl/day

Retentate recycled:
t Zn/day
t PEI/day
t water/day

Permeate:
t NaCl/day
t water/day
t HCl/day

Feed tank

Pump
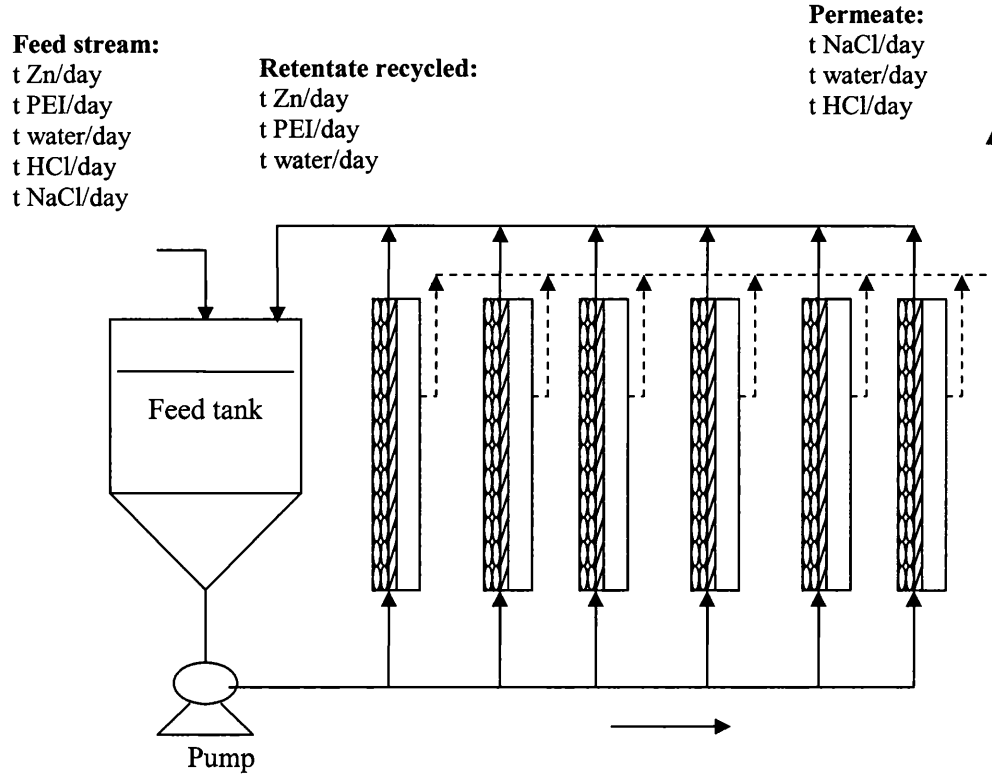
Figure 6-3: The schematic of continuous parallel array concentration ultrafiltration process in a plant.

For the PEI balance:

$$W_P C_{PEI,W_P} = P_C C_{PEI,P_C} + R_C C_{PEI,R_C} \qquad (6.19)$$

where $C_{PEI,Wp}$ = Polymer concentration in feed, g/L, $C_{PEI,Rc}$ = Polymer concentration in retentate, g/L and $C_{PEI,Pc}$ = Polymer concentration in permeate, g/L.

Several assumptions were made in order to simplify the calculations of optimum variables. These are:

- No interaction between the membrane surface and free metal ions.

- The formation of zinc hydroxide is neglected.

- The zinc-polymer complex is completely retained by the membrane and only NaCl passed through.

- Equilibrium between polymer and zinc ions is reached instantaneously.

- Cake thickness is not limiting flux at 6 g/L PEI and this was in fact observed at the early stages of the process during the lab work (see section 4.6)

The amount of retentate can be calculated by dividing the total feed input by volume concentration factor, VCR of 10:

$$R_C = \frac{W_P}{VCR}$$

(6.20)

Therefore, the amount of permeate can be found by rearranging equation (6.17) to yield:

$$P_C = W_P - R_C$$

(6.21)

Since the feed stream contain 6 g/L of polymer. Hence rearranging equation (2.19) for $C_{PEI,Pc} = 0.0$ yields:

$$C_{PEI,R_C} = \frac{W_P C_{PEI,W_P}}{R_C}$$

(6.22)

From the results obtained in table A5-1 the concentration of zinc entering the filtration system was found to equal 0.609 g/L. Hence from equation (6.18) for no zinc associated with the permeate:

$$C_{Zn,R_C} = \frac{W_P C_{Zn,W_P}}{R_C}$$

(6.23)

Based on the results of the batch ultrafiltration experiments discussed in chapter 4, permeate flux, J was found to be equal to 0.022 m^3/m^2.hr at a volume concentration factor, VCF of 10. Hence, the permeate flow can be determined as a function of membrane area as:

$$P_C = J \times A \tag{6.24}$$

where A is the membrane surface area in m^2, rearranging the equation (6.24) for A:

$$A = \frac{P_C}{J} \tag{6.25}$$

The amount of energy consumed by the unit is mainly due to pumping the feed to the membrane system. The total energy consumed by a concentration ultrafiltration unit can be presented as:

$$E = E_{Thermal} + E_F \tag{6.26}$$

where $E_{Thermal}$ represents the thermal energy by heating to maintain the process fluid at the required temperature, E_F, kW/m^2 is the pressure energy required to feed the system at specific transmembrane pressure or pumping energy which is the driving force for the ultrafiltration unit. This can be represented as:

$$E_F = \frac{\Delta P.W_P}{A.\eta} \tag{6.27}$$

where ΔP is the pressure drop across the module in psi, and η is the pump efficiency, Usually $0.5 - 0.85$ (Cheryan 1998).

6.1.3. Decomplexation and Washing Processes:

In Chapter 4, a diafiltration study was conducted in a batch container simply by adding acidified water to the feed solution in the container. In continuous systems, it could be done by the addition of acidic water at pH 2.5 and recycling the permeate stream in the same UF system again for further washing (see figure 6-4).

The unit is well mixed so that all added water with free zinc ions leaves the system as permeate each time. The results of the decomplexation and washing/ultrafiltration model using equations employed in the methodology are shown in table A5-3. If the incoming solution contains only Zn then it would be possible no washing stages would be required as no contaminate removal is required.

After the addition of acidic water to maintain the retentate solution at pH 2.5, the first washing process takes place via ultrafiltration. The mathematical model used considers the membrane unit as two linked membrane modules in series.

Acidic water:
t water/day
t 37% HCl/day

Acidic water:
t water/day
t 37% HCl/day

Retentate 1

Retentate 2
t Zn/day
t PEI/day
t water/day

Feed:
t Zn/day
t PEI/day
t water/day

Feed Tank

Feed Tank

Permeate 1

Permeate 2
t Zn/day
t ZnCl$_2$/day
t water/day
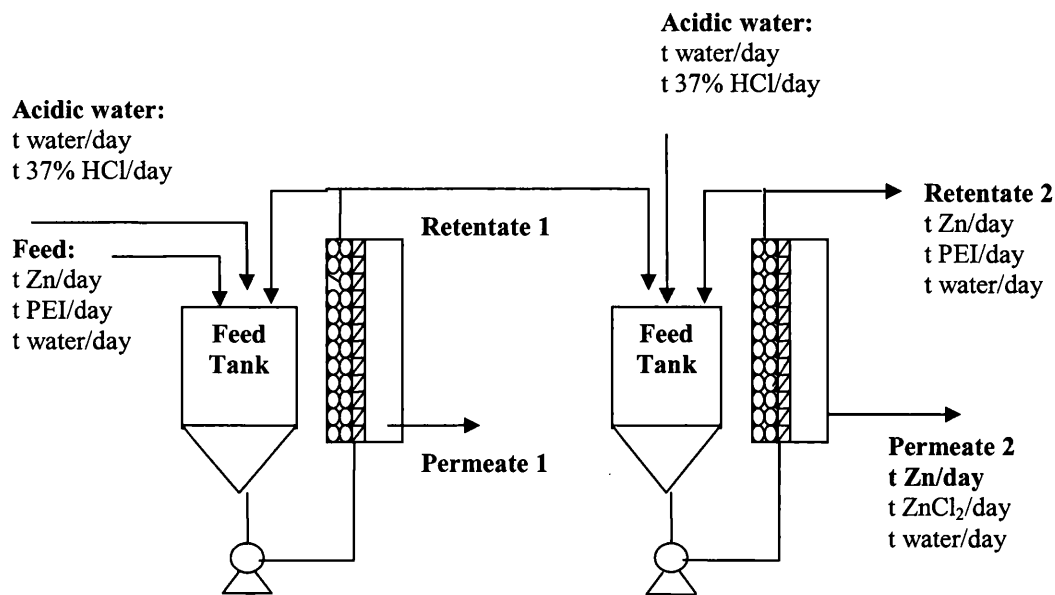
Figure 6-4: A decomplexation and washing scheme. All values were obtained from the results of batch filtration washing stages discussed in chapter 4.

Based on the results obtained in the concentration step, presented in section 6.1.2, the amount of complex retentate was used as feed to this unit and the concentration of zinc output in the permeate stream was taken from table 4-6. Taking a steady state mass balance around each stage and assuming that all added water leaves the filtration system as permeate, the relationships between input and output flow-rates and membrane area can be obtained as follows:

For the overall material balance around the first washing stage:

$$F_W + W_1 = R_1 + P_1$$

(6.28)

where: F_W is the concentrated feed mass rate entering the first stage, t/day, W_1 is the acidic water flow-rate at the first stage, t/day, P_1 is permeate mass rate from the first stage, t/day, R_1 is retentate flow-rate from the first stage, t/day.

For the zinc balance:

$$F_W . C_{Zn,F_W} = R_1 . C_{Zn,R_1} + P_1 . C_{Zn,P_1}$$

(6.29)

where $C_{Zn,Fw}$ is the zinc ions concentration in the feed stream, g/L, $C_{Zn,R1}$ is the zinc ions concentration at first stage retentate stream, g/L, $C_{Zn,P1}$ is zinc ions concentration at first stage permeate stream, g/L.

For the PEI balance results:

$$F_W . C_{PEI,F_W} = R_1 . C_{PEI,R_1} + P_1 . C_{PEI,P_1}$$

(6.30)

where $C_{PEI,Fw}$ is the polymer concentration in the feed stream, g/L, $C_{PEI,R1}$ is the polymer concentration in the first stage retentate stream, g/L and $C_{PEI,P1}$ is the polymer concentration in the first stage permeate stream, g/L. The amount of acidic water was calculated as:

$$W_1 = WR \times F_w - F_w$$

(6.31)

where WR is the washing ratio. The value of P_1 was then calculated by rearranging equation (6.28) and substituting the value of W_1. The membrane area can be calculated using the following equation:

$$A = P_1 / J_1$$

(6.32)

After computing the first time flow-rates and membrane area, the resulting retentate then becomes the feed for the second time washing and so on. The overall equations that describe the model for n number of washing times, (n = 2 in this case), can be generalised as:

Overall balance:

$$R_{n-1} + W_n = R_n + P_n$$

(6.33)

where: R_{n-1} is the concentrated feed mass rate entering the nth time, t/day, W_n is water mass rate added to n^{th} stage, t/day, P_n is permeate mass rate outlet the nth stage, t/day. R_n is retentate mass rate in the nth stage, t/day.

For the zinc balance:

$$R_{n-1}.C_{Zn,n-1} = R_n.C_{Zn,R_n} + P_n.C_{Zn,P_1} \qquad (6.34)$$

where $C_{Zn,Rn-1}$ is zinc ions concentration at feed stream to n^{th} stage, g/L, $C_{Zn,Rn}$ is zinc ions concentration at n^{th} stage retentate stream, g/L, $C_{Zn,Pn}$ is zinc ions concentration at n^{th} stage permeate stream, g/L.

For the PEI balance:

$$R_{n-1}.C_{PEI,n-1} = R_n.C_{PEI,R_n} + P_n.C_{PEI,P_n} \qquad (6.35)$$

where $C_{PEI,Rn-1}$ is polymer concentration at feed stream entering the nth stage, g/L, $C_{PEI,Rn}$ is polymer concentration at n^{th} stage retentate stream, g/L and $C_{PEI,Pn}$ is polymer concentration at n^{th} stage permeate stream, g/L.

For the amount of acidic water:

$$W_n = WR \times R_{n-1} - R_{n-1} \qquad (6.36)$$

The total volume of acidic water was estimated by multiplying the initial amount of water by the number of washing stages. However, the membrane area for the nth stage is assumed to be the same as the first stage since the process was repeated in the same unit. The volume of retentate before washing and both $C_{Zn,Fw}$ and $C_{Zn,Pn}$, (equal to 2.18 g/L after two times washing) are known from the experimental results presented in chapter 4. Hence the overall amount of zinc leaving in the permeate, $r_{D1,ZnFree}$ t/day was calculated as:

$$r_{D,ZnFree} = \frac{n \times W_1 \times C_{Zn,P_n}}{1000.0} \qquad (6.37)$$

From equation (6.29):

$$r_{D,ZnComplex} = F_W.C_{Zn,F_W} - r_{D,ZnFree} \qquad (6.38)$$

After the addition of 0.5 mol/L HCl solution, zinc ions released from the complex solution go through the membrane system with the permeate. Therefore, by knowing the amount of zinc ions liberated during this process, the amount of $ZnCl_2$ was calculated as:

$$wt_{ZnCl_2} = r_{D,ZnFree} \times \frac{Mwt_{Zncl_2}}{Mwt_{Zn}} \qquad (6.39)$$

where wt_{ZnCl2} is the amount of $ZnCl_2$ entering the unit in t/day, Mwt_{ZnCl2} is molecular weight of $ZnCl_2$ and Mwt_{Zn} is the molecular weight of the zinc element. Therefore, the amount of 37% concentrated HCl required was obtained by calculating the amount of HCl required to produce $ZnCl_2$ and employing equation (6.15) without multiplying by the concentration term. The energy consumption due to the feed pumping was calculating using equation (6.27).

