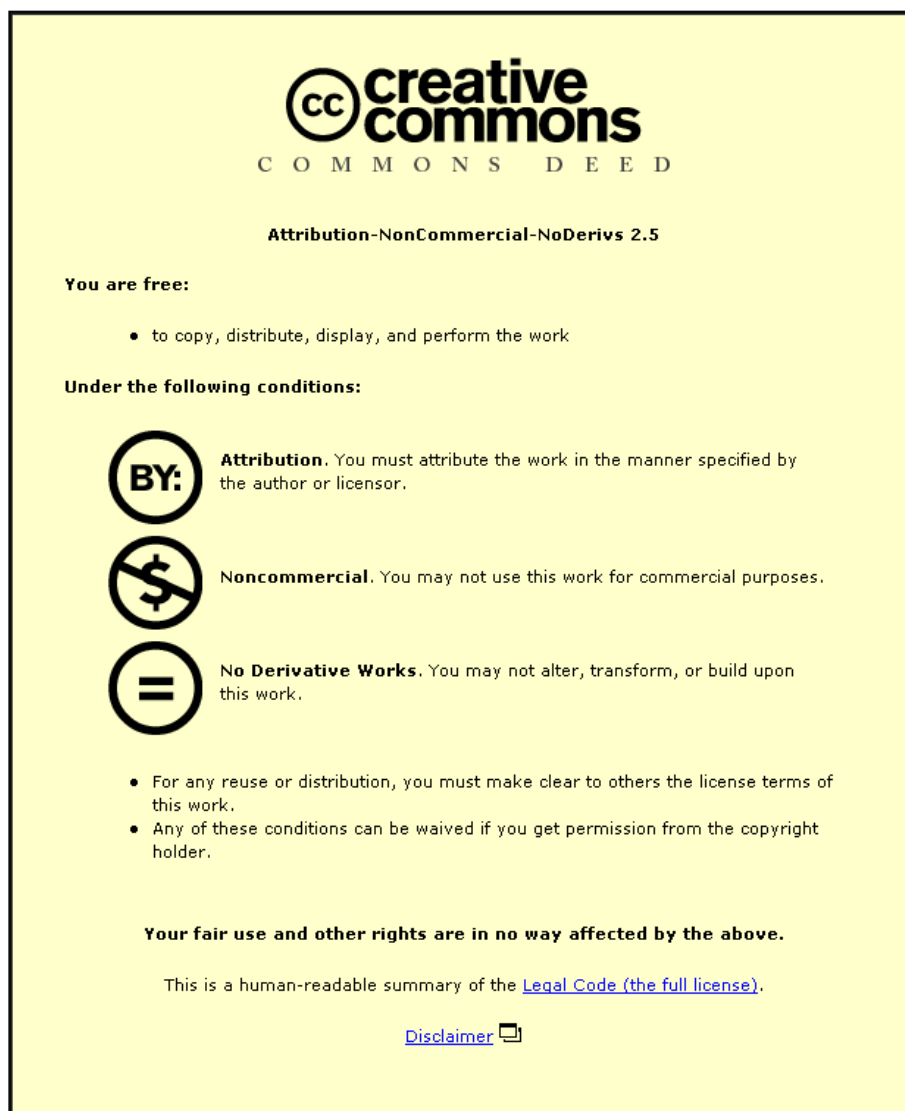


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An Experimental Study of the Design of an Electrochemical Ion Exchange Cell

by

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A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of
philosophy

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To you all a few words of dedication,

for past love and affection, my parents Reza and Pari

for present companionship and support, my wife Sylvie

for future hope and aspirations, my daughter Pareesa

"A process cannot be understood by stopping it. Understanding must move
with the flow of the process....."

Frank Herbert

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ABSTRACT

Electrochemical Ion Exchange (EIX) was studied to determine the viability of the process for treatment of metal bearing effluents containing Cu, Zn and Ni. Other metals used during the investigation were Na and Cs. The EIX process was examined at the laboratory scale and later in a pilot plant. Process performance and cell design were evaluated both in absorption and regeneration cycles. A mathematical representation of the system was developed based on the Nernst-Planck equation. Zirconium phosphate, Purolite S930, Purolite S950 and Purolite PrAOH were the ion exchangers used during the study.

The EIX cell was made of two perspex blocks, each 490 mm by 125 mm and 20 mm thick. Each block contained a half cell made up of an EIX electrode and a counter electrode on either side of a heterogeneous ion exchange membrane with dimensions of 280 mm by 63 mm by 5 mm. The EIX electrode consisted of a platinised titanium mesh, acting as a current feeder, embedded in the membrane. The counter electrode was a platinised titanium mesh placed on the opposite side to the current feeder. The process was operated by applying a potential across the membrane.

The Results indicated that the removal of target cations improved with decreasing flow rate, hydrogen ion concentration and feed concentration. The removal of cations increased with an increase in current density. The electrical efficiency was reduced by decreasing the flow rate, feed pH and increasing the current density. By decreasing the distance between the two half cells, the removal of cation was increased at low flow rates. Under alkaline conditions, sodium removal was improved by using one central counter electrode which also resulted in higher voltage requirements.

When using the hydrogen form of resins, pH and concentration steadily decreased in the direction of the flow. A high sodium concentration was obtained at the back of the cell which contaminated the bulk solution by leakage. Modifications were successfully carried out to reduce this leakage during absorption. Mixing within the cell was affected by the superficial velocity and the current density. Gas generation at the electrodes improved mixing within the bulk solution.

The current profile was found to be meniscus in shape with the minimum current flowing through the centre section of the membranes and the highest current readings obtained near the inlet and outlet. The results indicated that conditions outside the membrane did not influence the current distribution. The thickness and form of the membrane also affected the current flowing through the EIX membrane. The rate of regeneration was proportional to the applied current density. Reasonable elution efficiencies were obtained using acidic solutions. Model results indicated that there was good agreement between data generated experimentally and mathematically.

Pilot plant was operated over a period of up to 168 hours. Tests showed that there was scope for further improvement and optimisation. Poor regeneration, precipitation and electroplating were some of the problems encountered during long term experiments. Whilst operating the pilot plant, selectivity only occurred after the cationic resins had been converted to the sodium form.

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NOMENCLATURE

a_i Activity of species i

$$b, \text{ Constant} = \frac{d\Phi}{dx}$$

C_i Concentration of species i , $[\text{mol.m}^{-3}]$

D_i Diffusion coefficient, $[\text{m}^2.\text{s}^{-1}]$

d_a Length of the flow channel

d_b Width of the flow channel

d_m Hydraulic mean diameter = $2 d_a d_b / (d_a + d_b)$

F Faraday's constant = $96485 [\text{C.mol}^{-1}]$

k_i Proportionality constant

N_{i_x} Molar flux of the i th species in the x plane through a unit area of membrane per unit time $[\text{mol.m}^{-2}.\text{s}^{-1}]$

q Flow rate

R Gas constant = $8.31 [\text{J.mol}^{-1}.\text{K}^{-1}]$

Re Reynolds number = $u d_m \rho / \mu$

T Temperature, $[\text{K}]$

u Superficial velocity

u_x Velocity, $[\text{m.s}^{-1}]$

v_i Velocity of species i in the x direction,

x Linear direction

z_i Valency of species i

Φ_s Arbitrary solution potential

μ Viscosity of water = 10^{-3}Ns.m^{-2}

μ_i Chemical potential of species i

μ_i^0 Standard chemical potential

ρ Density of water = 1000kg.m^{-3}

$$\frac{d\Phi}{dx} = b \text{ Potential gradient, } [\text{V.m}^{-1}]$$

$$\frac{d\mu}{dx} \text{ Chemical potential gradient}$$

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

As the twentieth century draws to a close, human civilisation has realised the dependence of its fragile existence on the environment that surrounds it, as much as its own ingenuity. Environmental issues have become more important to governments as well as to the public at large. All aspects of human interactions with the environment have come under close scrutiny from industrial pollution to recycling of wastes.

The approach taken to deal with these problems has taken many forms. Handling of wastes has switched from one of disposal and elimination to reutilisation and minimisation. Industries have had to adapt to manage environmental problems better, under pressure from public and legislative bodies. The chemical industry has had to treat effluents by using end of pipe control, recycling, reduction of wastes at source and minimisation as an inherent part of process design.

All aspects of water treatment are periodically reviewed in a number of publications (e.g. Anon. (1998)). Water pollution is an environmental concern that has been increasingly examined to find solutions to age-old problems. In the last few years, wastewater treatment technologies have been developed and improved to handle a wide range of industrial effluents. One such method is Electrochemical Ion Exchange (EIX).

EIX is thought to be suitable for treatment of metal bearing effluents with the right characteristics for end of pipe control. It offered prospects of treatment without the need for additional chemicals and was easily reversible. The process was initially screened by AEA, Harwell for the treatment of low to

medium radioactive wastes in late 80's. Removal of base metal ions from effluent streams by EIX needed to be carefully considered before industrial application. The work described here was carried out to assess the performance of the EIX process under laboratory conditions and subsequently on a pilot plant scale. This chapter aims to put into perspective the reasoning behind development of such processes over the last few years, outlining briefly various wastewater treatment.

1.1 Management

Management of wastewater ranges from municipal to large scale industrial effluents. Since the onset of the industrial revolution, pollutants have been increasingly discharged into the environment. Initially, contaminants were airborne or released into open waters such as rivers. Large scale waste disposal on land is a comparatively recent development. It has been recognised that damage to any one of air, water and land cannot be dealt with separately and all must be taken into account when considering environmental issues. So, the trend is towards a more comprehensive approach to redress the harm done to natural surroundings.

Over the past few decades, new techniques have been examined to treat different wastes. Old processes have been modified and new ones developed to solve specific problems. However, the application of new technology may take a decade to work its way through from laboratory scale to full industrial plant. Overall the chemical industry along with many other industrial sectors is in a state of flux to meet environmental demands of tomorrow.

Public awareness of environmental issues has also increased to a high level. People have taken direct action on contentious issues and governments and industry have had to respond to a growing list of demands. Environmental measures are no longer just responding to local problems but addressing global

issues. International treaties and national laws have been drawn up to form a framework of legal and statutory boundaries.

1.2 The Law

Regulations are created by various means and originate from several bodies. Three main sources are international treaties, regional organisations such as the European Community and national laws.

International treaties are usually agreed upon and signed at organised conferences. Although, these have no direct bearing on national legislation they do influence the signatories to abide by and honour such agreements. Two main documents bear mentioning, the first is the 1972 Stockholm Declaration on the Human Environment and the second the 1992 Rio Declaration

Regional frameworks also exist for the setting up of laws and legal norms such as in the European Union. The legal system within European Union operates under the various treaties signed by member states. Different arms of the community's institutional apparatus are responsible for achieving the aims and objectives of the Union. Legally binding standards are adopted in the form of regulations and directives. Regulations are the laws which can be implemented without the interference of any national regulations.

Directives state objectives for member states but leave the means and the methods to the control of the individual state. Article 4 of EC directive 91/156/EEC states:

"Member states must take necessary action to ensure that waste is recovered or disposed of without risk to water, air or soil...."

Directives are sometimes broad or discretionary standards that contain vague definitions and terms. This results in members states using different criteria to implement the directives. Member states of the European union have passed laws to enforce these directives. Elsewhere limits of pollutants allowed to be released freely are being reduced to ever lower levels.