6.1.4. Metal Hydroxide Sedimentation Process:

Zinc ions associated with permeate flow-rates resulting from the washing stage can be completely precipitated as a slurry of zinc hydroxide, $Zn(OH)_2$, ($Zn(OH)_2$ is nearly insoluble in water), by the addition of NaOH solution as shown in figure 6-5 and then is filtered. The formation of $Zn(OH)_2$ is governed by the following equation:

$$ZnCl_2 + 2NaOH \rightarrow 2NaCl + Zn(OH)_2 \qquad (6.40)$$
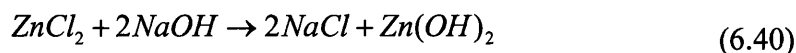
It can be seen from the above equation that 1 mole of zinc chloride, $ZnCl_2$ requires 2 moles of NaOH. Therefore, the amount of NaOH required to convert all $ZnCl_2$, resulting from the diafiltration unit to $Zn(OH)_2$ can be determined. The above material balance step is a straightforward procedure and all the results of such calculations are presented in table A5-4. From equation (6.40), the amounts of $Zn(OH)_2$ and sodium chloride, NaCl, produced and NaOH required can be determine as:

Feed stream 1:
t $ZnCl_2$/day
t water/day

Feed stream 2:
t NaOH/day
t water/day

Metal
hydrodroxide
unit

Product steam 1:
t NaCl/day
t water/day

Product stream 2
t $Zn(OH)_2$ solid/day
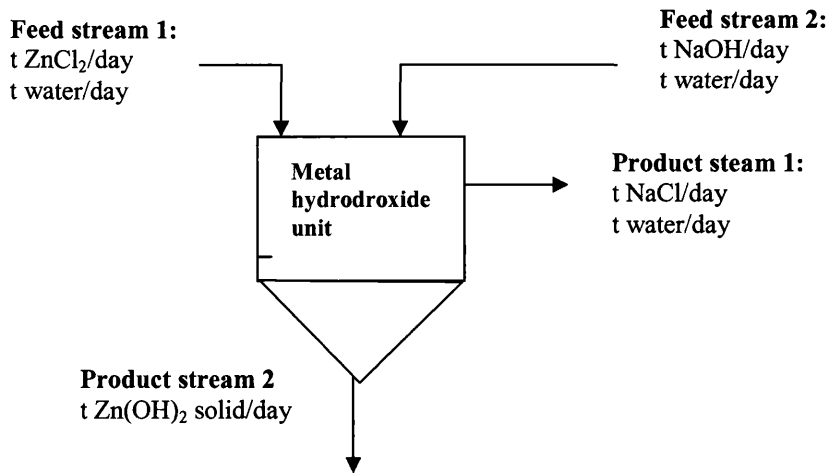
Figure 6-5: Continuous metal sedementation unit diagram.

$$wt_{Zn(OH)_2} = wt_{ZnCl_2} \times \frac{Mwt_{Zn(OH)_2}}{Mwt_{ZnCl_2}}$$

(6.41)

where $wt_{Zn(OH)2}$ is the amount of $Zn(OH)_2$ produced, t/day, wt_{ZnCl2} is the amount of $ZnCl_2$ produced, t/day and $Mwt_{Zn(OH)2}$ and Mwt_{ZnCl2} are molecular weight of $Zn(OH)_2$ and $ZnCl_2$ respectively.

$$wt_{NaOH} = 2 \times wt_{ZnCl_2} \times \frac{Mwt_{NaOH}}{Mwt_{ZnCl_2}}$$

(6.42)

where wt_{NaOH} is the t/day of NaOH required and, Mwt_{NaOH} is molecular weight of NaOH.

$$wt_{NaCl} = 2 \times wt_{ZnCl_2} \times \frac{Mwt_{NaCl}}{Mwt_{ZnCl_2}}$$

(6.43)

where wt_{NaCl} is the amount of NaCl in t/day resulted in liquid stream, P_1 and Mwt_{NaCl} is molecular weight of NaCl.

By knowning the initial concentration of NaOH used in this system, the amount of NaOH solution entering the unit, N_O, t/day is defined as following:

$$N_O = 1 \times 10^3 \times \frac{wt_{NaOH}}{C_{NaOH} \times Mwt_{NaOH}} \times \rho$$

$$(6.44)$$

where C_{NaOH} is the amount of NaOH, (= 4 mol/L) and ρ is the density of product solution, (can be assumed as density of water), t/m^3. The amount of water required to prepare a 4 mole/L NaOH solution was calculated by subtracting the amount of NaOH solution entering the unit, N_O from wt_{NaOH}, the weight of NaOH solids required. It can be assumed that the amount of feed, F_O entering the system contains only $ZnCl_2$ solution and all the $Zn(OH)_2$ produced as precipitated solid, P_2. Hence, from the overall material balance, the amount of NaCl solution is calculated as:

$$P_1 = F_O + N_O - P_2$$

$$(6.45)$$

The above procedures were employed in the design of such a system and $Zn(OH)_2$ from this stage is then dissolved via a zincate formation unit which will be discussed in the following section.

6.1.5. Zincate Formation Process:

Generally, it is known that zinc hydroxide will be dissolved using a certain concentration of NaOH according to the following reaction:

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2Zn(OH)_4$$

$$(6.46)$$
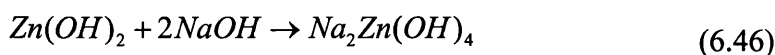
Therefore, the final zinc ion concentration of 20 g/L was found to be the optimum initial zinc concentration for the electrowinning unit as discussed in chapter 5. This also can be used to calculate the amount of NaOH needed to form zincate solution for electrowinning.

The results of the model for the unit shown in figure 6-6 are presented in table A5-5. From equation (6.46), 1 mole of $Zn(OH)_2$ produces 1 mole of zincate. Therefore, the total amount of zincate can be estimated as:

$$wt_{Zincate1} = wt_{Zn(OH)_2} \times \left(\frac{Mwt_{Zincate}}{Mwt_{Zn(OH)_2}} \right)$$

$$(6.47)$$

where $wt_{Zincate1}$ is the mass rate of zincate produced from the above reaction, t/day, and $Mwt_{Zincate}$ is the molecular weight of zincate.

Feed stream 1:
t $Zn(OH)_2$ Solids/day

Feed stream 2:
t NaOH/day
t water/day
t zincate/day

Zincate formation Process

Production stream:
t zincate/day
t water/day
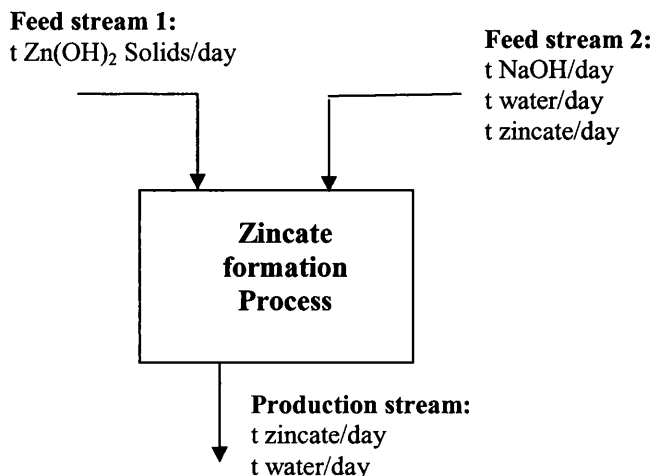
Figure 6-6: Continuous zincate formation unit.

Similarly, the amount of NaOH entering the system can be calculated as:

$$wt_{NaOH} = 2 \times wt_{Zn(OH)_2} \times \left(\frac{Mwt_{NaOH}}{Mwt_{Zn(OH)_2}} \right)$$

(6.48)

where wt_{NaOH} is mass rate of NaOH required to dissolve zinc hydroxide, t/day, and Mwt_{NaOH} is the molecular weight of NaOH. As was mentioned above, the optimum concentration of zinc in the product stream should be 20 g/L (or 55 g zincate /L), the amount of product stream, P can be calculated as:

$$P = 1 \times 10^3 \times \frac{wt_{Zincate}}{C_{Zincate}} \times \rho$$

(6.49)

where $C_{Zincate}$ is the concentration of zincate, (= 55 g/L) and ρ is the density of product solution, (can be assumed as density of water), t/m³. Since the amount of feed, F_Z entering the system contains only zinc hydroxide slurry, (this means $F_Z = wt_{Zn(OH)2}$), the amount of NaOH solution, N_Z is calculated as:

$$N_Z = P - F_Z$$

(6.50)

The results of zincate output solution was then employed in the calculations of metal production via electrowinning. The amount of water required to prepare a 4 mole/L NaOH solution was calculated by subtracting the amount of NaOH solution entering the unit, Nz from wt_{NaOH}, the weight of NaOH solids required.

6.1.6. Metal Electrowinning Process:

The final step in this proposal concerns the electrowinning from 20 g/L zinc ions, (or 55 g/L zincate) generated in the previous unit to produce pure metal from the alkaline solution of zincate. The results of alkaline electrowinning shown in figure 6-7 are listed in table A5-6.

The process of alkaline electrowinning may occur as follows:

$$Na_2Zn(OH)_4 \rightarrow Zn + 2NaOH + 2OH^- \qquad (6.51)$$

Feed stream:
t zincate/day
t water/day

Electrowinning reactor

Production 1:
t pure zinc/day

Production stream 2:
t NaOH/day
t zincate/day
t water/day
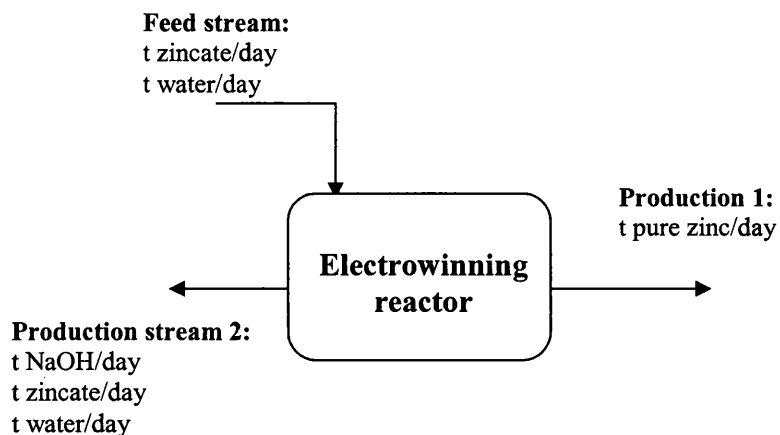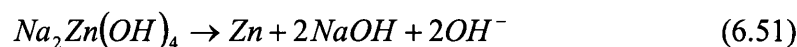
Figure 6-7: Continuous electrowinning reactor.

It can be seen from the above chemical reaction equation that 2 moles of hydroxide ions are produced. The system makes net OH that is used to precipitate $Zn(OH)_2$ from $ZnCl_2$. However, the amount of extra OH will in turn react with the electrode material, (in this case iron in stainless steel). This will increase the alkalinity of the system so that some fluid may be withdrawn and used for the precipitation of

$Zn(OH)_2$ from $ZnCl_2$ effective recycling the hydroxide solution (see figure 3.9) or used in the conversion of $Zn(OH)_2$ to zincate complex.

The amount of zinc metal attached to the cathode was calculated based on metal deposition model (limited cathode surface, see chapter 5). Results presented in table A5-6 suggests that the best zinc converted from solution to metal is 88.55% using an anaerobic zinc electrowinning at the recommended parameters. Thus, the amount of zinc metal produced, P_Z in t/day is:

$$P_Z = X_{elec} \times wt_{Zincate1} \times \left(\frac{Mwt_{Zn}}{Mwt_{Zincate}} \right)$$

(6.52)

where X_{elec} represents the fraction of removal of zinc metal from zincate solution, (= 0.8855). The remaining zincate, $wt_{Zincate2}$ leaving the unit is:

$$wt_{Zincate2} = wt_{Zincate1} + (X_{elec}/100) \times wt_{Zincate1}$$

(6.53)

Also, the electrolysis of zincate solution could regenerate NaOH which can be used in dissolving metal oxide discussed in the previous section. The total amount of NaOH generated (see equation (6.51)) is determined as:

$$wt_{NaOH} = 2 \times X_{elec} \times wt_{Zincate} \times \left(\frac{Mwt_{NaOH}}{Mwt_{Zincate}} \right)$$

(6.54)

and the total amount of solution product, containing zincate and NaOH, R_e in t/day is estimated via the overall material balance as:

$$R = F_e - P_Z$$

(6.55)

The current is estimated by rewriting equation (4.2):

$$I = \frac{P_Z \, n \, F}{M \, t \eta_I}$$

(6.56)

Hence, from equation (4.4), the cathode surface area required to produce P_Z amount of zinc is:

$$A_C = \frac{I}{C.D.}$$

(6.57)

6.1.7. Other Utilities:

6.1.7.1. Chemicals Regeneration and Distilled Water Re-production:

The amount of NaOH and HCl consumed by this process might be regenerated for further use. The principal method used for the manufacture of NaOH is electrolytic dissociation of NaCl produced via the electrodialysis process. During this process chlorine gas, Cl_2 is produced as a co product, as shown in the following equation:

$$2NaCl + 2H_2O \xrightarrow{\quad DC \quad} 2NaOH + Cl_2 + H_2$$

(6.58)
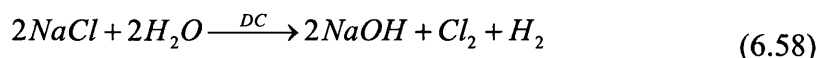
There are three different ways of producing NaOH; mercury, membrane and diaphragm cell. However, the first type produces effluent that might increase the danger of mercury pollution as well as more energy required. According to the European Commission (2001), the amount of energy used in kWh/t of Cl_2 produced was found to be 3360, 2720 and 2650 for mercury, diaphragm and membrane cells respectively.

An electrodialysis cell uses a steel cathode, and the reaction of NaOH with Cl_2 is prevented using a porous diaphragm, often made of asbestos fibres. In the electrodialysis cell process, the anode area is separated from the cathode area by a permeable diaphragm. The brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment. The chlorine is then burned in hydrogen to produce hydrogen chlorine, HCl according to the following equation:

$$Cl_2 + H_2 \rightarrow 2HCl$$

(6.59)

This process can be performed by several burners, such as the silica burner, the ceramic-lined burner and the graphite burner. The produced gas is cooled, absorbed and scrubbed in the purifying coke tower. HCl acid is then removed directly form the bottom of the cooler by means of a trap at a concentration of 37% (Lowenheim and Moran, 1975). Also, the unit can be utilised to provide the required quantity of

distilled water remaining after the concentration step. The results of this step are presented in table A5-8.

6.1.8. Concentration, Decomplexation and Washing Sequence as a Batch Process in One Vessel:

In order to reduce the cost concentration, decomplexation and washing processes can be performed using the same tank as shown in figure 6-8. This shows the valve system required to allow the stages to be carried out sequentially in a single vessel.
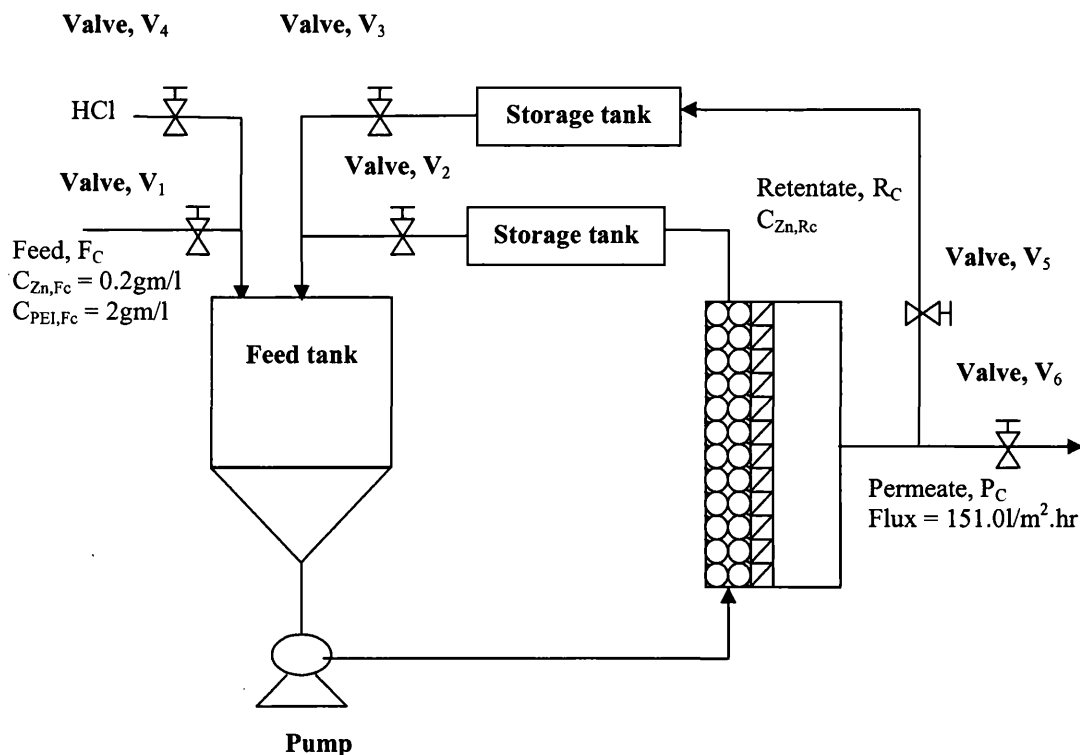
Figure 6-8: Concentration, decomplexation and washing sequence.

At the beginning, 33% of the liquid resulting from the leaching system can be concentrated by turning the feed and permeate valves, (V_1 and V_5) on and maintaining the other valves closed. After achieving a certain PEI concentration of 10 g/L, V_1 and V_5 should be closed and the retentate and HCl valves, V_2 and V_4 are then opened to allow all retentate to return to the feed tank and addition of HCl. This allows the decomplexation step to take place. Finally, the washing process is

performed by closing all the unit valves and opening valves V_3 and V_6. The above steps are then repeated for the rest of leached liquid in the order presented in table 6-1.

Table 6-1: Concentration, decomplexation and washing operations order.

Process	V_1	V_2	V_3	V_4	V_5	V_6
Concentration	Open	Close	Close	Close	Open	Close
Decomplexation	Close	Open	Close	Open	Close	Close
Washing	Close	Close	Open	Close	Close	Open

Similarly, the sedimentation and zincate formation processes may be performed in a certain order using the same reactor.

6.2. Economic Analysis:

An acceptable integrated zinc recovery unit design must be a process that is capable of operating under conditions which will give a profit. This section concerns a preliminary estimation and aims to obtain and present material and energy balances, initial estimates for equipment, piping and chemicals required. Some duty rating and sizing of the process equipment is also made. Even though the cost estimation might be expected in error (but no more than 25%), subsequent actions and decisions related to design and operation can be compared to this kind of estimation. Also, proposals to change from the original plan in terms of finance, time and/or improvements to the process can analysed by reference to this estimation (Gerrard, 2001).

The determination of the relative contribution of variable costs, fixed operating costs and capital investment to the total product costs allows cost-reduction efforts to be focused on those cost components that are likely to be most significant (Anderson, 2009). Therefore, an economic evaluation at any stage in the developments of a project could be indicated by determining capital investment, manufacturing and total cost, sales price and return on investment.

Using the information from the literature and work carried out in section 6.1 an economic evaluation was carried out to investigate the Zn recovery process.

The financial calculations of the integrated zinc recovery unit for the unit when 1000.00 t/day solids with 2% zinc were fed to the system with 0.01% polymer losses is indicated table A6-1. The model that performs such calculations can be manipulated in order to study the effect of varying extraction efficiency and production rate on the economy of such process.

The operating profit may be expressed as:

$$\text{Operating profit} = \text{Precess revenue} - \text{Total cost of the process} \qquad (6.60)$$

The process revenue may be obtained from:

$$\text{Process revenue} = \text{Zinc metal sales} \qquad (6.61)$$

The total cost is then:

$$\text{Total cost} = \text{Total variable cost} + \text{Total expenses} \qquad (6.62)$$

Several assumptions can be made to simplify and reduce the cost of the system. These are:

- Solids input to the leaching unit are mostly from waste where the cost of raw material only depends on the transportation expenses. This can also be ignored since the process in this work is located close to the source of the effluent.

- The amount of polymer solution losses should not exceed 0.1%.

- A safety factor is considered when estimating the size of each unit.

- Concentration, decomplexation and washing processes are performed in sequence as shown in section 6.1.9.

All data required to perform the economic evaluation are cited in appendix A. The prices of zinc and chemicals were regularly updated (London metal exchange, 2010, IChemE Education Subject Group, 2002, ICIS pricing, 2010) and the latest

prices were recorded in July 2010. Calculations of some variables in the table will be explained in the following sections.

6.2.1. Process Investment:

The process investment includes fixed capital and working capital. Fixed capital of purchased equipment, equipment installation, piping and building were included. Once the purchased costs were obtained, the other costs were estimated as an equivalent percentage of purchased-equipment cost (Aries and Newton, 1955). Working capital of raw material, which is the contaminated water or solid can be ignored in this type of process and replaced by materials start up including NaOH, HCl, distilled water and PEI. However, annual manufacturing costs of labour, supervision, maintenance and of electrical power used, were determined along side payroll overhead, laboratory, depreciation, property taxes and insurance. Equipment design for this preliminary process evaluation involves determining the size of the equipment in terms of volume, flow per unit time, or surface area. Some of the calculations associated with each unit were presented to indicate the extent of the calculations.

6.2.1.1. Purchased Equipments and-Plant Cost:

Results shown in table A6-1 were achieved by following certain calculation procedures. The size of all units are equal to the volume of inputs into each unit times number of day per cycles times a 10% safety factor recommended in the literature (Peters and Timmerhaus, 1991). The cost of each unit was determined applying six-tenth factor method on each equipment since the cost of equipment were given at one capacity (Aries and Newton, 1955, Matches, 2003). The cost of the actual size can be determined using:

$$E_b = E_a \left(\frac{c_b}{c_a} \right)^{0.6} \tag{6.63}$$

where c_a is capacity of equipment a, c_b is capacity of equipment b, E_a is the purchase cost of a and E_b is the purchase cost of equipment b. The cost of installation can be assumed to equivalent to 25% of the purchase price of the equipment. The price of piping for the fluid process is taken as 86% of equipment

cost whereas the cost of building is 40% of equipment cost (Aries and Newton, 1955).

6.2.1.2. Working Capital Cost:

As seen in previous sections, the PEI solution should be maintained at pH 5.5 (for complexation) or pH 2.5 (for decomplexation), so, acids or alkalis are used during the operation. The total amount of material utilized was estimated from the results of material balances for the chemicals and water (see section 6.1 and relevant appendices).

The chemicals required in this process are HCl, NaOH, PEI and ionized water. NaOH is used to change the polymer solution pH from 2.5 to 5.5, to promote metal oxide formation and zincate formation. HCl is employed twice, first, when polymer solution pH is required to be changed from 10 to 5.5 and second when the pH is to be changed from 5.5 to 2.5. The acid is also needed to separate NaOH from zincate solutions remaining from the electrowinning process. Distilled water is mostly used for the dilution purposes in the PEI pH convertor (see figure 3-9), washing, metal oxide formation and zincate formation.

The cost of chemicals and distilled water required to proceed with the extraction and their prices are listed in table A6-2 (IChemE Education Subject Group, 2002). Values presented in this table depend very much on the percentage of zinc extracted during the operation. All calculations are based on the material balance presented earlier around each unit and the summation of the chemical and the total amount of distilled water needed was obtained by summing the amount of water required by leaching, washing, zincate formation and dissolution units. All the cost of each material was then multiplied by the price to evaluate the overall cost of each substance. The total chemicals cost was calculated by summing the cost of the chemicals used. The calculations were carried out in a series of spreadsheets

6.2.2. Production Cost:

The process material in this case included the amount of PEI solution that might be discharged/lost from the production cycle, (which is assumed to be 0.1% of the total PEI solution input per cycle of absorption). The utilities required to proceed with

this plant were assumed to be the energy required to operate the filtration unit and the amount of electrical energy consumed by the electrowinning and electrodialysis processes. Daily pumping costs for concentration and washing ultrafiltration can be calculated using the following formula:

$$P_C = E_F(kW/m^2) \times A(m^2) \times$$
$$\text{operating time}(hr/year) \times \text{power cost}(£/kWhr) \qquad (6.64)$$

where P_C is the cost of pumping, £/year.

The cost of electrical energy consumed by electrowinning E_C is estimated as follows:

$$E_C = E_E(kWh/t) \times \text{Zinc production}(t/day)$$
$$\times \text{power cost}(£/kWh) \qquad (6.65)$$

The amount of energy consumed by electrowinning of zinc, E_E, £/year was estimated from the experimental work presented in chapter 4, (= 0.77 kWh/kg or 770.00 kWh/ton). The energy required to regenerate NaOH, HCl and distilled water from electrodialysis process can be calculated based on the data of the electricity used per ton of Cl_2 of 2720 kWh when employing the electrodialysis cell, (provided by European Commission (2001)). The amount of energy cost to run this process, D_c, £/year is evaluated using the following relationship:

$$D_C = E_D(kWhr/tons) \times \text{Chlorine produced}(tons/day)$$
$$\times \text{power cost}(£/kWhr) \qquad (6.66)$$

The results of energy expenses required to perform concentration, washing, NaOH and HCl regeneration and electrowinning processes are listed in table A6-3.

The estimation of labour and hourly wages was based on an average scale taking into account the possibility to increase the labour cost due to overtime, Sunday, holiday or night operation along side the level of skills. The average number of workers was assumed to be 15 with the average UK wage of £15/hr. Estimation of supervision was prepared by applying a percentage of the labour charge equal to 10% since the operation was assumed to be simple. Maintenance expenses included

the cost of all materials and labour employed in routine maintenance and incidental repairs was considered as 6% of the fixed capital cost. Other associated expenses which remain constant in total with regards to time, regardless of production level are also included. Depreciation was considered as 9% of total fixed capital investment, local taxes was also estimated to be 5% of fixed capital cost and insurance which is 1% of the fixed capital cost. Corporation tax in the UK was taken as 35% of taxable profit (Allen, 1991).

Generally, the process of profit analysis is based on a depreciated or amortised investment asset over its working life. i.e. each year there is a depreciated charge against the profit which is related to the capital investment so that the total investment is recovered from profits by the end of the life time. However, it has been argued that this procedure is not relevant to economic evaluation that is concerned with making investment decisions taking into account the expected future cash flow resulting from that decision. It was recommended to proceed with the profit analysis using an indirect way in which the concept of depreciation affects charges using depreciation based capital allowance in order to reduce the expenses via reducing taxable profits (Allen, 1991). This approach might be useful if the value of scrap is known after a certain life time.