Individual countries have different legal frameworks based on different systems and traditions. Environmental law in many countries is based on the European or United States legislation. By the way of example, the environmental laws in Britain can be taken as representative of rules and regulations governing such issues in industrial nations.

In Britain, there have been Acts which have played a part in the prevention of pollution such as the Alkali Act 1906, the Clean Air Act 1957 and 1968 and the Control of Pollution Act 1974. The latest being the Environmental Protection 1990 Act establishing a system of integrated pollution control. Under this Act, those industrial processes that have the potential for significant release of harmful substances are subject to centralised control.

These rules and regulations have affected a wide range of industries. Industry has had to invest heavily in research, capital and expertise to implement the changes required in process operating practices and design in response to the impact of their businesses on the environment. Shifting emphasis on treatment of wastes has led to a booming environmental industry. New processes have been discovered and old ones improved to meet present standards. Nowhere is this more so than the wastewater treatment industry.

1.3 Wastewater Treatment

Water is an essential ingredient for life with only a fraction, less than 2%, being available in the form of fresh water. The demand for a clean supply is

continuously growing. Providing sufficient potable water poses an ever increasing problem in most regions of the world and its treatment has become an important factor particularly in the developed countries.

The need for water can be fully appreciated by considering the numerous ways it is used, from industry to personal human consumption and as a result, a wide range of wastes are produced. The demand for water is steadily increasing which can be partially balanced by better management of existing resources by minimising its usage or recycling of treated water. In most cases, the treatment of wastewater gives rise to secondary effluents that need to be disposed of.

Industrial processes often produce the most difficult and the most costly of effluents to treat. The main considerations for their treatment are the pH, composition and temperature of the waste stream. In each case the waste is unique and often needs to be treated by a combination of processes to give the required effluent. Each process needs to be evaluated and audited on the quality and the quantity of wastes it produces. The influent and effluent characteristics define the point of treatment and the overall mass balance of the process. Hence, new design and modifications can be geared to produce the most economical solutions. In most cases, several processes are used to eliminate one or more particular pollutants. Goronszy et. al. (1992) gave a brief review of such processes.

In general, water borne pollutants are in the following form:

- Oil and grease
- Organic
- Suspended solids
- Toxic compounds
- Acid and alkaline
- Radioactive species
- Metals

Wastewater treatment involves one or more processes to remove these pollutants and to obtain a desired water quality, a brief outline of which is given here.

There are two basic types of oils, those that form emulsions and those that do not. Free oil and greases can be removed by flotation. At low concentrations, air injection can be used to enhance the performance of the process. The oil and greases are then mechanically removed by skimming the top of the flotation tanks or siphoning off the top layer. Emulsified mixtures need chemical coagulants to help agglomeration of the pollutants.

Volatile organic compounds (VOCs) are usually stripped from wastewater treatment by using steam or air. Activated carbon or resins can be used to adsorb organic micropollutants. Non-volatile organic can be removed by biological treatment. This can be carried out either in the presence or absence of oxygen.

Solid particles, ranging from 1 μm to 25 mm in diameter, are clarified by sedimentation. Chemicals or air assist smaller particles to form coagulates. Other methods used in removing large solids and particles are screening or filtration. The methods used depend on the size and nature of the materials.

Toxic compounds can be removed by chemical oxidation. Oxidising agents such as chlorine, ozone or hydrogen peroxide are used to destroy noxious materials which also eliminate bacterial organisms. Combination of oxidising agents and ultraviolet radiation are very effective in the destruction of organic contaminants. This method is used particularly when contaminants are present in low concentration. Oxidation can also assist in removal of metals by

releasing metals from any complexes formed with organic agents and increasing the oxidation state of metals to aid precipitation.

pH is an important parameter in waste water treatment. The general discharge requirements for pH are between 6 to 9. If the treatment plant includes a biological operation it is crucial to keep the pH between 4 and 9.

Removal of radioactive species has been greatly studied. Waste management of radioactive material includes treating the waste at source which involves segregation, recycling and point source reduction. Treatments used for low to medium level liquid waste are typical methods that can also be applied to metal removal. These include ion exchange, precipitation, coagulation, flocculation, evaporation and membrane processes.

Radioactive materials are only found in a few sites. However, metals pose a more general problem, as these are used extensively in a wide range of industries producing effluent streams of different composition. The legal requirements are often dependent on "the best available technology" and detection limits of target metal ions. Discharge limits on metals are approaching those of drinking water. There are a variety of waste treatments for metal removal discussed in the next chapter.

CHAPTER 2

LITERATURE REVIEW

2. INTRODUCTION

Metals present in water even in dilute concentrations can be toxic to many life forms. These water borne contaminants may also be ingested by aquatic life forms and enter the food chain. Processes and equipment are continuously being developed to recover metals from wastewater streams. The various processes can be categorised under the following broad categories:

- Chemical treatment
- Membrane processes
- Adsorption
- Biological
- Liquid-liquid extraction
- Ion exchange
- Electrochemical

This chapter will outline these techniques, their inherent advantages and limitations which have been summarised in Table 2.1. The applications of processes to remove metals from wastewater will also be discussed. This treatise is not an exhaustive discussion on available methods of metal removal from wastewater. It is merely used to highlight main treatment techniques and to place the application of Electrochemical Ion Exchange (EIX) into perspective. References will also be made to literature describing combinations of processes applied to removal of transition group metals in industry as well as different approach taken to handle large scale industrial wastes.

A summary of references can be seen in Table 2.2 at the end of this chapter. The table contains the treatment processes covered in this chapter. These have been classified under the four headings of authors, methods, metals and feed concentrations.

Table 2.1: Advantages and disadvantages of various treatment techniques

Process	Advantages	Disadvantages
i) Chemical Precipitation	Cheap Good overall removal of a wide range of metals Easily applied without the need for sophisticated technology Effective at high metal ion concentration and high pH	Excess chemicals used to obtain good recovery Further disposal and/or treatment Secondary treatment necessary such as filtration and dewatering necessary Requires high dosing to reduce concentrations below the legal limit Optimum conditions vary for different metals
i) Chemical Coagulation	Improves removal when used in combination with precipitation	Requires secondary treatment
ii) Membrane Processes	Selective Compact Contaminants can be selectively removed depending on their size Suitable for continuous separation Separation by size down to molecular level when pressure driven Separation can be combined with concentrating	Solids may need to be filtered prior to treatment High capital and operating costs Limited to high concentration Possible leaching of materials
iii) Adsorption	Cheap Effective for general treatment of combined organic and metal removal Effective at low concentrations	Sorbents require subsequent treatment and handling Low capacity of sorbents
iv) Biological	Renewable Can be widely incorporated into new systems	Sensitive to metal ion concentration Complex system of monitoring and control required
v) Liquid-liquid systems	Can be operated continuously Large volume reduction	Solvents may be toxic Can be expensive
vi) Electrochemical	Metals can be recovered in a	Limited by ionic concentration

Process	Advantages	Disadvantages
vi) Electrochemical (continued)	useful form Usually no chemicals are required	High capital and operating costs
vii) Ion exchange	Easily reversible and suitable for repeated use Can be selective Reduction in volume Suitable for treatment of variable feeds	High costs of resins Fouling a problem in high solid content treatment Secondary treatment required to obtain metal in suitable form pH sensitive

Various authors have reviewed processes for treatment of metal bearing solution such as Reed et. al (1998), Wei Lin et. al. (1998), Matsumoto et. al. (1993), Peters et. al. (1985) and Spearot and Peck (1984). Matsumoto et. al. (1993) and Reed et. al. (1998) reviewed a wide range of physicochemical processes for wastewater treatment. The main methods considered were precipitation, coagulation/flocculation, sorption, filtration and membrane processes. Peters et. al. (1985) described the full range of treatments available for removal of metals from waste waters. Wei Lin et. al. (1998) considered the range of processes available to the electroplating industry including ion exchange, electrolytic techniques and electrodialysis. Spearot and Peck (1984) considered recovery of copper from complex solutions by different technologies.

2.1 Chemical Treatment

Chemical treatment usually involves addition of chemicals to waste waters bearing metals. These assist or react with metal ions to form compounds that are insoluble in water. Invariably excess quantity of chemicals must be used to ensure good recovery. Although chemicals are usually cheap, the effluent needs further treatment and/or disposal. The capital costs are usually higher than ion exchange systems. These processes need to be carefully monitored to avoid blockages and ensure correct dosing of chemical reactants.

2.1.1 Precipitation

Precipitation is a low cost method of dealing with metals in solution. Hydroxide, carbonate and sulphide treatments are the most commonly used. Major disadvantages of the method are the secondary treatment steps required such as filtration and dewatering. The use of agents such as lime or ferrous sulphate is largely dependent on the type of waste. Large quantities of organic compounds may need to be broken down by oxidation prior to chemical precipitation. Metals such as copper, nickel and zinc readily precipitate out of solution while others such as mercury, lead and chromium may not. The optimum pH for streams containing different metals may be different for each contaminant, in which case the stream needs to be treated in separate steps under different pH conditions.

Lime is often used because of its low cost. Coagulants are generally added to improve the settling process. The most common coagulants are aluminium and iron salts. These attach to particles and cause smaller ones to coalesce and make larger aggregates that settle more rapidly. Both hydroxide and sulphide precipitation were used for removal of heavy metals in the presence of weak complexing agents by Ku and Peters (1986). In the presence of complexing agents, the chemical equilibrium was not affected but the particle size distribution was smaller.

Hexavalent chromium needs to be reduced to trivalent chromium before treatment. Chromium bearing streams are usually treated separately for this reason. Various parameters were studied by Lin et. al. (1992) in the treatment of hexavalent Cr (VI) bearing wastes. The effect of operating parameters such as pH, quantity of reductant and bases were investigated. The characteristics of the sludge produced were also examined.

Carbonate precipitates usually form at lower concentrations than hydroxide precipitation. They have better dewatering characteristics and separate from solution better. Sulphide precipitation occurs at lower pH than carbonate. The reaction time is also less but fine solids are formed and hence coagulants are needed at the separation stage. The main obstacles to sulphide precipitation are production of H_2S and toxicity effect of sulphides, although the sludge produced is subject to less leaching.

Chromium (VI) and nickel were removed from ground water by iron (II) sulphate (Zotter and Licsko (1992)). Iron (II) salts reduced Cr (VI) while being oxidised to iron (III). These then acted as coagulant agents forming aggregates of iron (III) and Cr (III) hydroxide which led to an easy solid-liquid separation. Feed concentrations were between 3 and 34 $mg.l^{-1}$ chromium and 10 $mg.l^{-1}$ of nickel and with aid of an anionic flocculant these were reduced to less than 100 $\mu g.l^{-1}$ for both metals with pH close to 11.

Schiller et. al. (1984) used magnesium oxide to precipitate heavy metals. MgO was found to form a compact precipitate with a three to five fold reduction in volume compared to lime precipitate. Compared to lime treatment, more metal was removed and less chemicals remained in solution. The disadvantages of using magnesium oxide is its high cost and the reaction occurs at the surface of the oxide so a plug flow reactor is required for continuous operation.

Whang et. al. (1982) considered the design of a plant to treat wastewater from a plating shop. The design considerations had to include handling of Cr (VI) and cyanide present in the waste streams. The main part of the plant comprised the following units: cyanide oxidation, chromium (VI) reduction, neutralisation, sulphide addition, flocculation, clarification and filtration. Any remaining sulphide was also oxidised at the end of the system by hydrogen peroxide.