6.2.3. The Profit Analysis:

The economic analysis performed in previous sections dealt with costs and profits calculated at a specified amount of feed rate and extraction efficiency for the integrated unit of a certain design capacity. This section presents the results of employed zinc recovery model constructed on an excel spread sheet to analyse the effect of feed input rate, which is a function of plant size and capacity output on plant profit. Payback time required to return the capital investment can be estimated using the following formula:

$$\text{Payback time} = \frac{\text{Total inventment, £}}{\text{Total yearly proft, £/year}} \qquad (6.67)$$

Feed input was plotted against zinc production rate, t/day and the process profit for various extraction efficiency and polymer solution losses of 0.1%, (see figures 6-9a

and 6-9b) increasing feed rate would lead to an increase in zinc production rate and the process profit at all extraction efficiencies.
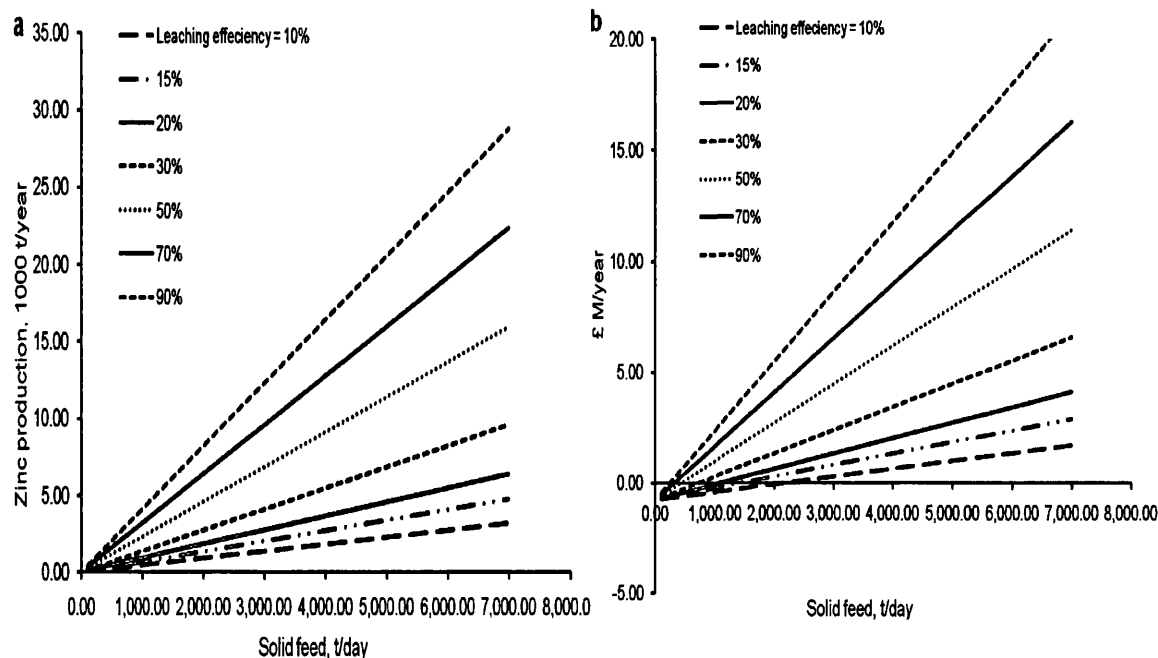
Figure 6-9: The effect of solids feed rate at various leaching extraction efficiency of zinc recovery plants with 0.1% polymer loss on a) zinc production rate and b) total plant profit.

From figure 6-9, the production rate and profit were as expected, to increase when increasing the extraction efficiency. However, the amount of feed required at low extractions efficiencies will be higher to get to the break-even point, (the point where the total profit is equal to zero at certain production rate). Values of breakeven feed rate were decreased when increasing the extraction percent as shown in table 6-2 and this is a critical factor in the success of this process. The quality and characteristics of the minerals is most important.

Table 6-2: The effect of extraction efficiency on the breakeven feed rate in the Zn recovery plant model.

Extraction efficiency %	Breakeven feed rate, t/day
10	2516.67
15	1510.00
20	1078.57
30	755.00
50	444.12
70	314.58
90	243.55

The effects of feed input rate on payback time are shown in figure 6-10 for each extraction efficiency percent. Number of years to payback is dramatically decreased from 8 years at 30% to 2 years at 70% extraction at a feed rate of 1000 t/day. However, the payback time becomes less effected, between 2 to 5 years when extraction efficiency increased to values higher than 50%. On the other hand, the payback time showed a dramatic decrease when increasing the solids input rate which becomes less sensitive at high feed rate values (>5000 t/day).

Overall, the recovery unit returns the investment in reasonable time when the extraction efficiency exceeds 50% at a feed rate higher than 1000.00 t/day.

It is important to point out the fact that the effect of extraction efficiency is such a crucial factor since it represents the type and the nature of solids input to the system. Therefore, it is required to conduct a study to identify the ability of zinc metal to separate from its environment. Preliminary experiments of waste tailings from two mines in Ireland have been carried out and there is a considerable variation in leaching efficiency (personal communication Dr R.W. Lovitt).
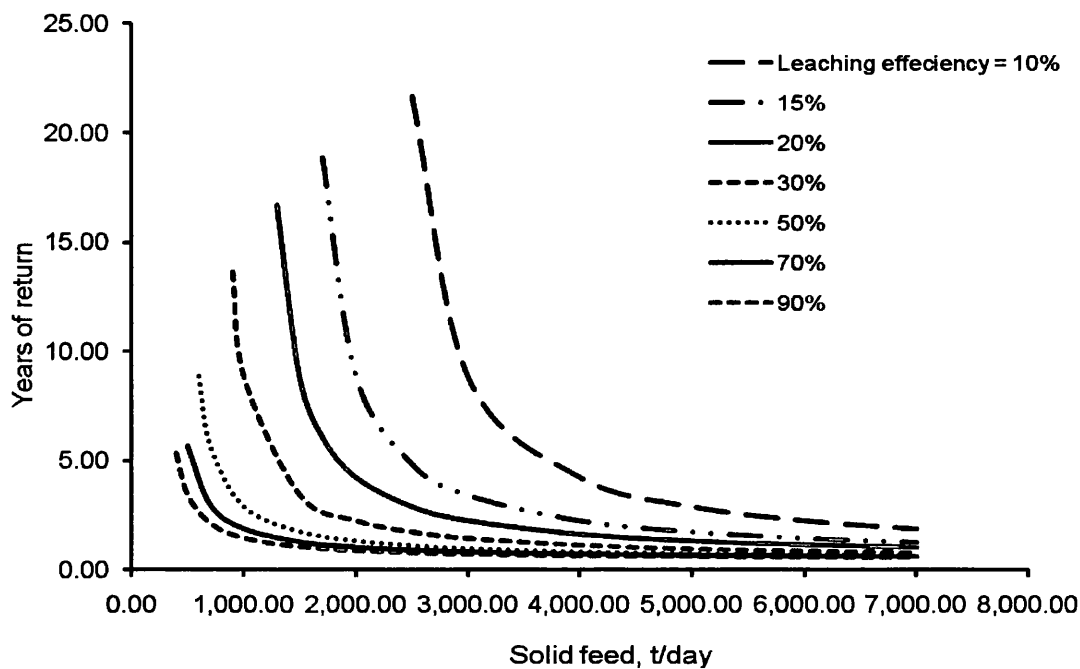
Figure 6-10: The effect of feed rate input on the year of return of zinc recovery plants with 0.1% polymer loss for various extraction efficiency percentages.

The above discussion is obviously dependent on zinc price (in this study £1243/t 99.99% Zn). The amount of zinc produced by this process studied here with the best conditions of 90% extraction efficiency and 7,000 t/day is estimated to produce 29,000 t/year Zn. This is very small in comparison to the 10,000,000 t per year of world zinc production (Tolcin, 2008). Therefore, the contribution of the plant proposed in this work would be very small and should not effect the price of zinc. Hence, the project proposed would continue to be profitable as long as the demand of zinc increases over the years.

Chapter 7

7. CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusion:

7.1.1. Introduction:

The topic of metal recovery is an important topic in a resource limited world and the approach depends on the nature and value of metal, process type and conditions and the source nature of metal. It is clear from the previous work presented in chapter 2 that some of metals used in industries were traditionally extracted using mining processes, the avaliability of which are now in decline. Consequently, there is the potential for substantial environmental and financial savings to be made through the reduction of metal wastes produced by industrial processes and the reprocessing of mining tails and recovery from wastes. This may be achieved by performing improvements in existing metal extraction units or by the design of a new integrated process coupled with appropriate optimisation routines.

The aim of this work was focused on the design of a suitable zinc recovery process in order to extract zinc metal from a low concentration solution to a high purity form. This is done by conducting a review of existing techniques and performing related experiments. Zinc metal is chosen in this study due to its industrial importance and resale value in the current economic situation. Examination of the literature suggested a versitile hydrometallurgical approach to this problem. Thus, a process for Zn metal recovery of the following steps was investigated:

1. leaching of the metal from its ores using the concept of complexation of the metal by means of polymeric ligands;

2. ultrafiltration of the complex, which produced a purified effluent and a concentrated metal complex solution;

3. decomplexation by acidification; followed by ultrafiltration of the concentrate after acidification allowing the recycling of the complexing agent;

4. precipitation and dissolving of metal ions using sodium hydroxide and finally,

5. electrolysis of the concentrated alkaline zinc solution (filtrate).

Two of the main process units were experimentally investigated, PEUF in chapter 4 and Zn electrowinning in chapter 5 while stright forward data and calculations were employed in the design other units, such as the process of precipitation and desolving metal ions. On the other hand, the leaching process is too complex for the study and individual study is required to study the effect of leaching conditions on the complexation process including the effect of Zn ore type.

The project intended to make a preliminary economic estimation of the unit in order to validate the process. The overall model constructed can be employed to predict the effect of feed rate input at various leaching extraction effeciencies on the process profit. These variables depend on the type of feed inputs and plant size.

7.1.2. The PEUF Process:

A model of the polymer binding/ultrafiltration process, PEUF, can describe the recovery of high zinc concentration solution from low concentration zinc chloride solution using a water-soluble polymer, to improve the membrane separation. Consequently, the effect of solution composition on the efficiency of the removal of zinc is experimentally studied and presented in chapter 4. Polymer binding agent can be recovered from its complex with the metal and regenerated. In addition, the metal-ion-retention properties of a water-soluble polymer depend on solution pH and polymer concentration as shown in figure 4-1. The efficiency of binding of metal ions increases when pH increases as shown in a previous study (Juang and Chen, 1996, Jaung and Shiau, 2000). However, pH values higher than 7, results in the formation of zinc hydroxide (Jones, 2005). This can lead to an increase in zinc retention alongside metal polymer complexation process. The experimental studies of pH and complexation are used to estimate maximum binding capacity of the polymer. This is governed by the Langmuir isotherm equation since it provided a better fit to the experimental data than the Freundlich isotherm (Jones, 2005, Almutairi, 2008).

The design engineering equations for ultrafiltration allows the prediction of the membrane permeation flux. The general membrane equation, equation (5.1), can be applied up to 30 psi pressure. Initial polymer concentration shows a significant effect

on the flux within the pressure controled zone at low polymer concentrations. However, the filtration mechanism increases concentration of the solute at the membrane surface with time and the flux will be pressure independent. However, the cake resistance-polymer concentration relationship can be obtained at various applied pressures and presented as shown in figure 4-7. This has slightly improved the fit with the observed data at various pressure and polymer concentration values, (see figures 4-5 and 4-8).

A volume concentration factor of 10 results in a suitable permeate flux during zinc concentration and washing stages and has been recommended previously (Baticle et al., 2000). However, increasing that value leads to a decrease in the flux to an uneconomically low value and this causes the pumping power and, in turn the cost to rise due to an increase in cake thickness above the membrane surface. A certain concentration of zinc solution can be obtained for further processing, while the complexing polymer can be returned to the leaching process to carry out a new treatment cycle.

The results of decomplexation and washing system presented in section 4.4.2 suggest that reasonable amount of zinc in terms of recovery percentage can be obtained when performing the washing stage at least twice at various washing factors. However, the output zinc concentration and differences in zinc recovery percentage become relatively small when performing the washing step more than three times or increasing the washing factor. This can be more costly for less zinc obtained since more pumping is needed. Therefore, two times washing seems appropriate to achieve reasonably high zinc concentration and removal with less cost possible.

Initial polymer concentration is proven to be an important variable since it can be used to estimate the membrane productivity for the overall diafiltration membrane system as shown in figures 4-17 and 4-18. Based on the results presented in section 4.4.2, membrane productivity seems to be less affected when increasing both washing factor and initial polymer concentration. This point has been used to identify a polymer concentration of 6 g/L that results in a zinc concentration solution of 2.3 g/L from 0.6 g/L, (by a factor of 3.8), and recovery percentage of 78%. The rest of Zn remains complexed with PEI and recycled.

The above process was performed using a synthetic zinc solution with no other metals included. However, further study is required to study the effect of interference on the process of complexation, e.g. complexation with naturally occurring chelators, competition with other ions (including other metals) and the potential PEI losses from the process. All these factors amount to a decrease in performance and additional costs, producing less robust process than would be expected, as indicated in section 2.3.3.1.

7.1.3. Electrowinning:

The metal electrowinning unit is one of the most important processes in the recovery of pure metals. Therefore, it is necessary to examine the behaviour of a zinc electrowinning cell using galvanostatic electrolysis strategy in order to select suitable cell conditions. It is well known that the choice of the cell type depends on three factors, viz. current efficiency, electrical energy consumption and metal recovery percentage. Therefore, it is apparent from this work that the recovery associated with alkaline electrowinning gives greater performance than the relevant recovery with the acidic process when controlling pH using sodium or zinc hydroxide. In addition many metals cannot form soluble alkaline complexes and so the conditions become even more selective for Zn. This work confirms the work conducted to develop and improve the electrowinning of Zn, by other workers (St-Pierre et al., 1985b, St-Pierre and Piron, 1992, St-Pierre et al., 1996). The poor performance of acidic electrowinning is mainly due to the hydrogen evolved on the cathode surface. Even though, the problem of chlorine attack on the cathode is solved using Ti/RuO_2 anode, the results of acidic electrowinning remain unsatisfactory in terms of zinc recovery. These types of side reactions can be inhibited when employing alkaline electrowinning strategy.

In the study of the effect of operating parameters on the performance of alkaline electrowinning cell (section 5.2.2), the cell provides good efficiency, deposited productivity and minimum electrical energy consumption at an initial zinc concentration of 20 g/L, current density of 2000 A/m^2 and sodium hydroxide concentration of 4 mol/L. Furthermore, it is still possible to use sodium hydroxide solution concentrations from 2 mol/L and up to 6 mol/L in order to achieve a

reasonable recovery. This is because the variation of NaOH concentration shows little effect on the cell performance.

Based on the above conditions, experimental results of concentration distribution of zinc metal as a function of time were used to confirm the predictions of a mathematical model using metal deposition kinetics equations for both first order and limited cathode area assumptions. The latter show better agreement with the experimental results since it considers the electrode surface limitations. This also confirms that the zinc electrowinning reaction does not follow the first order assumption after prolonged operation periods where equilibrium kinetics are approached. The metal deposition model can be employed in the development of such a unit, such as bubbling nitrogen gas through the solution in order to improve zinc deposition. The results presented in table 5-5 for such an approach indicate that the combination of anaerobic and alkaline electrowinning improves the deposition efficiency of the unit from 80 to 89% recovery with a decrease in electrical energy consumption as explained in section 5.4, (from 0.941 to 0.767 kWh/kg zinc). However, the effect of solution temperature is not considered in this work. Also the purity of Zn metal extracted in this unit strongly depends on the degree of metal solution purity results from PEUF system and the subsequent alkaline electrowinning conditions.