Peters and Ku (1987) examined the feasibility of seeding metal precipitation by activated carbon. Zinc hydroxide precipitation was investigated with an initial zinc concentration of 100 mg.l^{-1} for different activated carbon dosage and pH. For short settling time of less than 30 minutes, addition of activated carbon enhanced the process by reducing the residual metal concentration. Removals of 95% were obtained for pH of 10.5. Optimal carbon dosage was reported to be $\leq 50 \text{ mg.l}^{-1}$. The mechanism of removal ranged from direct adsorption to catalysis of precipitation by activated carbon.

Merrill et. al. (1987) applied iron co-precipitation to the removal of arsenic and selenium from effluents from a coal fired power station. The basic process involved the addition of iron salts that trapped or adsorbed other trace metals within the precipitate. Feed concentrations used were between 20 to $40 \text{ } \mu\text{g.l}^{-1}$ arsenic and 40 to $60 \text{ } \mu\text{g.l}^{-1}$ selenium. The iron dosage was between 7 and 56 mg.l^{-1} . Arsenic and selenium removal increased with higher iron dosing. Addition of polymeric coagulant enhanced the solids separation. Consideration was also given to mixing, sludge characteristics and handling. Arsenic removal of 90% was obtained for iron doses greater than 14 mg.l^{-1} while 89% was the maximum selenium removal obtained.

In general, the success of these methods depends on the nature of the metals concerned and the characteristics of the aqueous medium, particularly the solution pH. Sometimes combinations of all or some of these agents are used. Chemicals such as calcium carbonate help the co-precipitation of metals when used in combination with hydroxide or sulphides.

Other chemical methods are also used to either assist separation following a precipitation step or as stand alone methods for treatment of waste streams such as coagulation and flocculation.

Coagulation refers to charge neutralisation of suspended contaminants such that particles agglomerate forming flocs that drop out of solution. Most commonly coagulants are aluminium or iron salts. In flocculation, materials are added to aid the formation of flocs.

2.2 Membrane processes

Flynn and Way (1982) gave an outline survey of membrane processes in which driving forces and application were considered. The main advantage of membrane processes compared to conventional separation is the selective nature of the system. Membrane processes involve the flow of a permeate through a porous media induced by a driving force and retention of particle contaminants. Membrane process can be separated into three main types based on the applied driving force. These are pressure, electrical and concentration.

Membrane processes for wastewater treatment were considered by Ben Aim et. al. (1993). Membranes were suggested to offer alternatives to deep bed filtration and sand filtration. Problems of productivity and cost were discussed with references to case studies. Solutions were offered for fouling of microfiltration membranes ranging from back-flushing to unsteady flow. Pilot plant studies of membrane processes were used in conjunction with flocculation and biological treatment. Experiments were conducted to examine the dynamic filtration of clay suspension. Particle retention, flux and fouling were studied for a couette system consisting of two axial cylinders with one rotating within the other. The results indicated that a change in pore size and rotational speed had no influence on particle deposition within the pore.

2.2.1 Pressure

The pressure gradient processes can be categorised as reverse osmosis, ultrafiltration, microfiltration and nanofiltration. Reverse osmosis operates by applying a greater driving pressure than the osmotic pressure caused by

dissolved salts in water. The pressure must be considerably higher than the osmotic pressure to obtain reasonable fluxes. Reverse osmosis works well for low solid content solutions. The method removes a variety of contaminants but fouling of the membrane causes a decline in flux which can be reversed by chemical dosing.

In other membrane processes, the separation is achieved according to size of suspended solids. Particles smaller than a certain size are allowed to pass through the membrane while the larger solutes are retained. The pressure driven methods can be enhanced by using chemically active membranes, complexing agents or having a cross flow arrangement. The application of such processes is a comparatively recent development in the field of wastewater treatment.

The application of crossflow microfiltration was considered by Broom et. al. (1994) for treatment of heavy metal bearing waste waters. A pilot plant scheme using settling tanks, sand filters and crossflow microfiltration was assessed for a mixed effluent. Crossflow microfiltration offered a remedy for excessive cake build-up with a thinner cake retained producing a more acceptable flux. The filter media used was made of multi-filament polyester yarn with a thickness of approximately 0.33 mm. The cloth offered a surface for build-up of a cake inside the tube during operation hence increasing the filtration capacity of the membrane.

Broom et. al. (1994) used a combination of chemical precipitation, sand filtration and crossflow microfiltration to reduce the level of heavy metals to below the discharge limit. Mixed plating waste contained 2.44 mg.l^{-1} cadmium, 7.2 mg.l^{-1} chromium, 9.98 mg.l^{-1} calcium, 4.88 mg.l^{-1} lead, 8 mg.l^{-1} mercury, 13 mg.l^{-1} nickel and 71.2 mg.l^{-1} zinc. The waste was dosed with lime

and put through a microfilter with a filtration area of 0.25 m^2 . After 18 hours batch clarification, these concentrations were reduced to 0.04 mg.l^{-1} cadmium, $<0.08 \text{ mg.l}^{-1}$ chromium, 1.48 mg.l^{-1} calcium, 0.42 mg.l^{-1} lead, 0.08 mg.l^{-1} mercury, 1.16 mg.l^{-1} nickel and 1.63 mg.l^{-1} zinc.

On the basis of a pilot plant study, a full scale plant was designed to deal with $300 \text{ m}^3.\text{d}^{-1}$ of waste. The plant comprised of 9 filtration modules with total surface area of 136.8 m^2 . The feed was treated with calcium hydroxide and sodium hydrogen sulphide corresponding to a pH change from 8.5-9.5 to 11-12. Effluents from battery recycling plant were treated to reduce the metal concentration to below 1 mg.l^{-1} . The process was reported to work well under variable feed conditions.

Solutions containing transition metals were treated with polyelectrolytes followed by ultrafiltration to separate the metals from solution by Volchek et. al. (1993). A mathematical model of the process was also presented. Influences of solution composition on the performance of the process were studied. Metal concentration of 210 mg.l^{-1} copper, 135 mg.l^{-1} iron, 67 mg.l^{-1} nickel, 18 mg.l^{-1} zinc, 790 mg.l^{-1} magnesium, 1210 mg.l^{-1} sodium were reduced to 0.2 mg.l^{-1} iron, 0.02 mg.l^{-1} nickel, 0.07 mg.l^{-1} zinc, 790 mg.l^{-1} magnesium, 1280 mg.l^{-1} sodium and below the detection limit for copper. The pH was increased from 5.1 to 8.5.

The major disadvantages of a pressure driven membrane processes are the risk of fouling, large capital cost and high operating costs. These are very useful for relatively clean applications.

2.2.2 Electrical

In electrical methods, an electric current facilitates the transport of ion across a permeable membrane. In electrodialysis, a direct current is applied across a

stack of semi-permeable membranes. Depending on the membrane, cations or anions are allowed across the membrane while the passage of oppositely charged ions is blocked. Electrodialysis is widely used in desalination plants across the world. The process works well under high concentration driving forces but at lower concentration, polarisation across the membrane limits the process and affects the energy consumption.

2.2.3 Concentration

Babcock et. al. (1979) reported on a process for separation of heavy metals from electroplating rinse water. The process was carried out by using a microporous membrane containing complexing agents which facilitated the transport of metal ions from one side of the membrane to the other. Electric neutrality was preserved by passage of hydrogen ions in the same or opposite direction depending on the charge of the complex species. The transfer of material occurred due to a difference in pH or concentration prevailing on either side of the membrane. A range of complexing agents was used to decontaminate a solution containing copper, nickel and chromium with concentrations between 50 to 5000 ppm.

Recent developments have lead to supported or emulsified liquid membrane separation or purification of metals from aqueous solutions. Yi and Tavlarides (1992) used 2 hydroxy-5-nonylcelophenoneoxime supported by α -alumina silica to study the transport of copper and model the metal flux through the chemically active membrane. A linear model was developed based on the external mass transfer and interfacial kinetics. Fluxes of $5.4\text{--}22 \times 10^{-5} \text{ mol.cm}^{-2}$ were reported for a copper feed solution of 0.03 mol.l^{-1} and pH of 3. The pH of the stripping solution was 0.3.

Kedem and Bromberg (1993) studied the extraction of metal cations by liquid cation exchange membranes. A commercial hydroxime reagent was used for

recovery of copper. The copper was removed by liquid ion exchange and stripped by acid solution. This was carried out by having an aqueous solution in one chamber separated by a cation ion exchange membrane from another chamber containing liquid ion exchanger in dodecane. A second process involved three chambers with outer chambers filled with aqueous solution and a central chamber filled with liquid ion exchanger separated by a membrane from a second outer chamber containing an aqueous phase. A third set up examined was similar to the first two chamber process but the two phases, organic and aqueous, were forced to flow parallel to the membrane.

The first technique demonstrated a flux of $1.1 \times 10^{-9} \text{ mol.cm}^{-2} \text{ s}^{-1}$ for an initial feed concentration of 4.9 mM copper sulphate in water. The extractant phase was 10% by volume liquid ion exchanger in dodecane. In the second technique, the flux was $1.7 \times 10^{-9} \text{ mol.cm}^{-2} \text{ s}^{-1}$ and Copper was selectively extracted from 200 ml of CuOAc_2 and NiOAc_2 with about 4.5 mM each in solution. At a higher flow rate of 1.2 l.h^{-1} , a larger flux of $5.6 \times 10^{-9} \text{ mol.cm}^{-2} \text{ s}^{-1}$ was obtained as compared to $7 \times 10^{-10} \text{ mol.cm}^{-2} \text{ s}^{-1}$ at a flow rate of 400 ml.min^{-1} . Nickel was not transported across the ion exchange membrane.

Although no ion exchanger was lost there was cross contamination of solvents into the aqueous phase. The three compartment set up was used successfully for removal of copper and silver. Different ion exchange membranes were used with different capacities and thickness. The membranes were usually saturated with target ion before the start of the experiments. The technique was also applied to recovery of mineral acids from wastewater by using extractant and anion exchange membranes. The method was not tested for a more complicated system with ions that may interfere with the transfer of target ions.

2.3 Adsorption

Adsorption usually involves the fixation of the metal ions onto the surface of a medium. This occurs in the form of physical or chemical interaction between the metal ion and surface of the adsorbent. The method is dependent on the pH and surface of the material. The most frequently used adsorbent is activated carbon. Activated carbon has traditionally been used for removal of organic compounds and dyes but it has also been considered for removal of heavy metals. This is chiefly due to the high surface area and relatively low cost of the material compared to ion exchange resins. The capital cost of the process is a function of contact time needed. The process is expensive to operate and is dependent on the pH. Other materials such as clay, zeolites and metal silicates have also been used.

Following precipitation process to remove heavy metals, Ku and Peters (1987) studied the feasibility of using activated carbon as a polishing step. Several types of activated carbon were used in the presence of ammonia and cyanide preceded by a lime or sulphide precipitation. The activated carbon reduced the concentration by about 50 to 80%. Sulphide concentration was also reduced by the polishing step. The residual concentrations were all below 0.5 mg.l^{-1} at $\text{pH} > 9$ with initial metal ion concentration of 100 mg.l^{-1} .

Bhattacharyya and Cheng (1987) investigated the adsorption of several metals by activated carbon. A two component system was used to study the effect of surface charge, ligand to metal ratio, pH and kinetics. The experiments were conducted in the presence of chelating agents ethylenediaminetetraacetic acid (EDTA) and triethylenetetramine (TRIEN). Initial concentrations of metals were 0.8 mM and carbon dosage was 20 g.l^{-1} . In the presence of EDTA, 98% removal of cadmium (II) and nickel (II) was achieved, with a solution pH of 5.

Cadmium (II) and nickel (II) could be successfully removed in presence of complexing agents.

Huang and Blankenship (1984) studied the removal of mercury ions for eleven activated carbons. The average removal was about 90% between pH 4 and 5 by all activated carbon used. The mechanisms of removal was also studied and found to be adsorption and reduction which were pH dependent. Adsorption was dominant in the mid pH range. The extent of reduction was greater at pH of <3 to 4 and >9 to 10 than the adsorption reaction. In the presence of complexing agents the total removal of mercury (II) decreased. A carbon concentration of 1 g.l⁻¹ was used with a mercury feed concentration of 1×10^{-5} to 1×10^{-4} M.

Laboratory scale studies were carried out by Netzer et. al. (1974) to remove aluminium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, silver and zinc from aqueous solutions. The technique involved using lime and discarded automotive tyres. Removals greater than 99.5% were achieved. Feed concentration of 100 mg.l⁻¹ of each metal was prepared and pumped round the system at 300 ml.min⁻¹. The maximum removal of each metal depended on the pH. The suggested mechanism of removal was the adsorption of metal by carbon black in the tyres and the reaction with the constituents such as sulphur to produce insoluble products.

2.3.1 Biosorption

Biosorbents offer a natural and inexpensive sorbents material for metal removal. These are another class of sorbents that have been used to remove trace levels of metal ions from water which include alginates, lignin, chitin and chitin derivatives.

Aldor et. al. (1995) used harvested *Sargassum fluitans* (brown sea weed) to study the elution of cadmium after loading the sorbent with cadmium. The pH was reduced to 1 for the elution process by the addition of acid. A solution of hydrochloric acid was found to be the most appropriate eluant. After several sorption and desorption cycles, the ability of the material to remove cadmium was not diminished. The ratio of biomass to eluant volume was found to be important.

Deans and Dixon (1993) compared a number of biological materials for removal of lead (II) and copper (II) ions. Biosorbents evaluated were cellulose, alginic acid, chitin, chitosan and carrageenan as well as carboxymethyl and hydroxamic acid derivatives of these materials. Feed concentrations of 1 to 1000 mg.l⁻¹ of lead and copper were used. The test solution was buffered to between pH of 5.5 and 7. No single material was found to perform well at all feed concentrations and for both metal species. This was explained by the complex nature of the materials and size to charge ratio of the metal ions. However, two compounds showed overall general removal better than others. These were hydroxamic acid derivative of carboxy-methyl cellulose and chitin. The experiments were conducted for 0.015 g of adsorbents mixed with 15 ml of solution for 2 hours and then centrifuged, decanted and analysed. The final concentrations were between 0.27 to 11.56 mg.l⁻¹ of copper and 0.15 to 10.55 mg.l⁻¹ lead, for feed concentrations of 10.95 mg.l⁻¹ copper and 10.55 mg.l⁻¹ lead.

D'Avila et. al. (1992) considered the removal of heavy metals by activated peat. A satisfactory model was obtained for the process by using a Langmuir isotherm to define the equilibrium relationship. An improvement in adsorption was demonstrated by comparing the results for activated and natural peat.

Exhausted tea and coffee were among the adsorbents used by Orhan and Büyükgüngör (1993) to remove chromium (VI), cadmium (II) and aluminium (III) from synthetic waste water.

Corn starch was used to produce soluble and insoluble starch xanthates. These were examined for removal of cadmium (II), copper (II) and chromium (VI) by Tare et. al. (1992). The pH range used was between 3 and 7. the capacities of the insoluble xanthates was reported to be better than the soluble xanthates, particularly for cadmium. Heavy metal adsorbed onto the surface of the insoluble xanthates and formed a precipitate with soluble xanthates. For insoluble xanthates, removal of cadmium was 94% for a feed pH of 4 and initial concentration of 7 to 10 mg.l⁻¹. Copper was removed to below the detection limit over a pH range of 3 to 7 with a feed concentration of about 10 mg.l⁻¹. For soluble xanthates, 94% of cadmium (II) and 67% copper were removed with a feed pH of 4 and feed concentration of 7 to 10 mg.l⁻¹ of each metal.

Couillard (1994) reviewed properties and uses of peat in wastewater treatment. One application was the removal of heavy metals by peat.

2.4 Biological Metal Removal

The presence of substantial amount of heavy metals in wastewater can adversely affect biological waste treatment processes. Most systems can cope with moderate concentrations of about 10 to 30 mg.l⁻¹. Biological removal of heavy metals is most effective at a solution pH of between 6 and 9. These processes usually require good monitoring and control to keep a viable biological culture. This adds to the cost and the complexity of these processes. The mechanism of biological removal of heavy metal is thought to be by extracellular adsorption and incorporation within the intracellular material.

Ghosh and Bupp (1992) investigated microbial uptake of heavy metal at high concentrations. Concentration of cadmium, copper and lead ranging from 30 to 40 mg.l⁻¹ were used along with a mixed culture system. Some cultures were exposed to metal ions (cadmium) before the experiments and others were left unexposed. A mixture of amino acids namely cysteine and cystine were used to simulate metal uptake by micro-organisms. Organisms were killed at metal concentration higher than 30 mg.l⁻¹ but the metal uptake was unaffected. Simulated solution of proteins generally showed better metal removal compared to either micro-organisms exposed or unexposed to metal solution prior to treatment. Metal binding occurred in the following order Cu>Pb>Cd by the micro-organisms.

Immobilised micro-organisms can remove trace quantities of heavy metals. Martin (1991) reported on wastewater systems using naturally occurring bacteria and fungi. Non-pathogenic bacteria and fungi were fixed within a porous matrix, which also contained potassium alumino-silicates. The potassium was exchanged with metals and trapped the metal inside the matrix. Hence, the metal ions were not readily leachable.

Barnes et. al. (1991) used a method which involved removal of heavy metal and sulphates from contaminated water by anaerobic microbes. Ethanol was used as the growth substrate and the process reduced the sulphate to sulphides. The heavy metals precipitated out of solution in the form of sulphides. The Optimum pH was 7.5 with the method being viable between 5 and 9. The sludge offered some buffer capacity. A pilot plant scheme was set-up demonstrating the removal of a range of heavy metals. The residence time required for the settling stage was shortened by addition of flocculant. Maximum operating temperature was 42 °C and feed concentrations used were between 107 to 1070 mg.l⁻¹ of zinc and 0.46 to 6.8 mg.l⁻¹ of copper. The feed

pH ranged between 3 to 6.7. After 11 hours, the zinc concentration was reduced from 1070 to 0.22 mg.l⁻¹ and copper from 6.8 mg.l⁻¹ to 0.02 mg.l⁻¹, with feed pH of 4.9.

Blais et. al. (1992) compared the removal of heavy metals from municipal sludge by acid or microbial leaching. Two bioleaching processes were used, one with elemental sulphur and the other with ferrous sulphate. The methods reduced the quantity of acid needed for metal extraction. The sulphur process performed better with only 5 days reaction time needed compared to the 10 days taken for the ferrous sulphate process. The metal was recovered by using large quantities of acid. The metal solubilisation yield with iron oxidising bacteria was lower than for sulphur oxidising bacteria.

Rivera (1983) reported on the biological treatment of wastewater containing heavy metals. The process was based on an anaerobic bioreactor using immobilised bacteria. Removal efficiency of 85 to 95% was obtained for zinc, with feed concentration of 100 mg.l⁻¹ to 1000 mg.l⁻¹.

Pradhan and Levine (1992) evaluated uptake of metals by a microbial biosorption system. It was found that significant quantity of binding occurred with extracellular material.

2.5 Liquid-liquid Systems

The introduction of liquid-liquid extraction has led to a variety of new processes described by Warshawsky (1987). Researchers in the Soviet Union pioneered early work on the use of liquid amines for analysis and recovery of platinum group metals.

Liquid ion exchange has also been used in recovery of metal ions. Two phases are usually involved, an aqueous phase containing the metal and an organic

phase which contains water insoluble active compounds. There are several advantages with this system. It can operate at high concentration in aqueous phase and the concentration can usually be increased by ten fold.

Guha et. al. (1994) used liquid ion exchange to remove copper, chromium and mercury in organic phases such as *n*-heptane, tri-*n*-octylamine and xylene. The metals were then recovered and concentrated in an aqueous phase. Yin and Blanch (1989) described design, synthesis and characterisation of calcium chelating thiolate groups found in common proteins for the application of metal ion removal.

Silica gel-bonded macrocycles were considered for removal and separation of metal ions by Izatt et. al. (1988). These systems were applied to concentrating cations at the part per billion level before analysis.

Macrocycle compounds have been used for solvent extraction. A chromatography column was used to fix the macrocycle silica gel material after loading the material with metal ions. The metal ions were then eluted by EDTA. Activity was not changed after repeated cycles over a pH range of 0 to 11. Barium (II), strontium (II), lead (II) and thallium (II) were removed and concentrated in the presence of alkali earth cations such as magnesium (II) and calcium (II). Silver was removed to below the detection limit with a feed of $1 \mu\text{g.l}^{-1}$ silver nitrate in the presence of a hundred times greater concentration of alkali earth metals. The pH was less than or equal to 7.0. Experiments with silica gel showed that silver ion removal at pH 2 was due to the silica gel and mercury ion removal was primarily due to the macrocycles.

2.6 Electrochemical

Electrochemical methods usually recover metals in a useful form as opposed to in sludge or filter cake. These processes are costly mainly due to high energy

consumption and can be labour intensive. Dilute solutions cause cathodic polarisation which results in low electrical efficiencies. The reason for the polarisation is due to poor mass transfer and large potential drop across the solution electrode interface.

There are measures that can reduce the polarisation effects such as better mixing to improve the mass transfer within the cell. Causing turbulence in the system either by rotating the electrodes or conventional stirrers can also improve mixing within the cells. Rough electrodes have also been used to promote mass transfer. Using low current densities improves the efficiency but increases the capital costs. At high current densities, the current efficiency is low resulting in higher running costs but reduced capital cost.

The basic principle of electrochemical methods lies in the oxidation and reduction reactions occurring at the electrodes and transport of ions across the cell due to the applied voltage. The reactions offer electrons to convert metal ions to their elemental state and applied voltage facilitates the transport of ions to the reaction sites. Therefore, electrochemical techniques needing no chemicals other than those involved in the reactions.

Fleet (1988) outlined a range of electrochemical systems available for environmental applications. Engineering aspects of design of such reactors was discussed in relation to their technical and economical merits. Surfleet and Crowle (1972) described the alternative cell design for electrolytic recovery of metals from dilute solutions. The advantages of the electrochemical treatments were outlined. Basic current densities were given along with limiting currents and diffusion layer thickness. Several systems were described for recovery of copper from acid waste.