7.1.4. Overall Process Integration and Economics:

In order to estimate the relative performance of an integrated metal recovery unit two experimental investigations were conducted on two main processes in the recovery system shown in figure 3-9.

The process described in chapter 6 allows the treatment of large volumes of effluent containing zinc at low concentrations using an initial PEI concentration of 6 g/L for leaching and ultrafiltration, followed by an electrowinning process. Based on the optimum conditions of PEUF and zinc electrowinning obtained experimentally and mathematically, an integrated zinc recovery unit model developed in this work estimates the design parameters and predicts the profit of the plant. The size of the unit depends on the amount of feed rate and zinc extraction efficiency in this model. Moreover, the leaching process can be used as a complexation unit at pH 5.5 and the

amount of PEI depends on the extraction efficiency of the unit which in turn depends on the amount of zinc contained in the solids feed input and the nature of the ore.

Some modifications can be proposed to reduce the cost of the process. The addition of an electrodialysis unit to the system can regenerate sodium hydroxide, hydrochloric acid and distilled water consumed by the whole zinc recovery process. It is found that electrodialysis unit consumes relatively high energy (European Commission, 2001). Nevertheless, this approach can be useful since the cost of charging the overall process with the new chemicals is relatively high. Another suggestion can also be made concerning the concentration, decomplexation and washing processes using the same equipment at a certain sequence as shown in figure 6-8. This reduces purchase equipment expenses and allows the water removed by the concentration step to be reused by the decomplexation and washing stages.

Preliminary designs are ordinarily used as a basis for determining whether further work should be done on the proposed process. The design in this work is based on approximate process design methods, and rough cost estimates are prepared. However, the time spent on calculations is kept at a minimum. In considering the overall costs or profits in the plant operation, one of the factors that have an important effect on the economic results is the fraction of total available time during which the plant is in operation. When the plant operates at low capacity, certain costs, such as utility and labour, can be reduced, but the cost for maintenance continues essentially at the same rate even though the plant is not in full use.

The size of each unit in this plant was estimated based on the output conditions. However, it is recognised that this way of estimating the size is not practical since the design is not finalised and any changes that occur may make previous calculations meaningless. Nevertheless, the purpose of the preliminary design is to provide enough information in order to decide on the viability of the plant. It can be seen from figures 6-9 and 6-10 that the size of the plant that has small extraction efficiency is uneconomical since the total operating cost will certainly remain higher than the process income due to high maintenance cost. On the other hand, a plant with higher than 50% extraction efficiency can provide optimum product schedule at the maximum size beyond the break-even point.

The profitability of the products obtained from the zinc recovery process employed in this study also depends on value of the zinc selling price. The amount of zinc produced by this project at the best conditions is estimated to equal to 29,000 t/year which is very small when comparing it to 10,000,000 t per year of the world zinc production (Tolcin, 2008). The contribution of the plant proposed in this work would be very small and should not effect on the price of zinc. Therefore, it is desirable to operate the plant at maximum capacity while simultaneously meeting market demand. From this point, the profit will increase with increased rate of production and leaching extraction efficiency at varied plant size.

The model described in chapter 6 can be used to predict the economical outcome of the plant before taking the decision to operate in order to cover the demand of zinc. An increase in the amount of zinc produced may lead to an increase in the profit therefore adjustment of the production rate is required, at certain extraction efficiency, in order to improve the process profit. However, below a certain level of extraction efficiency, the process will become loss making and thus uneconomic.

The results of the economic study in this project indicated that production rate can be adjusted in order to provide a high profit at certain conditions. However, further development might be required in order to increase the range of products, or to extend the production capacity since the plant will be operating for some time and become outdated. Therefore, some constraints on the design and cost estimating will be necessary because of the requirement to match the standards of the old plant. This involves the construction of a duplicate to an existing line so that the cost exercise becomes similarly duplicated.

Finally, the described process can be economic and the profit certainly depends on the metal extraction methods and efficiency, product selling prices and cost of the operation. Also this integrated unit can be applied with minor modifications and adjustments in order to remove other cations, such as copper, cobalt and nickel. The process may also be applied to treatment of electrical wastes and the recovery of Zn from scrap metals. However, it cannot easily be applied to solutions containing stable complexes, such as cyanide solutions.

7.2. Recommendations:

Based on the conclusions and the knowledge gained from the present study, further study and economic analysis is required in order to cover the following suggestions for future investigations:

- **Further optimising process conditions**: More work should be done in order to study the effect of process temperature on the productivity of the zinc recovery plant since polymer viscosity decreases by increasing the solution temperature. This might raise the possibility to reduce thickness of the cake at the membrane surface and increase the separation of the metal (Canizares et al., 2005). It might also improve the productivity of the electrowinning cell.

- **Real vs. Synthetic process streams**: All solutions used in this study were synthetic. Therefore, further work is required to study the selectivity and efficiency of such a process to remove metals from an environment that contains multi metal components, and provides a general model that considers the cost of recovering these metals to validate the integrated unit economically. Leaching extraction efficiency of this process depends on the type and nature of metal ore. This means that the more zinc recovered from its solids, the better the economic outcome. Therefore, further study is required to define and optimise the effective parameters of the leaching process using PEI as a leachate solution.

- **More realist costing and process analysis**: It is well known that prices may vary widely from one period to another, and this factor should be considered when the costs for an industrial process are determined. Therefore, price of chemicals used and process products and wage fluctuations must be kept up-to-date. Also the remaining solid stream should be treated for further metal(s) extractions. For example, to avoid the increasing cost due to polymer losses, the solid inert stream produced by leaching should be passed through a sedimentation unit in order to recover the polymer for further reuse by the leaching stages.

- **Other problems associated with contaminationing ions**: Problems associated with electrodialysis: Species of concern include calcium and magnesium hardness, suspended solids, silica, and organic compounds that coat, precipitate onto, and foul the surface of the ion exchange membranes in electrodialysis

systems. This fouling decreases the efficiency of the electrodialysis system and cause the electrodialysis process to become less economical. Therefore, regular feed pre-treatment of electrodialysis is required to remove these species or the unit might be replaced by other systems, such as reverse osmosis, to improve the economy of the whole system.

Clearly the study indicates that metal recovery from low concentration solutions is a fruitful area of research for the future in a world limited by resources. This is because:

a) Metals are essential for a successful world wide economy

b) The future is good for this approach since recycling is becoming more important and processing of new ores becomes more difficult (politically and economic processing)

c) Technologies need to be improved to make low impacts on the environment.

Therefore, hydrometallurgical processing techniques have a tremendous potential in solving the metal resource problems.

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NOMENCLATURE

A	The membrane surface area in m^2
A_c	The electrode area, m^2
A_D	*HCl* solution mass rate into decomplexation unit, t/day
a_O	The activities of the electron acceptor
a_R	The activities of the electron donor
c_a	The capacity of equipment a in equation (6.65)
C_b	The bulk concentration of particles in the feed (particle volume/feed volume)
c_b	The capacity of equipment b in equation (6.65)
C_{ia}	Concentration of metal i in the feed solution, mg/L
C_{if}	Concentration of metal i in the permeate, mg/L
C_{iu}	The metal residual concentration in solution, mg/mL solution
C_{NaOH}	The concentration of NaOH, mol/L
C_{PEI}	Initial PEI concentration in solution required performing the complexation step, in t/m^2
C_{PEIf}	Polymer concentration after dilution, (= 18.0 g/L)
$C_{PEI,Fw}$	Polymer concentration at feed stream, g/L
C_{PEIi}	Polymer concentration before dilution, (= 20.0 g/L)
$C_{PEI,Pn}$	Polymer concentration at n^{th} stage permeate stream, g/L
$C_{PEI,P1}$	Polymer concentration at first stage permeate stream, g/L
$C_{PEI,Pc}$	Polymer concentration in concentration unit permeate, g/L
$C_{PEI, PD}$	Polymer concentration in decomplexation unit product, t/m^3
$C_{PEI,R1}$	Polymer concentration at first stage retentate stream, g/L
$C_{PEI,Rc}$	Polymer concentration in concentration unit retentate, g/L
$C_{PEI, RD}$	Polymer decomplexation unit feed concentration, t/m^3
$C_{PEI,Rn-1}$	Polymer concentration at feed stream entering the nth stage, g/L
$C_{PEI,Rn}$	Polymer concentration at n^{th} stage retentate stream, g/L
$C_{PEI,Wp}$	Polymer concentration in feed, g/L
$C_{Zincate}$	The concentration of zincate, (= 55 g/L)
$C_{Zn, FD}$	Zinc feed concentration, t/m^3
$C_{Zn,Fw}$	Zinc ions concentration at feed stream, g/L
$C_{Zn,P1}$	Zinc ions concentration at first stage permeate stream, g/L
$C_{Zn,Pc}$	Zinc concentration in concentration unit permeate, g/L
$C_{Zn, PD}$	Zinc concentration in the product stream, t/m^3
$C_{Zn,Pn}$	Zinc ions concentration at n^{th} stage permeate stream, g/L
$C_{Zn,R1}$	Zinc ions concentration at first stage retentate stream, g/L
$C_{Zn,Rc}$	Zinc concentration in concentration unit retentate, g/L
$C_{Zn,Rn-1}$	Zinc ions concentration at feed stream to n^{th} stage, g/L
$C_{Zn,Rn}$	Zinc ions concentration at n^{th} stage retentate stream, g/L
$C_{Zn,Wp}$	Zinc concentration unit feed concentration, g/L
D	The dielectric constant
E_a	The purchased cost of a in equation (6.63)
E_b	The purchased cost of equipment b in equation (6.63)

E_F	The pressure energy required to feed the system at specific transmembrane pressure or pumping energy which is the driving force for ultrafiltration unit kW/m^2.
$E_{O/R}$	The equilibrium electrode potential
$E_{O/R}^{\theta}$	The standard electrode potential
$E_{Thermal}$	The thermal energy by heating to maintain the process fluid at required temperature kW/m^2
e	Ion size
F	Faraday's number, (96500)
F_L	The total amount of solids fed to leaching unit, t/day
$f_{L,PEI}$	The amount of PEI in the solid feed stream to leaching unit, t/day
$f_{L,solid}$	The amount of solid without zinc in the solid feed stream to leaching unit, t/day
$f_{L,Zn}$	The amount of zinc in the solid feed stream to leaching unit, t/day
F_O	The mount of $Zn(OH)_2$ feed entering zincate formation system, t/day
F_{PEI}	The total amount of polymer solution fed to leaching unit, t/day
$f_{PEI,PEI}$	The amount of PEI in the polymer stream input to leaching unit, t/day
$f_{PEI,solid}$	The amount of solid without zinc in the polymer stream input to leaching unit, t/day
$f_{PEI,Zn}$	The amount of zinc in the polymer solution stream input to leaching unit, t/day
F_W	The concentrated feed mass rate entering the washing stage, t/day
F_Z	The mount of feed entering zincate formation unit contains only zinc hydroxide slurry, t/day
H	Pump efficiency, (usually $0.5 - 0.85$)
I	The total current, Am
$[I]$	The concentration of ion in solution, (mol/L)
i_{0c}	Cathodic exchange current densities, A/m^2
i_{0a}	Anodic exchange current densities, A/m^2
i_{La}	Anodic limiting current densities, A/m^2
i_{Lc}	Cathodic limiting current densities, A/m^2
J	The permeate flux, expressed as volumetric rate per unit area, $m^3/m^2.hr$
k_{df}	The deposition constant for forward reaction, (a dynamic or pseudo-equilibrium constant expressing the relationship between the actual steady state concentrations)
k_{dr}	The deposition constant for reversible reaction, (a dynamic or pseudo-equilibrium constant expressing the relationship between the actual steady state concentrations)
K_{eq}	Equilibrium constant
K_L	The dissociation constant, mg/mL
L	The optimum polymer capacity

M	The molar mass of the deposited metal
m	The mass of metal deposited in grams
Mwt_{NaCl}	Molecular weight of NaCl
Mwt_{NaOH}	Molecular weight of NaOH
Mwt_{Zn}	The molecular weight of zinc element
$Mwt_{Zincate}$	Molecular weight of zincate
Mwt_{ZnCl2}	Molecular weight of $ZnCl_2$
$Mwt_{Zn(OH)2}$	Molecular weight of $Zn(OH)_2$
n	Number of electrons transferred in the cell reaction
N_O	The amount of 4 mol/L NaOH solution entering sedimentation unit, t/day
N_Z	The amount of 4 mol/L NaOH solution to form zincate solution, t/day
P	The amount of product stream from zincate formation unit, t/day
P_1	Permeate mass rate from the first washing stage, t/day
P_2	Precipitated solid produced by sedimentation unit, t/day
P_D	Product mass rate from decomplexation unit, t/day
P_n	Permeate mass rate outlet the nth washing stage, t/day
Q	The amount of metal complexed, mg metal/mg polymer
Q_{max}	The maximum capacity of polymer, mg metal/mg polymer
R	Gas constant, 8.314 J/mol K
r	The specific resistance of the deposit
R_1	Retentate flow-rate from the first washing stage, t/day
R_c	The resistance of layers deposited on the membrane or cake resistance, the filter cake and gel foulants, m^{-1}
$r_{C,Zn}$	The total zinc input to decomplexation stage, t/day
$r_{D,ZnFree}$	The amount of zinc freed from polymer, t/m^3
R_e	Total amount of solution produced by electrowinning unit containing zincate and NaOH, t/day.
R_i	Retention of solute i
R_m	The resistance of the membrane, m^{-1}
r_{max_f}	The maximum velocity of the forward reaction, mg/L.min
r_{max_r}	The maximum velocity of the reversible reaction, mg/L.min
R_n	Retentate mass rate into the nth washing time, t/day
R_{n-1}	The concentrated feed mass rate entering the nth washing time, t/day
T	The cell temperature, K
t	The deposition time
V	The operating cell voltage, volt
V_f	The total volume filtered, m^3
$V_{HCl,\ elect}$	The amount of HCl required to produce $Zn(OH)_2$ from zincate, m^3
W	The electrical energy consumed, kW.h/kg Zn
W_1	The amount of water added to the first filter, (=2.5 times F_W), t/day
W_n	Water mass rate added to n^{th} washing stage, t/day
W_P	The amount of complex solution output leaching system, t/day