Figuerola et al. (1994) examined the recovery of copper from chopped scrap by an electrochemical cell with titanium supported electrode. Concentrated copper solutions were treated by using a monopolar cell to recover copper from scrap in concentrated sulphuric acid solution. The copper sulphate feed concentration was 180 g.l^{-1} with the same concentration of sulphuric acid present. The applied current density was 2 A.m^{-2} with an electrode spacing of 3 cm. High quality copper was recovered with a reported purity of 99.98%. The electrical efficiency was between 98.5 and 99 %.

Three dimensional electrodes were used by Trivoli et. al. (1993) for removal of silver from photographic process wastes. The reactor was a flow through type with graphite felt electrodes. Three dimensional electrodes offer a combination of high surface area accessible to electrochemical reaction and high permeability to solution. This allows the electrochemical reactor to be optimised with respect to size and efficiency. Typical three dimensional processes are those that use porous electrodes or fluidised beds electrodes. Reticulated vitreous carbon, a glass like material combining properties of glass and carbon also offers a three dimensional surface. The material has good chemical inertness, high surface area, stability and low resistance making them suitable for electrochemical applications.

High current efficiencies were obtained for recovery of copper from scrap metal pickling wastewater by Huang et. al. (1993). The concentration of copper, iron, nickel and zinc were between 1 to 14 g.l^{-1} with solution pH of 1.4. After four stage electrolysis these were reduced to between 0.7 and 1.8 g.l^{-1} with a solution pH of 2.3. Huang et. al. studied the effect of current density on current efficiency, electrodeposition rate and surface loading. It was demonstrated that the current efficiency decreased with increasing current density.

Allen and Chen (1993) used an electrochemical method to recover EDTA and the metal associated with it from a stream containing the complex of the two. The complexes were generated by using EDTA to remove metals from contaminated soil. Cation exchange membranes separated the anolyte and the catholyte. A supporting electrolyte, 0.1 M sodium hydroxide solution, was placed in the anode compartment while the cathode compartment contained metal-EDTA solution. A voltage was applied across the cell making the sodium ions move through the ion exchange membrane into the cathodic section. EDTA was then converted to sodium form releasing the heavy metal which precipitated or electrodeposited. For a 0.01 M EDTA-Cu solution, 98% of copper and 99% of the EDTA were recovered. The current was 0.75 A at a current efficiency of 3.2%. The initial copper concentration was 437 mg.l⁻¹ and feed pH was 3.27. The copper concentration was reduced to 10.2 mg.l⁻¹ with a final solution pH of 12.8. The current efficiency decreased with increase in current density.

Karavasteva and Karaivanov (1993) studied the recovery of zinc from a solution containing surfactants. Current densities of up to 1000 A.m⁻² were used with feed zinc concentration of 45-49 g.dm⁻³. Using a variety of surfactants, current efficiencies were between 10 and 15 %. The addition of surfactants allowed a pore free and fine grain zinc deposit to be formed. Voortman et. al. (1992) applied an electrochemical membrane cell to treat a range of effluent streams. The cell comprised an anolyte and a catholyte compartment separated by an ion permeable membrane. It differed from electrodialysis in that the electrode reactions were a part of the process. The process was used to recover sodium hydroxide from textile scour effluent. The current efficiencies were between 70 to 80 % for current densities of 300 to 1000 A.m⁻².

A stainless steel consumable electrode system was used to treat mine acid water containing a number of metals by electrodeposition (Jenke and Diebold (1984)). A 100% removal of aluminium and copper was achieved with 90% removal of zinc while the solution pH increased from 2.8 to 4.7. For the same experiment 25% manganese and 10 % magnesium were removed while the concentration of iron ions increased. It was concluded that the removal of heavy metals by adsorption was minimal and coprecipitation was the major factor in the reduction of metal concentration. The major proposed advantage of the system was that the waste products could be reclaimed rather than disposed of.

Metal recovery of up to 100% was achieved for copper, uranium, cadmium, chromium and zinc by Agarwal et. al. (1984) using electrochemical means. The number of passes needed for 100% removal varied for different metals ranging for 1 pass for copper to 20 passes for cadmium. Both initial feed solutions contained supporting electrolyte of 0.5 M sodium sulphate. Increase in flow rate resulted in a lower amount of electrodeposition. Different optimum voltages were found for each metal. Increasing the supporting electrolyte concentration decreased the applied voltage needed.

Horner and Duffey (1983) reported on electrochemical reduction and precipitation used to treat wastewater containing chromium (VI). A sacrificial carbon steel electrode was immersed in spent liquor. By passing current through the system, ferrous ions were generated by the steel electrodes. These reduced the hexavalent chromium (VI) to trivalent chromium (III). Chromium hydroxide was then precipitated along with other metals (Cu, Ni, Zn, Pb, Sn, V etc.). Coprecipitation of metals also took place with ferric hydroxide. The pH increased between 0.5 and 1.0 unit during the process. The feed concentrations used ranged from 6.7 to 198 mg.l⁻¹ of chromium, 2.3 to 10.4 mg.l⁻¹ of zinc, 0.2

to 11 mg.l⁻¹ of copper and 9.4 to 189 mg.l⁻¹ of nickel were treated. The discharge concentrations of metals were 0.03 mg.l⁻¹ of chromium, 0.17 mg.l⁻¹ of zinc, 0.4 mg.l⁻¹ of copper and 0.06 mg.l⁻¹ of nickel.

The electrical energy required was 5 kWh per pound of metal removed, with cells operating at about 25 A and applied voltages of 50 to 400 V. The wastewater was delivered to the cell at about 25 psig. Two modes of operation used were continuous and batch. The metal feed concentration were between 10 to 50 mg.l⁻¹. The solution was put through the cell with a residence time of about 10 sec. Flocculant was added to aid the solid liquid separation in the clarifier. The batch mode was used for metal concentrations above 50 mg.l⁻¹. Horner and Duffey (1983) estimated the cost of the plant based on an average electrode consumption of 3 lb. of electrode per lb. of metals. Capital cost depended on the quantity of wastewater to be treated. The overall cost was found to compare favourably when compared to chemical precipitation.

A full range of electrochemical methods for environmental management were discussed by Rajeshwar et. al. (1994). These included a range of cathodic processes for metal ion recovery from water. The mass transfer limit of the standard electrochemical techniques was considered to be at a metal ion concentration of about 1 mg.l⁻¹. Below this concentration level, three-dimensional electrodes were thought to be more appropriate.

Stankovic and Stankovic (1991) examined the recovery of metal by a spouted bed electrode cell. The spouted bed was a modified fluidised bed which consisted of an upper cylindrical or rectangular section with a conical base. The electrolyte was fed into the bottom of the reactor. This created a central region where particles are transported upwards and a dense region on the side of the reactor where the particles flowed downwards. The two walls acted as

current feeders with an electrode placed in the centre of the bed acting as the counter electrode.

The initial concentration of the electrolyte was 1 g.dm^{-3} in 0.5 M sulphuric acid. The volume of the electrolyte used was 4 dm^3 . The variation of the concentration and current efficiencies was examined under constant current and constant electrode potential. The current efficiencies were as high as 90% in constant electrode potential mode. The results showed a better electrowinning rate and energy consumption in potentiostatic mode compared to constant current conditions. The process occurred at a constant rate when the applied current was less than the limiting current. When the current was higher than the limiting current, hydrogen evolution took place and the current efficiency decreased.

Under constant electrode potential, the process began at a higher current which decreased with time but hydrogen evolution was avoided. The required cell voltage was higher with increasing electrolyte flow rate. The increase in cell voltage was because of higher resistance experienced with bed expansion.

Fibrous carbon electrodes were used to remove hexavalent chromium from contaminated solutions by Abda et. al. (1991). The carbon electrodes consisted of mounted felt on copper foil. The two electrode compartments were separated by a Nafion cation exchange membrane. The cell was tested for a concentration range of 1 to 60 mg.l^{-1} chromium (III) or chromium (VI) as oxides in the presence of 0.05 M sodium sulphate. Concentration of chromium (III) was reduced from 9.5 mg.l^{-1} to lower than $25 \text{ }\mu\text{g.l}^{-1}$. The voltage was higher than 1.6 V . The flow rate was 1 ml.min^{-1} and the initial pH was 3.2.

The chromium (III) readily precipitated at a higher pH than 6. Chromium (VI) effluent was reduced to $\mu\text{g.l}^{-1}$ level for a feed pH of 3 to 3.5 and applied voltage of 1.4 to 1.6 V. The location of the precipitate moved towards the outlet as the flow rate was increased. The peak of the precipitate also moved towards the outlet as the current was reduced. This was thought to be due to the pH values suitable for efficient precipitation being attained further into the cell. Abda et. al. used a combination of columns under different conditions such as flow rate and the current to adjust pH and chromium removal.

Pletcher et. al. (1991) studied mass transport properties of reticulated vitreous carbon cathodes for cathodic deposition of copper from acid sulphate solution. The solution also contained copper (II) ions. The carbon electrode was mounted on a lead anode and a steel plate acted as the cathode. The anolyte and catholyte compartments were separated by a semi-permeable Nafion membrane. At low concentrations, Pletcher et. al found that approaching the limiting current evolution of oxygen was unavoidable. The carbon electrode had a large surface area because of the highly porous structure. This enhanced the performance of the process with regards to limiting current and mass transfer.

Pletcher et. al. (1993) further studied the removal of metal ions by reticulated vitreous carbon cathodes, using a single pass cell. As in the earlier work the electrodes were mounted onto a steel plate. The anode was a lead and antimony plate. The catholyte feed solution was made up of copper sulphate in 0.5M sodium sulphate adjusted to pH 2 by sulphuric acid. The anode compartment was filled with 0.5 M sulphuric acid and was separated from the anode compartment by a Nafion membrane. Using a linear flow velocity of 3.5 mm.s^{-1} , the copper concentration was reduced from 100 to 0.1 mg.l^{-1} by passing the solution along 400 mm electrodes. Current efficiencies as high as

96% were reported. The electrodes worked well at dilute feed concentrations. At high feed concentrations, the porous structure of the electrode may be blocked which would degrade the performance of the cell. Copper was selectively removed from a solution bearing copper complexes by electrochemical displacement (Spearot and Peck (1984)).

2.7 Ion Exchange

Ion exchange is a chemical reaction where the metal ion in the water is exchanged for an equivalent number of ions on the resin. It is reversible and an effective way of removing metal ions present in wastewater. Resins are regenerated by washing the ion exchanger with acid or alkali, depending on the nature of the resin (cationic or anionic). The resulting solution is higher in concentration and smaller in volume but it has to be treated to recover the metals. This means that the process is simple to operate and control but needs secondary treatments.

Ion exchange offers an economical way of treating dilute solutions under different process conditions. The process has a broad scope for different contaminants and it is a simple and economical process to apply. Ion exchangers are usually resistant to chemical attack even under severe chemical conditions. For ion exchange to be effective it must operate within a given pH range. Solids must be removed to reduce the risk of fouling. The mass transfer can be improved by using smaller ion exchanger beads. The relative cost of an ion exchange system is lower than an equivalent membrane process.

Removal and reduction of wastes can be carried out by using a combination of ion exchangers (Fries and Chew (1993)). It was found that by using a number of ion exchangers, the process water could be recycled and the usage of fresh water was reduced from 65 USg.min⁻¹ to 25 USg.min⁻¹. The hazardous waste was also reduced by a third by using a combination of resins. The whole

process consisted of three different stages with different ion exchange units making up each individual section. The recovery of copper was about 99% successful. The effluent from the treatment process contained less than 2 mg.l⁻¹ meeting the local regulatory requirements.

Chelating resins were compared to ion exchange resins for heavy metal removal in toxicity fractionation by Mazidji et. al. (1992). The resins were iminodiacetate chelating Chelex 50-100 and Dowex 50W-X8 ion exchangers. Chelating resin removed cadmium, copper, mercury, lead and zinc completely. Mercury was not removed by the resins efficiently. Neither resin provided complete removal of silver. The pH range used was between 7.0 to 7.5. The fractionation was carried out in the presence of organic toxicants and the metal feed concentrations were 1 g.m⁻³ Ag, 1.2 g.m⁻³ Cd, 3.5 g.m⁻³ Cu, 0.25 g.m⁻³ Hg and 6 g.m⁻³ Zn. Hardness of water did not affect the performance of the ion exchangers at low concentrations but the chelating resin performance was not as effective above a hardness of 195 g.m⁻³. The resins were tested over a pH range of 4 to 8 and were effective between pH values of 5 and 8.

Verweij et. al. (1992) described the synthesis and characterisation of two ligand materials onto the silica. The ligands used were grafted onto the silica either before or after modification. The exchangers selectively removed copper from a solution containing copper, cadmium, zinc, nickel, and cobalt at a pH higher than 2. The capacity of the material containing one extractant decreased with a reduction in pH while the capacity remained high at low pH for the second ligand. The materials were tested for metal uptake and regeneration. Capacity for copper of 0 to 0.25 mmol Cu²⁺.g⁻¹ of resin were observed for a pH range of 1 to 6. The material prepared by modifying the ligand prior to grafting onto the silica surface performed better than the ligand modified after being attached to silica surface.

Micron range ion exchange beads were used to remove metals to parts per billion levels in simulated wastewater by Grinstead and Paalman (1989). Ion exchange material was introduced into the system and supported by a screen, either ultrafiltration or Millipore (3 μm diameter pore) membranes. Limits of throughput and pressure drop were the main obstacles to the process. Parameters such as bed depth and applied pressure could be optimised. The elution was carried out by 1 to 3 M hydrochloric acid solution. Zinc was not eluted completely from iminodiacetic based ion exchanger. The reason was the formation of anion chlorocomplexes on the surface of the ion exchanger. Removals were between 80 to 90% for a feed concentration of 0 to 2 mg.l^{-1} .

Takeuchi et. al. (1988) studied the adsorption of heavy metal ions by hydroxyapatite, a calcium phosphate compound. The calcium is exchanged with heavy metals. Hydroxyapatite dissolved by reaction with acid below pH of 3.

Other materials such as ferrocyanide have also been investigated for removal of heavy metals from wastewater bearing heavy metal ions. Srivastava et. al. (1980) found chromium ferrocyanide gels showed selectivity for cobalt, manganese, zinc, cadmium, iron, thallium, and lead. The kinetics of the process depended on the metal ions being used. The removal of copper and lead was irreversible while cobalt, cadmium, manganese, zinc and lead could successfully be eluted.

Blanchard et. al. (1984) achieved simultaneous ammonium and heavy metal removal by natural zeolites. The zeolites showed good removal of lead and nickel. The effect of flow rate was investigated on a pilot plant scheme. Conditions of regeneration were also examined for the zeolite bed by using sodium chloride solution. Pilot plant tests were carried out using a dilute

solution containing 2.63 mg.l^{-1} ammonia, 0.261 mg.l^{-1} lead, 0.235 mg.l^{-1} zinc, 0.241 mg.l^{-1} copper and 0.216 mg.l^{-1} cadmium. After 4 hours, heavy metal ions were released by zeolites using a 50 g.l^{-1} solution of sodium chloride at a pH of 4 and a flow rate of 10 BV.h^{-1} .

Other methods such as evaporation and distillation are primarily used for product recovery. These techniques are energy intensive and only economically viable when the ionic concentration is high or volume low.

2.8 Overall Considerations

Metal bearing solutions can be treated by numerous methods. Overall the techniques are varied and geared towards particular systems. Factors such as level of contamination, volume of wastewater, ionic species, capital costs and operating costs influence the type of process used. The treatment methods suitable under one criterion may not be under another. The most appropriate design depends on considering the whole system. It must also be determined whether waste streams need to be treated individually or together, minimised or recycled. Various authors have discussed how treatment methods can be used in relation to particular industrial application.

Cushnie et. al. (1994) highlighted results of a survey by the National Centre for Manufacturing Sciences, US, of approaches taken by plating shops to deal with their effluents. The two most pressing problems facing the industry were reported to be the cost of complying with legislation and frequently changing regulations. A wide range of methods were used by the industry to deal with their wastewater discharges including end of pipe control as well as advanced technologies.

2.8.1 Process Considerations

Valenti (1992) discussed different approaches taken by different industries to handle metal contamination. Equipment and processes were considered for a number of case studies. These ranged from car battery recycling to reclaiming contaminants from soil. Janson et. al. (1982) discussed the alternative wastewater treatment methods available to the electroplating and finishing industry. The discussion evolved around handling waters containing heavy metals. General considerations for evaluating waste systems were discussed by Moleux (1993). Factors were outlined which influence the capital and operating costs. Point source recovery was also compared to centralised treatment system.

Alternative small treatment systems were discussed based on capability and costs by Logsdon et. al. (1990). Small systems were classified as those handling less than 1×10^5 USg per day. The main processes were coagulation, filtration, ion exchange, activated carbon, air stripping, reverse osmosis, lime softening and activated alumina. These were selected based on their capital cost, operating cost, simple operation, low maintenance and low labour requirements.

Alternative treatment of effluents containing organics and heavy metals were considered by Meardon et. al. (1989). The main objective was to produce a liquid effluent which could be freely discharged and a solid sludge which could be disposed of in a landfill. The principle processes were evaporation, crystallisation, activated carbon adsorption, reverse osmosis and ultraviolet peroxidation.

Hannah et. al. (1977) applied physico-chemical methods to removal of trace metals. Using coagulant the waste stream was passed through filtration and

carbon columns. Although the techniques were effective in removing trace metals it was concluded that if low concentration of metals were required then the coagulant dosing and operating conditions must be selected to optimise removal. Xue et. al. (1992) evaluated the recovery and treatment of cadmium and nickel by application of some techniques discussed in this chapter.

2.8.2 Others

Apart from process considerations, other aspects of a treatment system need to be considered as well. Centralised treatment of wastes was considered by Saltzberg (1982) as opposed to an end of pipe treatment which may be more costly. A centralised water treatment system was an approach considered for handling of waste from industrial plant by a main processing facility saving on costs because of economics of scale. The main criteria for waste treatment were striking a balance between cost of transport to volume of the waste to be treated. Waste reductions were based on water and chemicals savings.

Management of industrial hazardous waste was considered by Overcash and Eagleton (1984) with three main options of elimination or reuse of wastes, conversion to less or non- hazardous material and perpetual storage. It was considered that some assessment of wastes should be based on the risk factor of the hazards. Various technological needs were also addressed based on the review carried out by US national Academy of Science Committee.

Daniels et. al. (1982) considered the management of wastes for chemical manufacturing complexes. Among the consideration put forward were the classification and characteristics of such facilities. Daniels et. al. suggested ways of identifying wastes by degree of hazards and facilities as part of a comprehensive environmental management audit. The main objectives of waste management by recycling and reduction at source were discussed by Cornwell and Lee (1994) and Underwood (1994) respectively.

Cornwell and Lee (1994) considered several water treatment plants and management treatment by equalisation and monitoring of the influents and effluents. Underwood reported good cost savings and environmentally sound options. Waste reduction had the benefits of cost saving on avoiding waste treatment and enhanced the performance of the process.

2.9 Conclusions

A wide range of applications and methods are available to remove metal from waste streams. The application of treatment techniques depend on the nature of the problem. Each method has its own advantages and disadvantages which allow a selection to be made based on the factors discussed in Section 2.8. Environmental implications as well as regulatory demands are also important. Chemical engineering considerations are paramount to achieving an effective treatment for the most economical solution. Each treatment can be geared to have the optimum results concerning any specific application. Apart from prevention, end of pipe management is probably one of the most cost effective way of managing waste which also minimises the environmental impact.

Based on the information gathered in this chapter, Electrochemical Ion Exchange (EIX) seems to be a suitable method for an end of pipe treatment that requires volume reduction. EIX combines the characteristics of an electrochemical process and an ion exchange method. It is appropriate for industrial application where a combination of these process can be used. It offers an alternative for the treatment of solutions bearing low metal concentrations which would not be economically viable using an ordinary electrochemical process.

This thesis investigates the technique developed to remove metal from water with minimum amount of chemicals used. It can be used as polishing step in conjunction with other methods to obtain the effluent metal concentration

required. A detailed description of the EIX technique is given in the next two chapters.

Table 2.2: List of authors, methods, metals and concentration ranges of referred material

Authors	Methods	Metals	Concentration range
Abda M., et. al.	Electrochemical	Cr	1-60 mg.l ⁻¹
Agarwal I. C., et. al.	Electrochemical	Cu, Cd, Cr, Pb, U, Zn	<0.5mM
Aldor I, et. al.	Adsorption (Biosorption)	Cd	-
Allen H. R., Chen P. H.	Electrochemical	Cu, Cd, Pb	400 – 1950 mg.l ⁻¹
Babcock, W.C. wt. al.	Membrane	Cu, Ni, Cr	50 - 5000 mg.l ⁻¹
Barnes L.J., et. al.	Biological	Zn, Cd, Co, Cu, Mg, Ca	< 1100 mg.l ⁻¹
Ben Aim R., et. al.	Membrane	-	-
Bhattacharyya D., Cheng C. Y.	Adsorption	Cd, Ni, Ba, Ca	< 0.86 M
Blais J. F., et. al.	Biological	Al, Cd, Cr, Cu, Mn, Ni, Pb, Zn	-
Blanchard G., et. al.	Ion exchange	Pb, Cu, Cd, Zn, Co, Ni, Hg	<3 mg.l ⁻¹
Broom G. P. et. al.	Membrane	Pb, Cu, Cd, Zn, Co, Ni, Hg	2 - 72 mg.l ⁻¹
Couillard D.	Review (Peat)	-	-
Deans J. R., Dixon B. G.	Adsorption (Biosorption)	Cu, Pb	1-1000 mg.l ⁻¹
D'Avila J. S., et. al.	Adsorption (Biosorption)	Pb, Cd, Zn, Ni, Cr, Cu	-
Figuerola M., et. al.	Electrochemical	Cu	180 g.l ⁻¹