$w_{P,PEI}$	The amount of PEI in the liquid product stream from leaching syatem, t/day
$w_{P,solid}$	The amount of solids without zinc in the liquid product stream from leaching unit, t/day
$w_{P,Zn}$	The amount of zinc in the liquid product stream from leaching unit, t/day
W_S	The amount of solids output from leaching unit as inert, t/day
$w_{S,PEI}$	The amount of PEI in the solid inert stream output leaching system, t/day
$w_{S,solid}$	The amount of solid without zinc in the inert stream output leaching system, t/day
$w_{S,Zn}$	The amount of zinc in the solid inert stream output leaching system, t/day
wt_{NaCl}	The amount of NaCl resulted in liquid stream from sedimentation unit, t/day
wt_{NaOH1}	The amount of NaOH required to generate $Zn(OH)_2$, t/day
wt_{NaOH2}	Mass rate of NaOH required to dissolve zinc hydroxide, t/day
$wt_{Zincate1}$	The mass rate of zincate produce by zincate formation unit, t/day
$wt_{Zincate2}$	The amount of remaining zincate leaving the electrowinning unit, t/day
wt_{Zn}	The amount of zinc input to sedimentation unit, t/day
wt_{ZnCl2}	The amount of $ZnCl_2$ entering sedimentation unit, t/day
wt_{Znd}	The amount of zinc deposited on cathode in grams
$wt_{Zn(OH)2}$	The amount of $Zn(OH)_2$ produced by sedimentation unit, t/day
x	The depth of electric double layer
$X_{complexation}$	The fraction of zinc complexed with PEI
$X_{decomplex}$	The fraction of zinc freed from PEI during leaching process
X_{elec}	The fraction of removal of zinc metal from zincate solution
$X_{Extraction}$	The extraction efficiency of leaching unit
$X_{PEI,losses}$	The fraction of polymer losses during the recovery operation
z	The ion valence
$[Zn^{2+}]$	The concentration of zinc ions at time t
$[Zn_{metal}]$	The concentration of zinc metal produced at time t

Greek Symbols:

α_c	Cathodic charge transfer coefficients
α_a	Anodic charge transfer coefficients
$\eta_{c'}$	Cathodic overpotentials, volt
η_a	Anodic overpotentials, volt
φ	Ionic strength of solution, (mol/L)
$|\Delta P|$	The pressure difference applied across the membrane, atm
η_I	The current efficiency
ΔP	The pressure drop across filtration module, psi
ρ	The density of product solution, (can be assumed as density of water), t/m^3

Acronyms and Abbreviations:

AEM	Anion exchange membrane
BECTU	Butyl ethoxycarbonyl thiourea
CD	Current density
CEM	Cation exchange membrane
CV	Cyclic voltammtrey
ECTC	Ethoxycarbonyl thionocarbamates
DETA	diethylnetriamine
EW	Electrowinning
IBECTC	O-isobutyl-N-ethoxycarbonyl thionocarbamate
IPETC	O-isopropyl-N-ethyl thionocarbamate
LIX	A hydroxyl-oxime complex
MIP	Molecular imprinted polymer
NTA	Nitrilotriacetic acid
PCB	Printed circuit board (
PEI	Polyethylenimine
PEUF	Polymer enhanced ultrafiltration
PWB	Printed wiring board
TBP	Tri-*n*-butyl phosphate chelating compound)
VCF	Volume concentration factor
VCR	Volume concentration ratio
WF	Washing factor

APPENDICES

Appendix 1: Zinc Integrated Recovery Unit Data:

	Variable	Amount	Unit
Leaching input	Initial solid input	1000.00	t/day
	Zinc content%	2.00	
	Zinc in solid	20.00	t/day
	Polymer concentration	6.00	g/L
	Polymer solution losses%	0.1	
	PEI capacity	0.1051	
	Extraction efficiency%	50	
Electrowinning	Current density	2000.00	Am/m^2
	Electrowinning energy usage	0.77	kWh/kg
	Current efficiency%	98.00	
	Zinc electrowinning Recovery%	88.55	
	Zincate initial concentration, $C_{Zincate}$	55.00	g/L
	NaOH input concentration, C_{NaOH}	4.00	mol/L
	Number of Zn electrons, n	2	
	Faradays number	96500.00	Faraday/mol
PH change	HCl Concentration, C_{HCl}	0.50	mol/L
	NaOH Concentration, C_{NaOH}	0.50	mol/L
	Polymer-HCl volume ratio, 10-5.5 complex	5.63	
	Polymer-HCl volume ratio, 5.5-2.5 complex	16.00	
Molecular weights	Mwt_{Zn}	65.37	
	Mwt_{ZnCl2}	136.37	
	Mwt_{ZnO}	81.37	
	Mwt_{NaOH}	40.00	
	Mwt_{NaCl}	58.50	
	Mwt_{H2O}	18.00	

	Variable	Amount	Unit
	Mwt_{Na}	23.00	
	Mwt_{HCl}	36.50	
	$Mwt_{Zincate}$	179.37	
	Mwt_{Cl2}	71.00	
	$Mwt_{Zn(OH)2}$	99.37	
Ultrafiltration	Zn-PEI ratio	0.1051	mg Zn/mg PEI
	Volume-concentration ratio, VCR	10.00	
	pressure	20.00	psi
	Concentration and washing permeate flux	0.022	$m^3/m^2.hr$
	pump efficiency	0.50	
	Total zinc decomplexed%	84.86	
	Zinc Complexation%	98.57	
	Zinc concentration after concentration	6.12	g/L
	Zinc concentration in 2 washing permeates	2.18	g/L
	PEI concentration after washing	61.18	g/L
	Zn remained in complex concentration after washing	1.76	g/L
	Washing feed/retentate ratio, WR	2	
Prices	Zinc selling price	1243.11	£/t
	NaOH price	332.80	£/t
	HCl price	133.12	£/t
	PEI price	6416.67	£/t
	Dionised water price	60.99	£/t
	Power cost	0.034	£/kWh
other data	Water density	1.00	t/m^3
	37% HCl Cp. Gr.	1.18	
	Electrodialysis energy consumption	2720.00	$kWh/t \ Cl_2$
	NaOH concentration in metal oxidation units	4.00	mol/L

Appendix 2: Electrolysis Parameters and Design:

A2.1: Parameters Definitions:

Metal deposition can be accompanied by any other cathodic reaction, such as hydrogen evolution. Thus, metal deposition uses only a part of the total current through the cell.

A2.1.1: Current Efficiency:

The efficiency of the deposition process can be defined as the ratio of the current used for the reduction of the ion for the intended deposit to the total current passed through the cell. This can be represented by the following relationship:

$$\eta_I = \frac{I_{Me}}{I} \tag{A2.1}$$

where I is the total current and I_{Me} is the actual current used for metal deposition.

The other part of current is consumed in the formation of hydrogen gas and other side reactions. Therefore, it is important to reduce the effect of this reaction in order to increase the deposition efficiency and then the deposition rate. The formation of hydrogen bubbles can be difficult to remove from the sample surface. This will hinder further deposition.

A2.1.2: Faraday's Law:

Faraday's law relates the quantity of electricity passed through the cell and the quantity of chemical substances that react on the electrodes. It states that the mass of metal, m, electrodeposited on the cathode is given by:

$$m = \frac{\eta_I ItM}{nF} \tag{A2.2}$$

where I is the total current, t is the deposition time, M is the molar mass of the deposited metal, η_I is the current efficiency defined by equitation A2.1, n is the charge of deposited ions and F is the number of Faradays per mole of consumed ions. It follows from equation (A2.2) that η_I can be easily determined by measuring the electrodeposited mass of metals and supplied quantity of electricity. However, it

is still required to distinguish between the current density that is due to metal deposition and hydrogen evolution since hydrogen evolution occurs simultaneously with the deposition reaction. Reducing the effect of hydrogen evolution by any mean and increasing the current efficiency of the process might achieve higher recover percentage.

The recovery of metals R can be defined as the actual amount of metal deposited onto the cathode divided by the initial amount of metal in the electrolyte. Hence, the current efficiency can be related to the metal recovery amount as following:

η_I = actual amount of metal deposited onto the cathode / amount of metals deposited based on faraday's law $\qquad$ (A2.3)

The above relationship could be employed to estimate the current used to deposit the metal.

A2.1.3: Energy Usage (Consumption):

Energy consumption by electrochemical cell is one of the most important energetic parameter in metal electrowinning and electrorefining technologies in the electrodeposition processes. It is clear that electric power requires some kind of energy to produce unit weight of metal. Therefore, energy consumption is function of both electrolysis conditions and cell design.

The mathematical representation of energy usage in electrochemical cell can be derived by defining the electrical work, W required to deposit m quantity of metal on the cathode. This can be written as following:

$$W = UIt \qquad (A2.4)$$

where U is the operating cell voltage, I is the total current and t is the deposition time. By combining the above equation with equation (A2.2), the specific energy consumption can be found as following:

$$It = \frac{mnF}{\eta_I M} \qquad (A2.5)$$

From equation (A2.4):

$$It = \frac{W}{U} \tag{A2.6}$$

By equating (A2.5) to (A2.6) the result is as following:

$$\frac{W}{U} = \frac{mnF}{\eta_I M} \tag{A2.7}$$

Rearranging the above equation yields:

$$w = \frac{W}{m} = \frac{nFU}{\eta_I M} \tag{A2.8}$$

where w represents the specific energy consumption. It can be seen from the above equation that the energy consumption does not depend directly on current density. This is due to the fact that the passage of current is essential to the conversion of material to product. In other word, the charge required to produce one mole of product can be determined by Faraday's law. On the other hand, the effect of cell voltage and current efficiency can be clearly recognised. It is important to point out that the minimum energy required to produce a desirable amount of certain metal should be counted.

A2.1.4: The Cell Voltage:

As it has been mentioned above, the cell potential plays an important role in reducing energy consumption in the cell. Consequently, it is required to estimate the value of cell voltage in order to improve the efficiency and in parallel reducing the energy usage by the cell. The cell voltage can be defined by the following equation:

$$U = E_e^C - E_e^A - |\eta_A| - |\eta_C| - I \sum_{1}^{n} R_i \tag{A2.9}$$

where: E_e^A and E_e^C are the equilibrium potentials for the anode and the cathode respectively, η_A and η_C are the anode and the cathode overpotential respectively, $\sum_{1}^{n} R_i$ represents the sum of ohmic resistance of the electrolyte, electrodes, contacts and connecting wires, I is the current.

The term $E_e^C - E_e^A$ is considered to be a part of the cell voltage that can be reduced by changing the overall cell reaction and may be changing the counterelectrode reaction. On the other hand, η_A and η_C can contain the contribution from the electron transfer process and mass transfer. It is assumed that simple electron transfer reaction occurs. Therefore, the electrode overpotential can be defined the following equation:

$$\left|\eta_{electrode}\right| = \frac{2.3RT}{\alpha nF}(\log I - \log I_0) \tag{A2.10}$$

Where I_0 is the exchange current density, α is the transfer coefficient (it has a value between o and 1, commonly 0.5). Equation (A2.10) is called Tafel equation and I_0 and α can be determined via experimental methods.

The ohmic drop in equation (A2.9) could be defined as the following:

$$I \sum_1^n R_i = \frac{1}{k}LI \tag{A2.11}$$

where L refers to the electrode gap and k is the specific conductivity of the electrolyte. The above equation shows that the ohmic drop is proportional to the electrode gap, current density and is inversely proportional to the specific conductivity of the electrolyte. However, varying both electrode gap and current density could be difficult due to restraints associated with cell design limitations and production rate requirements. Nevertheless, higher electrolyte conductivity could allow the electrowinning to perform at lower applied voltages. This means choosing the electrolyte and other solution is important in terms of reducing energy for an already designed cell for specific production.

A 2.2: Cell Design Principles:

The design of the cell will effect on the performance of electrolytic processes. The principles factors of cell design could be outlined as following:

- The presence or absence of separators and its type
- Mass transport regime

- The arrangement of the electrodes
- Anode-cathode gap
- Potential distribution at the cathodes
- Material of construction

A 2.2.1: Mass Transfer in Electrochemical Unit:

Liquid convection, diffusion, and migration can determine mass transfer. The liquid convection directed parallel to the electrode surface determines the thickness of the Nernst diffusion layer, δ, where as the concentrations of species can usually be assumed to be constant outside this layer.

The electrochemical cell can be controlled by mass transfer at the electrode surface. In the electrochemical cell, for example, a metal ion concentration at the cathode surface is decreased by electrolysis. If the concentration of the supporting electrolyte is a factor 10 higher than the concentration of the selected species to be oxidised or reduced, the migration of the selected species can be neglected. This could be applicable when experiment is in run with one of tow cases. The first involves no stirring equipments and the second case is when using forced convection to the solution (Kentish and Stevens, 2001).

For the first case, the electron transfer process at the surface leads to a boundary layer where the concentration of the oxidant specie is lower than that of the reductant one. The transport rate can be determined by diffusion given by Fick's first law at the electrode surface:

$$flux = -D_i \frac{dC_i}{Dx} \tag{A2.12}$$

where D_i is the diffusion coefficient of the specie. The above equation can be used to relate the current to the chemical change where the flux of the specie is equal to the electron flux. Therefore, the above equation can be rewritten as following:

$$\frac{I}{nF} = -D_i \frac{dC_i}{dx_{x=0}} \tag{A2.13}$$

Rearranging the above equation for the current density:

$$I = -nFD_i \frac{C_i^0 - C_i^\infty}{\delta} \qquad (A2.14)$$

where C_i^0 and C_i^∞ are the concentration of oxidant specie on the surface, which is function of potential, and in the bulk respectively. The limiting diffusion current density is given by:

$$I_L = \frac{nFD_i C_i^\infty}{\delta} \qquad (A2.15)$$

In the absence of supporting electrolyte, migration and diffusion determine the transport of selected species. For solutions containing exclusively a 1:1 valency electrolyte the mass transfer coefficient of the cation is given by:

$$k_m = 2D_i / \delta \qquad (A2.16)$$

The above equation shows that the contributions of migration and diffusion to the total mass transport are equal. Generally, $k_m = \gamma D_i / \delta$, where $\gamma \geq 1$ and the parameter γ depends on the composition of solution.