Authors	Methods	Metals	Concentration range
Fleet B	Electrochemical (Review)	-	-
Flynn T. M., Way J. D.	Membrane (Review)	-	-
Fries W., Chew D.	Ion exchange	Cu	< 100 mg.l ⁻¹
Ghosh S., Bupp S.	Biological	Cu, Pb, Cd	15 – 400 mg.l ⁻¹
Grinstead R. R., Paalman H. H	Ion exchange, Membrane	Cu, Ni, Pb, Zn, Cr	0.2 mg.l ⁻¹
Guha A. K., et. al.	Membrane	Cu, Cr, Hg	90 – 2000 mg.l ⁻¹
Hannah S. A., et. al.	Chemical, Filtration, Adsorption	Ag, Cr, Pb, Ba, Cd, Cu, Zn, Ni, Mn, v, Tl, Ti, Sn, Se, Hg, Co, Bi, Be	0.05 – 2.5 mg.l ⁻¹
Horner G. D., Duffey J. G.	Electrochemical precipitation	Cr, Zn, Cu, Ni, Pb	0.1-200 mg.l ⁻¹
Huang J. S., et. al.	Electrochemical	Cu, Fe, Ni, Zn, Pb, Cr, Cd, Mn, Ag	0.8 – 13900 mg.l ⁻¹
Huang C.P., Blankenship, D.W.	Adsorption	Hg	0.01-0.1 mM
Izatt R. M., et. al.	Liquid membrane, Adsorption	Ba, Sr, Pb, Tl, Mg, Ca	0.1-10 mM
Janson C. E., et. al.	Various (Review)	-	-
Jenke D. R., Diebold F. E.	Electrochemical, Precipitation	Al, Cu, Zn, Fe, Mg, Mn	300 – 1000 mg.l ⁻¹

Authors	Methods	Metals	Concentration range
Karavasteva M., Karaivanov St.	Electrochemical	Zn	45-49 g.l ⁻¹
Kedem O., Bromberg L.	Ion exchange	Cu, Ni, Ag	< 325 mg.l ⁻¹
Ku Y., Peters R. W. 1987	Adsorption, Precipitation	Zn, Cd	<100 mg.l ⁻¹
Ku Y., Peters R. W. 1986	Precipitation	Zn, Cd	100-106 mg.l ⁻¹
Lin C. F., et. al.	Chemical	Cr	<100 mg.l ⁻¹
Matsumoto M. R., et. al.	Review	-	-
Mazidji C. N., et. al.	Ion exchange	Cd, Cu, Zn, Pb, Hg, Ag, As, Cr	< 7 mg.l ⁻¹
Merrill D. T., et. al.	Precipitation	As, Se	20-60 µg.l ⁻¹
Netzer A., et. al.	Precipitation, adsorption	Al, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Ag, Zn	100 mg.l ⁻¹
Orhan Y., Büyükgüngör H.	Adsorption (Biosorption)	Cr, Cd, Al	5 mg.l ⁻¹
Peters R. W., Ku Y. 1987	Precipitation, Adsorption	Zn	<100 mg.l ⁻¹
Peters R. W., et. al. 1985	Review	-	-
Pletcher D., et. al.	Electrochemical	Cu	10-63 mg.l ⁻¹
Pradhan A. A., Levine A. D.	Biological	Cu, Pb	10-30 mg.l ⁻¹
Rajeshwar K., et. al.	Electrochemical (Review)	-	-

Authors	Methods	Metals	Concentration range
Reed, B.C., et. al.	Review	-	-
Rivera A. L.	Biological	Zn	100 –1000 mg.l ⁻¹
Schiller J. E., et. al.	Chemical	Fe, Cu, Zn, Ni, Mn, Co, Cd, Pb	< 41 mg.l ⁻¹
Spearot R.M., Peck V. J.	Various (Review)	Cu	-
Srivastava S. K., et. al.	Ion exchange	Tl, Hg, Mg, Fe, Cu, Zn, Cd, Pb	0.005 M
Stankovic V. D, Stankovic S.	Electrochemical	Cu	1 mg.l ⁻¹
Surfleet B., Crowle V. A.	Electrochemical (Review)	-	-
Takeuchi, Y., et. al.	Ion exchange	-	-
Tare V., et. al.	Adsorption (Biosorption)	Cd, Cu, Cr	-
Trivoli, V., et. al.	Electrochemical	Ag	0.005 M
Verweij P. D., et. al.	Ion exchange	Cu, Cd, Zn, Ni, Co	0.16 M
Volchek K., et. al.	Membrane	Cu, Ni, Zn, Co	various
Voortman W. J., et. al.	Electrochemical, Membrane	Na	-
Wei Lin et. al.	Review		
Whang J. S., et. al.	Precipitation	Pb, Cr., Zn, Cd, Cu, Ni	2-33 mg.l ⁻¹
Yi J., Tavlarides L. L.	Liquid membranes	Cu	0.3M

Authors	Methods	Metals	Concentration range
Yin J., Blanch, W. W.	Ion exchange (Liquid)	Cd	<1 mM
Zotter K., Licsko I.	Chemical	Cr, Ni	3-34 mg.l ⁻¹

CHAPTER 3

EARLIER STUDIES

3. INTRODUCTION

Coeuret (1993) described a process employing the concept of the flow through porous electrode patented by Hulin over a century ago. The original patent was entitled "Electrolytic process and equipment for the immediate separation of liquid or dissolved electrolysis products". Almost a century later electrochemical membrane processes are being used as waste water treatment techniques.

Electrochemical Ion Exchange (EIX) is an electrochemically enhanced ion exchange process. The main constituents of EIX cell are half cells. Each half cell consists of two electrodes with an ion exchange membrane placed between the two. One electrode is embedded in the membrane and the other is placed on the opposite surface of the ion exchange membrane. An essential part of the EIX process is the reactions that occur at each electrode due to the potential difference applied across them.

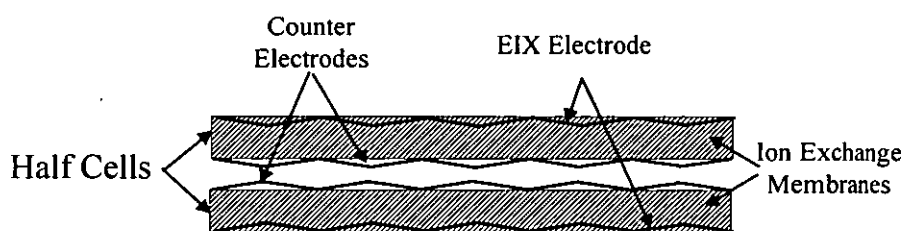


Figure 3.1: Basic components of an EIX cell

The principle and the development of the process are discussed in the next two chapters.

3.1 Demineralisation

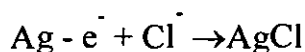
Early work on electrochemical ion exchange was conducted in the USA by Evans and Hamilton (1966). The original idea was developed by Murphy

(1960) at University of Oklahoma and patented (Murphy (1964)). The process involved passing saline water between suitable electrodes to produce an effluent with a lower salt content. The electrodes consisted of a conductive backing and chemically treated carbon. The demineralisation process occurred at the carbon particle surface. Treated carbon paste was later replaced by carbon felt because the felt material offered a greater surface area. Finally, commercial ion exchangers were used.

The early work concentrated on the mechanism of removal as well as regeneration and electrode materials. An electrode covered by carbon paste, acting as a cathode, removed sodium ions from solution. The sodium was released back into solution by making the electrode anodic and not when the current was switched off. The mechanism for regeneration is discussed in more detail in Chapter 4.

Strong cation exchangers were ruled out since they were not amenable to electrochemical control i.e. release of sodium ions under anodic potential. For weak cation exchangers, demineralisation and regeneration occurred efficiently. The Faradic efficiency was based on the ratio of the charge carried by the amount of ions removed to the charge calculated based on the current passed. Carboxylic acid base resins were reported to be 80 to 100 % efficient up to a loading of 5 meq.g^{-1} . At higher loadings, the efficiency was lower and accompanied by a change in pH.

Evans and Hamilton (1966) suggested that there was no change in solution pH since the exchange of sodium ions occurred such that any hydrogen ions released by the reaction were neutralised by the hydroxyl ions produced at the cathode. The circuit was completed by the following reaction at the Ag-AgCl electrode:



hence, there was no net change in hydrogen ion concentration. There was no indication as how the pH was determined. pH measurements were not made during the operation of the cell as the cell design presented in the report did not allow for intrusion of a pH electrode and no mention of use indicator paper was made. In later part of the program the determination of pH was made within the system with inclusion of indicator paper by Evans, et. al. (1969). Also, Faradic efficiencies greater than 100 % were reported which would suggest that either the determination of concentration of sodium and chloride ions were wrong or the current measured was less than the actual current flowing through the cell.

Carbon materials that could be regenerated using sodium hydroxide solution could also be regenerated by electrochemical means. A range of carbons, strong and weak cation exchangers were examined by using a cell consisting of three electrodes, a cation responsive electrode, an auxiliary silver-silver chloride electrode and a silver-silver chloride reference electrode. With carbons, the exchange capacity was lower than that of weakly acidic resins. For acid treated carbons, the exchange process was less efficient and accompanied by a change in pH above loading of 3.3 meq.g^{-1} . The process was 80 to 100% efficient only up to 1.2 meq.g^{-1} when using graphite, above this the efficiency dropped to between 20 and 30% accompanied by a change in pH. The weak cation exchanger performed well up to a loading of 4.7 meq.g^{-1} with no change in pH. It also showed good regeneration and no leaching when the current was off.

During the constant current experiments, the electrode potential increased in the first few minutes of the experiment until it reached a steady state value. Thereafter, the constant potential for weak acid resin was reported to be twice

that of electrodes containing carbon paste.

It was found that demineralisation occurred efficiently when the ohmic potential drop was high and no pH change was detected on the surface. The applied voltage was generally lower for regeneration. Constant current experiments were carried out using cells containing anion responsive material and combined anion-cation responsive electrodes.

3.1.1 Combined Cell

Evans et. al. (1968) further developed the electrochemical demineralisation process. The main areas covered included anion responsive electrodes, combined cell, performance of the overall cell and rough cost estimate of the process. Anionic weak base and cationic weak acid resins were also examined in this study. The resulting electrodes had high exchange capacity, ease of regeneration and long-term service life. A cost estimate was also presented based on the experimental results obtained for a small cell.

Electrochemically controlled ion exchange was defined as Evans et. al. (1968) “essentially undissociated fixed groups (weak acid or base) are ionised as a result of electrochemical reactions and participate in an ion exchange process”. The cation responsive electrode consisted of Norit graphite, cation exchange resin and binder fixed onto a graphite backing. The anion responsive electrode was similarly made with an anionic resin.

Acid treated carbon showed the best performance from all the carbons tested during the early part of the programme. A combination of electrodes were tested in the study by Evans et. al. (1968). The capacities of the electrodes were determined chemically by loading the electrodes with sodium and regenerating with hydrochloric acid solution. The electrochemical capacity was found to be between 65 to 90% of the chemical capacity. It was possible to regenerate the electrodes completely i.e. all the sodium adsorbed by the

membrane was completely eluted. The potential of the electrode increased with each successive demineralisation step but was lower for a regeneration step following a demineralisation step.

Different materials were used as binder. The quantity of binder used in the manufacture of electrodes was changed to obtain electrodes of different compositions. The performance of these electrodes was then investigated and their capacity also determined. Electrodes with ion exchange resin had a higher electrochemical capacity than electrodes where no ion exchange resin was used. High efficiencies were obtained for sorption and desorption at applied current density of 1 mA.cm^{-2} . Carboxyl groups were converted to amine groups on acid treated Norit carbon. The electrodes had low electrochemical capacity for sodium and chloride.

Anion and cation responsive electrodes were examined in a combined cell. These were set up with a silver - silver chloride reference electrode placed in between the two ion responsive electrodes with the active surface of each electrode facing each other. Using this set up, good demineralisation was achieved with high electrical efficiency and very small change in pH. Anion responsive electrode potential showed dependence on the sequence of cycles similar to those observed in the cation responsive electrode. Cell potential was reported to be between 0.8 and 1.4 V for a current of 0.5 mA.