For an electrolyte in the absence of supporting electrolyte for the migration of the cation the factor γ is given as follows (Pak et al., 2001):

$$\gamma = 1 + z_C / z_A \qquad (A2.17)$$

where z_C is the charge of the cation and z_A is the charge of the anion.

A 2.2.2: Electrochemical Cell and Chemical Reactor:

There are three types of chemical reactors employed in several electrochemical operations. The first type of reactors is called batch reactor where the reactor is charged with reactants and then mixed and left for a period of time. The concentration of reactants and products will change smoothly with time but the composition remains uniform throughout the reactor volume. This kind of reactors is suited to small scale operations.

The second type is called plug flow reactor. The reactant mixture is flowed steadily through the reactor and the products are extracted from the mixture leaving the

reactor. Hence, the composition of the mixture changes with distance through the reactor and the residence time is the same for all species. CSTR reactors are the most popular reactors in the industry. It consists of a well stirred tank for the composition to remain uniform through the reactor.

With the majority of electrochemical processes only one of the electrode reactions is desired. Therefore, the change of the environment which attends either of the reactions might have little effect on the progress of other. In this case, most of reactor design can be perform by considering the desired reaction alone. It all starts by writing the mass balance for the targeted ion. This can be generalised as following:

(mass of ion input) – (mass of A output) + (mass of A Generated) – (mass of A Removed) = (mass of A accumulated)   (A2.18)

From the above formula, the design equation can be derived for any type of reactor depends on the reactor conditions. The design equation procedure must enable the electrode area, current efficiency, energy consumption, etc, to be specified for certain conversion reactant. However, some other factors, such as initial reactor size and conversion of given operating voltage could be related problems but not usually the fist aim in the design procedures. Pickett (1979) reviewed all the above in his book in more details. This will be discussed in the following sections.

A 2.2.1.1: Basic Design Equation for Electrochemical CSTR:

Figure A2-1 represents an electrochemical CSTR reactor of volume V with equal flow rate of solution entering and leaving the reactor, N with constant concentration of reactants in both streams, C_1 and C_2. Generally, it is required to make an overall mass balance in order to study the design equation for several cases. This can be done by employing equation (A2.18) as following:

$$N(C_1 - C_2) = \frac{iA}{nF}$$ (A2.19)

The above equation was derived under certain assumptions of uniform primary current distribution. It can be seen from the above equation that the concentration changes over a differential CSTR but not the concentration distribution within it.
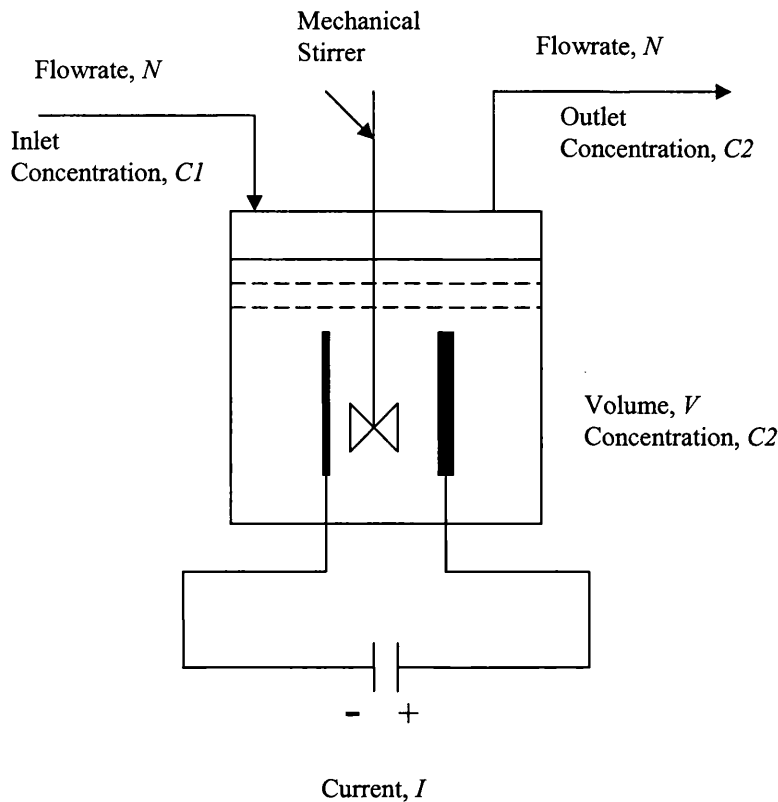
Figure A2-0-1: Electrochemical CSTR reactor.

When fast reaction, (reaction that has high current density and is limited by mass transfer of species to and from the electrode), occurs under limiting conditions, equation (A2.19) can be rewritten under limiting current density defined by equation (A2.16). The resulting equation could be as following:

$$N(C_1 - C_2) = k_m C_2 A \qquad \text{(A2.20)}$$

where k_m mass transfer coefficient defined by equation (A2.17) and A represents the minimum electrode area. The above equation can be rearranged for the output concentration yields:

$$C_2 = \frac{C_1}{1 + k_m A / N} \qquad \text{(A2.21)}$$

And the reactor conversion can be defined as following:

$$\% \ conversion \quad = \frac{C_1 - C_2}{C_1} \qquad (A2.22)$$

From equation (A2.21) and (A2.22):

$$\% \ conversion \quad = \frac{k_m A / N}{1 + k_m A / N} \qquad (A2.23)$$

A 2.2.2.2: Basic Design Equation for Electrochemical Batch Reactor:

The operation of this kind of reactors started when electrolyte is charged, electrochemical process takes place and finally the reactor is emptied. The natural convection in this reactor can be achieved by using stirrer in the tank. Ion concentration and tank temperature change with time and frequent adjustment of voltage to maximise the current efficiency is required.

From equation (A2.18), the input and output flows are zero since the operation occurs within the reactor volume. This also means that there is accumulation term in the equation. For a cathodyte volume, V with initial concentration of C_0, the process aims to reduce the amount of ions to value C at time t. The mass balance over the reactors becomes as following:

$$- V \frac{dC}{Dt} = \frac{I}{nF} \qquad (A2.24)$$

where I is the total current at that time. It can be assumed that mass transfer coefficient is constant and primary current distribution is uniform and:

$$I = nFk_m A(C - C_S) \qquad (A2.25)$$

where C_S is the ion concentration at the cathode surface. The above equation can be rearranged in terms of a factor called dimensionless current density or mass transfer deriving force, γ. This yield:

$$I = nFk_m A \gamma C \qquad (A2.26)$$

$$\gamma = \frac{I}{I_L} = \frac{C - C_s}{C} \qquad (A2.27)$$

By substituting equation (A2.26) into (A2.24), equation (A2.24) can be integrated and the result is as following:

$$t = \frac{-V}{k_m A} \int_{C_0}^{C} \frac{dC}{\gamma C} \qquad (A2.28)$$

As it can be seen from the above equation, time is function of the current density and therefore concentration in this reactor. The above equation could be rewritten to suit specific operation conditions. For instance, when the reactor operates at a limiting current or above it, the value of γ goes to unity and the above equation could be written as following for the minimum time of electrolysis:

$$t = \frac{V}{k_m A} \ln(C_0 / C) \qquad (A2.29)$$

Therefore, the minimum electrode required for the process in a given time could be evaluated as following:

$$A_{min} = \frac{V}{k_m t} \ln(C_0 / C) \qquad (A2.30)$$

Batch reactors are suitable for small scale operations where they are more economic than continuous reactors. They are also suitable in certain relatively large scale processes where intermittent operation is available, such as metal electrowinning. One of the important applications of the batch electrochemical reactor is an analytical instrument, where rates of reaction can be followed as function of electrolyte composition.

A 2.2.2.3: Basic Design Equation for Electrochemical Plug Flow Reactor:

This type is intensively employed in the real industry. It is the most widely used for high production rate. The idea of this kind of reactors is that element of fluid flows through the tube, which has specific size and conditions depend on the conversion required.

The operation of plug flow reactor can be shown in figure A2-2. The overall mass balance, equation (A2.18), can be applied around the system. It is assumed that the system is study state which means the concentrations and temperature will remain the same at any position.

From the above figure, a volumetric flow rate, N of electrolyte solution enters the reactor with reactant concentration, C_1 and leaves with reactant concentration C_2. The principal axis of the reactor is straight and corresponds to x-axis over the length L, from $x = 0$ to $x = L$. The cross section area normal to the electrolyte solution flow, s and the electrode area per unit length, A both remain constant since the diameter of the reactor is constant. The overall mass balance around the system can be given by:
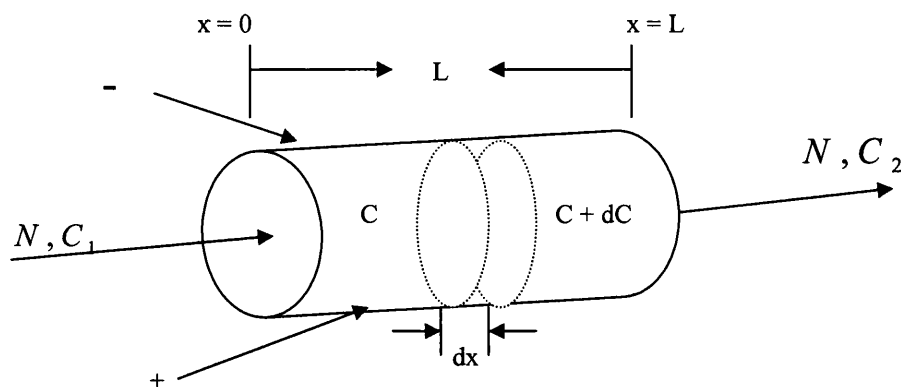
Figure A2-2: Electrochemical plug flow reactor

$$NC_1 - NC_2 = \frac{I}{nF} \qquad (A2.31)$$

It is also required to write the material balance over a small element of the reactor in order to obtain the differential equation for the concentration distribution inside the reactor. This procedure can be done as following:

$$\left\{ NC - Ds\left(\frac{Dc}{Dx}\right)_x \right\} - \left\{ N(C + dC) - Ds\left(\frac{dC}{dx}\right)_{x+dx} \right\} = \frac{I_x A}{nF} dx \qquad (A2.32)$$

where I_x represents the current density at x distance in Adx and it can be assumed constant over that element. By dividing the above equation by dx and taking the limits when $dx \rightarrow 0$, the following equation results:

$$\frac{-Ndc}{dx} + Ds\frac{d^2C}{dx^2} = \frac{I_x A}{nF} \tag{A2.33}$$

In many cases, the diffusion term in the above equation can be ignored since most of the reactor operation happens via the electrochemical reaction and the electrolyte flow. Therefore, the above equation becomes:

$$\frac{dC}{dx} = \frac{-I_x A}{nFN} \tag{A2.34}$$

When the reaction is fast, the local current density is function of mass transfer coefficient and the relationship can be presented as following:

$$I_x = nFk_m(C - C_S) \tag{A2.35}$$

where C_S is the ion concentration at the cathode surface. From equation (A2.35) and (A2.34):

$$\frac{dC}{dx} = \frac{-Ak_m}{N}(C - C_S) \tag{A2.36}$$

When the surface concentration approaches to zero, the reactor operates at minimum current and minimum electrode length required can be estimated as following:

$$-N\int_{C_1}^{C_2} \frac{dC}{C} = A\int_0^{L_{min}} K_m\, dx \tag{A2.37}$$

The result of the above integration gives:

$$a_{min} = AL_{min} = \frac{N}{k_m}\ln\frac{C_1}{C_2} \tag{A2.38}$$

Then by eliminating the flow rate N by equation (A2.31), viz:

$$\frac{I}{nF} = \frac{k_m a_{min} (C_1 - C_2)}{\ln(\frac{C_1}{C_2})}$$

(A2.39)

Also, the concentration at any distance inside the reactor can be obtained as following:

$$C_x = C_1 \exp\left[\frac{k_m A x}{N}\right]$$

(A2.40)

From equation (A2.22), the fraction conversion of reactant can be defined by following relationship:

$$\% \, conversion \; = 1 - \exp\left[\frac{k_m a_{min}}{N}\right]$$

(A2.41)

The total current can be defined by combining equations (A2.31) and (A2.41) yields:

$$I = nFNC_1 \left(1 - \exp\left[\frac{-k_m a_{min}}{N}\right]\right)$$

(A2.42)

Appendix 3: Polarographic Aspects of Cyclic Voltammetry:

A 3.1: Principles and Fundamentals:

Polarographic or voltammetric analysis involves the recording of current intensity-electric tension diagram under suitable conditions. However, the term polarography is reserved for the interpretation of current-potential curves obtained with dropping mercury electrodes and voltammetry should be used to study current-potential curves obtained with any indicator electrode. It has been pointed out that the dropping mercury electrode has limitation that it can not be used beyond a potential of about $+0.4V$ with respect to the saturated calomel electrodes.

A simple potential wave often used in electrochemical experiments is the linear wave form, (i.e., the potential is continuously changed as a linear function of time. The rate of change of potential with time is referred to as the scan rate (v)). The simplest technique that uses this wave form is linear sweep voltammetry. The potential range is scanned in one direction, starting at the initial potential and finishing at the final potential. A more commonly used variation of the technique is cyclic voltammetery, CV, in which the direction of the potential is reversed at the end of the first scan. Thus, the waveform is usually of the form of an isosceles triangle. This has the advantage that the product of the electron transfer reaction that occurred in the forward scan can be probed again in the reverse scan. In addition, it is a powerful tool for the determination of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction and evaluation of electron transfer kinetics.

A cyclic voltammetry can be obtained by measuring the current at the working electrode during the potential scan. The voltage is first held at the initial potential where no electrolysis occurs and hence no faradic current flows. As the voltage is scanned in the positive direction, so the reduced compound is oxidised at the electrode surface. At a particular set value, the scan direction is reversed and the material that was oxidised in the outward excursion is then reduced. Once the voltage is returned to the initial value, the experiment can be terminated. In conformity with normal voltammetric practice, cathodic (reduction) current are shown as positive and anodic (oxidation) current as negative.

A 3.2: CV as a Concentration Measurement Tool:

Cyclic voltammetric method can be used for measuring concentrations of subcomponents of additive mixtures, comprising the steps of: (a) Preparing a basis solution which contains all of the components of an unknown solution to be measured, except a component of interest; (b) Preparing a calibration solution which contains the component of interest in a known concentration near that which would be expected in the unknown solution; (c) Adding measured amounts of the calibration solution to a first defined volume of the basis solution and plotting a first cathodic charge against the added volume of the calibration standard; (d) Adding measured amounts of the unknown solution to a second volume of the basis solution and plotting a second cathodic charge against the added volume of the unknown solution; and (e) Comparing the slopes of the first and second curves to determine the concentration of the component of interest in the unknown solution.

The important parameters obtained from a cyclic voltammograms are the anodic peak current (i_{pa}), cathodic peak current (i_{pc}), anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}). All of these values can be readily obtained from the voltammogram. The peak current for an electrochemically reversible system (rapid transport of electrons on the surface within the framework of the experiment) is described by the following equation:

$$I_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}c \qquad (A3.1)$$

where: I_p= peak current (in mA), n = electron stoichiometry, D = diffusion coefficient (cm^2/s), c = concentration (mol/cm^3), A = electrode area (cm^2) and v = potential scan rate (V/s).

The above equation is called Randles-Sevcik equation. It describes the peak current for reversible systems for forward sweep of the first time. A plot of i_p vs. c should give a straight line with an intercept of zero. Large deviation from zero could indicate adsorption. A plot of i_p vs. $v^{1/2}$ should give a straight line, the slope of which can be used to determine the diffusion coefficient, if n, A and c are known.

Appendix 4: Prediction of Diafiltration System Model for Various Washing Factors:

1) WF = 2.5

[PEI], g/L	Membrane productivity, kg Zn/m².hr	Outlet zinc concentration, mg/L	Total permeate flux, m³/m².hr	Zinc recovery %
0.500	0.017	123.735	0.136	93.094
1.000	0.037	292.940	0.126	95.651
2.000	0.063	594.786	0.105	98.047
3.000	0.077	964.328	0.080	97.657
4.000	0.082	1286.726	0.063	95.491
6.000	0.083	1962.397	0.042	97.700
8.000	0.076	2556.848	0.030	94.740
10.000	0.069	3205.082	0.021	95.304

2) WF = 2.0

[PEI], g/L	Membrane productivity, kg Zn/m².hr	Outlet zinc concentration, mg/L	Total permeate flux, m³/m².hr	Zinc recovery %
0.500	0.024	180.711	0.135	87.928
1.000	0.043	355.532	0.122	79.137
2.000	0.076	770.765	0.098	83.345
3.000	0.086	1161.298	0.074	78.054
4.000	0.089	1546.591	0.058	76.168
6.000	0.087	2328.975	0.037	77.686
8.000	0.078	3086.830	0.025	76.239
10.000	0.070	3837.270	0.018	75.961

3) WF = 1.5

[PEI], g/L	Membrane productivity, kg Zn/m².hr	Outlet zinc concentration, mg/L	Total permeate flux, m³/m².hr	Zinc recovery %
0.500	0.037	278.197	0.134	63.122
1.000	0.074	631.721	0.117	64.111
2.000	0.100	1095.622	0.092	60.010
3.000	0.118	1753.236	0.067	56.884
4.000	0.116	2345.070	0.050	57.581
6.000	0.106	3501.180	0.030	56.877
8.000	0.095	4646.297	0.020	57.119
10.000	0.084	5770.805	0.015	56.810

Appendix 5: Results of Material Balance Calculations of Zinc Recovery Plant Units:

Table A5-1: Results of material balance calculations of leaching of 1,000 tons of solid contains 2% zinc using 6 g/L of polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Material	Unit	Input stream 1	Composition input 1	Input stream 2	Composition input 2	Product stream 1	Composition product 1	Product stream 2	Composition product 2
Zinc	t/day	20.000	0.020	2.791	0.0003	9.857	0.0010	12.934	0.013
Non zinc solids	t/day	980.000	0.980	0.000	0.000	0.000	0.000	980.000	0.977
PEI	t/day	0.000	0.000	48.557	0.005	48.508	0.005	0.049	0.0000
6 g/L PEI solution	t/day	0.000	0.000	8092.775		0.000	0.000		0.0000
0.5 mol/L HCl solution	t	0.000		1348.796		0.000	0.000		0.0000
HCl	t			21.327					
37% HCl	t	0.000	0.000	57.641	0.006	39.265	0.004	0.058	0.0001
0.5 mol/L NaOH	t/day	0.000		505.798		0.000	0.000	0.000	0.0000
NaOH solids	t/day	0.000	0.000	10.116	0.001	0.000	0.000	0.000	0.000
NaCl	t/day	0.000	0.000	0.000	0.000	14.780	0.001	0.015	0.015
Distilled water	t/day	0.000	0.000	9879.613	0.988	9869.733	0.989	9.880	0.010
Total	t/day	1000.000	1.000	9998.717	1.000	9982.143	1.000	1002.935	1.000

Table A5-2: Results of the continuous concentration/ultrafiltration process model calculations for solution resulted from leaching of 1,000 tons of solids contains 2% zinc using 6 g/L of polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Material	Unit	Feed stream	Feed composition	Retentate	Retentate composition	Permeate	Permeate composition
Zinc	t/day	9.857	0.0005	9.857	0.005	0.000	0.000
PEI	t/day	97.016	0.005	97.016	0.049	0.000	0.000
NaCl	t/day	29.560	0.001	0.000	0.000	29.560	0.002
Distilled water	t/day	19642.450	0.993	1871.015	0.946	17771.435	0.998
Total	t/day	19778.882	0.999	1977.888	1.000	17800.994	1.000

Table A5-3: Results of the continuous decomplexation and two times washing processes calculations resulted from leaching of 1,000 tons of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Material	Unit	Feed stream	Feed composition	Acidic water stream	Acid water composition	Permeate	Permeate composition	Retentate	Retentate composition
Zinc	t/day	9.857	0.010	0.000	0.000	7.066	0.003	2.791	0.003
PEI	t/day	48.508	0.048	0.000	0.000	0.000	0.000	48.508	0.049
$ZnCl_2$	t/day	20.563	0.020	0.000	0.000	14.741	0.007	0.000	0.000
HCl	t/day	0.000	0.000	7.891	0.000	0.000	0.000	0.000	0.000
37% HCl	t/day	0.000	0.000	15.659	0.008	0.000	0.000	0.000	0.000
Distilled water	t/day	935.923	0.922	1998.384	0.992	1998.384	0.989	943.691	0.948
Total	t/day	1014.851	1.000	2014.042	1.000	2020.190	1.000	994.990	1.000

Table A5-4: Results of the continuous metal hydroxide sedimentation process calculations for solution resulted from leaching of 1,000 tons of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Material	Unit	Feed stream 1	Feed composition 1	Feed stream 2	Feed composition 2	Production stream 1	Production composition 1	Production stream 2	Production composition 2
$ZnCl_2$	t/day	14.741	0.004	0.000	0.000	0.000	0.000	0.000	0.000
NaOH solids	t/day	0.000	0.000	8.647	0.160	0.000	0.000	0.000	0.000
NaCl	t/day	0.000	0.000	0.000	0.000	12.647	0.003	0.000	0.000
$Zn(OH)_2$	t/day	0.000	0.000	0.000	0.000	0.000	0.000	10.741	1.000
Distilled water	t/day	3965.584	0.996	45.399	0.840	4010.984	0.997	0.000	0.000
Total	t/day	3980.325	1.000	54.047	1.000	4023.631	1.000	10.741	1.000

Table A5-5: Results of the continuous zincate formation process calculations for solution resulted from leaching of 1,000 tons of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Material	Unit	Feed stream 1	Feed composition 1	Feed stream 2	Feed composition 2	Production stream	Production composition
Zincate, $Na_2Zn(OH)_4$	t/day	0.000	0.000	2.220	0.005	21.609	0.052
$Zn(OH)_2$	t/day	10.741	1.000	0.000	0.000	0.000	0.000
NaOH solids	t/day	0.000	0.000	8.647	0.021	0.000	0.000
Distilled water	t/day	0.000	0.000	394.829	0.973	392.883	0.948
Total	t/day	10.741	1.000	405.696	1.000	414.492	1.000

Table A5-6: Results of the continuous anaerobic zinc electrowinning and Zn(OH)₂ production reactors calculations for solution resulted from leaching of 1,000 tons of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Material	Unit	Feed stream	Feed composition	Production stream 1	Production composition 1	Production stream 2	Production composition 2
Zincate, Na$_2$Zn(OH)$_4$	t/day	21.609	0.052	0.000	0.000	2.220	0.005
NaOH solids	t/day	0.000	0.000	0.000	0.000	8.647	0.021
Zn pure	t/day	0.000	0.000	6.973	1.000	0.000	0.000
Oxygen, O$_2$	t/day	0.000	0.000	0.000	0.000	1.729	0.004
Distilled water	t/day	392.883	0.948	0.000	0.000	394.829	0.969
Total	t/day	414.492	1.000	6.973	1.000	407.426	1.000

Table A5-7: Electrodialysis process productivity results for solution resulted from leaching of 1,000 tons of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Material	Unit	Feed stream	Feed composition	Production stream	Production composition
NaCl	t/day	43.655	0.002	0.000	0.000
Cl$_2$	t/day	0.000	0.000	26.491	
NaOH solids	t/day	0.000	0.000	29.849	0.001
HCl	t/day	0.000	0.000	8.556	
37% HCl	t/day	0.000	0.000	54.051	0.002
Distilled water	t/day	22136.664	0.998	22123.232	0.996
Total	t/day	22180.319	1.000	22207.132	1.000

Appendix 6: Economic Analysis Results:

Table A6-1: Equipments cost calculations of zinc recover units to recover zinc from 1000 t of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Fixed capital cost

Item	Description	Feed input, m³/day	day/cycle	Size required, m³	Purchased cost, £	Installation, £	Piping, £	Building, £
Leaching	Vertical tank, conical roof	10998.717	0.500	6049.294	261942.7	65485.7	225270.8	104777.1
Concentration, Decomplexation and Washing	Horizontal, round end	9942.878	0.031	341.786	246155.7	61538.9	211693.9	98462.3
Sedimentation and Zincate formation	Mixer/settler	2067.171	0.010	23.686	33217.5	8304.4	28567.0	13287.0
Electrowinning	Electrowinning cell	414.492	0.031	14.248	279933.5	69983.4	240742.8	111973.4
Electrodialysis	Electrowinning cell	11005.020	0.031	378.298	11192.6	2798.1	9625.6	4477.0
Total					832441.9	208110.5	715900.1	332976.8

Table A6-2: Chemicals cost calculations of zinc recover units to recover zinc from 1000 t of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Chemicals

Chemical substance	Amount, t	Price, £/t	Cost, £
NaOH	27.411	332.800	9122.363
Distilled water	12316.278	60.000	1639542.993
HCl	73.300	133.120	3648.945
PEI	97.113	6416.670	623144.002
Total chemical Investment			**635915.311**

Table A6-3: Energy consumption cost by zinc integrated unit with 50% zinc extraction efficiency contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Energy cost

Process	Energy term	Unit	Area, m^2	energy amount	cost, £/year
Concentration	E_{F1}	kw/m^2	16948.087	0.235	2974.909
Washing	E_{F2}	kw/m^2	3826.118	0.106	303.643
Electrowinning	E_E	kWh/t	0.438	767.000	11.414
Electrodialysis	E_D	kWh/t Cl_2		45270.569	1539.199
Total					**4829.166**

Table A6-4: Zinc extraction integrated unit cash flow for 1000 t of solids contains 2% zinc using 6 g/L polymer solution with 50% zinc extraction and 0.1% PEI solution losses.

Variable	Amount	Unit
Zinc production	2545.312	t/year
Total production	2545.312	t/year
1. Fixed cost investment :		
a) Purchased equipment	832441.927	£
b) Installation	208110.482	£
c) Piping	715900.057	£
d) Building	332976.771	£
e) Start up Materials	635915.311	£
Total investment, I	2725344.547	£
2. Process revenue		
Zinc pure metal	3510545.473	£/year
Total Process revenue	3510545.473	£/year
4. Manufacturing cost:		
a) Utilities		
1. Energy	4829.166	£/year
Total utilities	4829.166	£/year
b) Extra chemicals		£/year
1. NaOH extra	0.000	£/year
2. HCl extra	2800.700	£/year
3. PEI extra	113723.780	£/year
4. Water	216363.514	
Total chemicals	332887.994	£/year
c) Labour and supercision		
Labour number	15.000	
Salary	15.000	£/hr
working hours	8.000	hr/day
1. Labour salaries,	657000.000	£/year
2. Supervision, at 10% salaries	65700.000	£/year
Total salaries	722700.000	£/year
Maintenance, 6% of investment	163520.673	£/year
Overheads		

Variable	Amount	Unit
1) Insurance, 1% of fixed capital cost	27253.445	£/year
2) Depreciation, 9% of fixed capital cost	245281.009	£/year
3 Property tax, 5% of capital cost	136267.227	£/year
Total overheads	**408801.682**	
6. Total operating cost	**1632739.514**	£/year
Operating profit, (before taxes)	**1877805.958**	£/year
U.K. Corporation tax, 35% of profit	657232.085	£/year
Profit after tax	**1220573.873**	£/year
Pay out time	**2.233**	years