The cationic electrode composition was as follows Evans et. al. (1968):

10 % Kraton (co-polymer of styrene and butadiene) binder
40 % Acid treated Norit
30 % Amberlite CG-50 resin
20% Graphite

This electrode composition gave a better performance in terms of efficiency

and lower total cell potential. A series of experiments were conducted with the combined cell with the electrode area of 1.5 cm^2 , cell current of 1 mA and total cell potential of 1.0 to 1.6 V obtaining an electrochemical capacity of 0.21 meq.g^{-1} .

Doubling the current did not result in doubling of the total cell potential. Electrodes deteriorated as a result of prolonged electrochemical testing with active material separating from the graphite backing. This was reported to be due to the ion exchange resin swelling and shrinking during the process. These volume changes affected the adhesion material with graphite backing. Epoxy resins were used as binder material. This was because of their low molecular weight and they could be cured at low temperature.

In the case of anion active electrodes, the Faradic efficiencies were below 50%. The loading of just ion exchanger was abandoned. Polymer based material were used to improve the durability of the electrodes. Some improvement of electrode life was obtained by addition of adhesion additive Picotex and by ball milling the mixture before application onto a graphite surface. The efficiency of the process was better when graphite was used in the fabrication of the electrodes. This was partly due to conductance of graphite and electrochemical reaction occurring throughout the electrode rather than just at the graphite backing surface. No relationship was found between the cell potential and the electrical efficiency of the cell.

A cost estimate was carried out for a plant treating $20\,000 \text{ USg.d}^{-1}$ of water containing 2500 ppm of sodium chloride solution and reducing this to 500 ppm. Estimate of the electrode surface area was based on results obtained from experiments using an electrode with a surface area of 1.5 cm^2 operating with a current of 2 mA. In total, four demineralisation units were required each with

300 compartments in a bipolar arrangement. The assumption was made that the process was 90% efficient. The surface area of each unit was 4.58 ft^2 with an applied current density of 1.24 A.ft^{-2} . The total capacity of each unit with a surface area of 4.58 ft^2 was taken as 0.85 eq. The applied current density was taken to be 1.24 A.ft^{-2} . Detail calculations were given by Evans et. al. (1968). The design of cells, plant and process were also discussed.

3.1.2 Further Investigations

Evans et. al. (1969) continued their work into understanding the electrochemical ion exchange and modelling of the transport processes associated with it. Experimental results were compared with model data to evaluate the applicability of a model. Studies were also conducted to obtain the limiting current. New binder materials were investigated for electrode fabrication.

The original cost estimate was based on a low current density of 1.33 mA.cm^{-2} (Evans et. al. (1968)). Further work was carried out to increase the limits of the process with respect to higher current densities and enhanced mass transport properties. Different fabrication techniques and binders were also tested. A binder used in the electrochemical system needed certain characteristics such as high mechanical strength, good stretch properties, good adhesion, hydrolytic stability to withstand attack from acid and bases and high permeability. The original Kraton (co-polymer of styrene and butadiene) binder had good strength and flexibility. However, it lacked good ion transport capabilities.

Ion exchange kinetics of the process were chemically determined by using ion exchange resin, binder and graphite backing. The studies were carried out in batch tests using mixed ion exchange systems. Demineralisation was carried out at different pH values.

Removal of chloride ions increased with a reduction in pH when using a weak base resin. At pH of 1.74, 696 ppm of chloride ions were removed from solution after 15 min. with a feed solution of 810 ppm chloride. Regeneration was also quickly obtained for the anion exchange system.

For a weak cation exchange resin, 0.05 g of the resin removed 0.018 moles of sodium from a test solution of 0.022 N sodium hydroxide, at a pH of 12.08. Quite good regeneration of the resins took place within 15 min. of placing them in 0.022 N hydrochloric acid solution, at a pH of 1.74.

Tests were carried out using electrodes with binder and ion exchanger on a graphite backing but no current was passed. The results indicated a good chemical capacity of electrodes. This meant that blockage of ion exchange sites did not occur as a result of the various fabrication techniques. Similar chemical capacities were obtained for pieces of electrode mixtures during batch experiments as compared to mounted electrode mixture on graphite backing.

Following some experiments, Evans et. al. (1969) found that by exposing only the area of the graphite covered by active material improved the performance of the process. They also concluded that ion exchangers could be used without any chemical treated carbon so long as the electrochemical reaction could be confined to the area containing the paste mixture. Good efficiencies were obtained for sodium removal when some bubbling occurred at the cation responsive electrode. The gas was generated at the cathode which must have been oxygen.

The electrodes fabricated with resin coated with Polyvinylpyridene (PVP) had lower electrode potential during regeneration than electrodes formed with non-coated resins, at the same current. This was thought to be due to better access

by water to the resin surface due to the water soluble nature of PVP.

Work was conducted on fabrication and optimisation of ion active electrodes. Flow cells were designed and manufactured. The cell consisted of three main parts, anion responsive electrode, cation responsive electrode and a spacer between the two. The spacer had a zig zag path cut out from the centre section to allow the passage of solution (Evans et. al. (1969)).

Two mathematical models were proposed. The first was based on the transport of ions described by particle diffusion. The second considered the transport of ions under film diffusion. The film diffusion model gave a film thickness ranging from 10^{-2} to 10^{-3} cm. The model assumed a homogenous system and the complication of the system were borne out by considerations for the model.

The model developed was based on a continuous ion exchange phase. The conductive material imbedded in the resin phase formed a continuous conducting material from the graphite backing to the solution interface as shown in Figure 3.2.

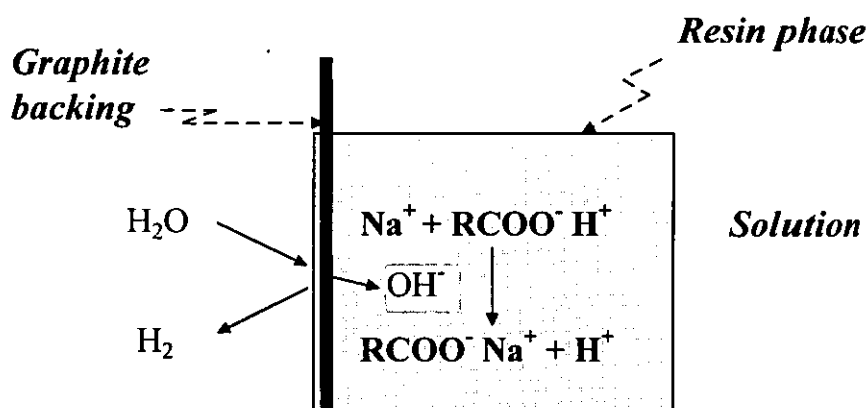


Figure 3.2: Cation responsive electrode in absorption mode

Cation responsive electrode had negative potential during operation. The following was the electrochemical reaction at the cathode:



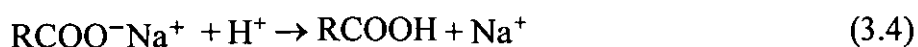
This caused an increase in pH which lead to ion exchange reaction:



The hydroxyl and chloride ions kept the electroneutrality. The efficiency of the process depended on the participation of these ions in carrying the current. The reaction front moved from the solution interface at the outside surface of the electrode towards the graphite backing. Once all the resin had been converted, the hydroxyl ions would then carry the current. During regeneration, the reverse reactions would occur at the positive cation responsive electrode acting as the anode.



This reaction would then produce acidic conditions conducive to regeneration of the cations from the resin of the form.



Other ions such as chlorides were present to keep electroneutrality. Participation of hydrogen and chloride ions in carrying the current reduced the efficiency of the process.

Based on the model presented ,the limits of the process were external mass transport. Expressions representing the system were derived based on film and particle diffusion control by Evans et. al. (1969). The results indicated that there was reasonable agreement between model and the experimental results when using the weakly acidic ion exchange resin but not for the strong acid or weakly basic resins.

Evans et. al. (1969) coupled anion responsive electrode with a cationic active electrode with a greater area. It was found that the process was limited by the cationic electrode when both electrodes had the same effective area. It was also considered that the process was more efficient when electrochemical reaction

occurred within the paste of active material rather than just at the graphite backing. This was supported by better performance of the cell when acid treated carbon was used. This could have also been due to the adsorption capacity of the treated carbon. Lower potentials were found when using carbon within the matrix of the electrode. This could have been due to higher conductivity of carbon.

The work was continued into electrochemical ion exchange by Evans et. al. (1970). The model was improved to represent the transport processes associated with the process. Electrochemical experiments were carried out to obtain a limiting current. Combinations of binder, ion exchange resin and carbon were used to examine the process in relation to ions other than sodium and chloride such as calcium and sulphate ions.

Anion active electrodes were made to perform efficiently between currents of 2 mA to 10 mA. The potential was lower for the anion responsive electrode fabricated with PVP precoated resin than the resin made without any precoating.

In cation active electrodes, the substitution of chemically treated carbon for non-treated carbon improved the electrochemical characteristics of the electrodes. A combination of methods and binders were used to obtain enhanced performance from anion active electrodes. Demineralisation and regeneration cycles were carried out for the electrodes with different compositions and materials. Higher potentials were needed for electrodes containing larger quantities of resin.

Various materials were deployed to improve the performance of the cation active electrodes. These included plating the resins with nickel, using different

resins, acid treated carbons and binder material. The efficiency of the cation responsive electrode with a surface area of 1.5 cm^2 was increased at higher current of 6 mA. Freeze drying and vacuum drying were other techniques used in the fabrication of electrodes but they were found to be unsuitable.

Kinetic responses of ion active electrodes were studied along with swelling characteristics. Large swelling was found for both types of resins. Advantages of using polymeric materials were highlighted in the manufacture of electrodes containing ion exchange material. None of the polymers used proved to be as good as Kraton. In continuous operation the anion active electrodes performed well with their chemical and electrochemical activity unchanged after a large number of cycles. However, the cation responsive electrodes degraded during the experiments by some separation of paste mixture from graphite backing. The potential for electrode during demineralisation and regeneration were relatively unchanged over 25 days of continuous operation.

The earlier work on demineralisation was discontinued for several reasons as high Faradic efficiencies were only obtained at low current densities. Overall, the program was probably halted due to the limited range of material available for the development of the process.

3.2 Radioactive Treatment

In the early 80's AEA, Harwell, were screening a range of electrical processes for the treatment of low to medium radioactive liquid wastes (Turner (1981)). Electrical methods had the ability to be remotely controlled by a change in potential difference.

Turner (1981) reviewed a broad range of electrical methods. Among the methods tested by Harwell were electrosmosis and electrochemically controlled ion exchange which both showed promising performances (Turner (1983)).

Electrochemical ion exchange was suggested to be used in series with cells reducing the ionic content of target solution in steps. The mode of operation suggested for elution was batch.

Evans described that during the absorption cycles, the reaction at the cathode would increase the local pH generating active ion exchange sites. During elution, the role of the cathode would be reversed to an anode decreasing the pH so as to promote exchange of hydrogen ions for the adsorbed cations. Electrochemical ion exchange was proposed because it could be applied to a wide range of wastes. Coupled with advances in new materials, i.e. selective ion exchange resins, the work started by Evans et. al. (1966) could be continued.

Turner et. al. (1983) reported on experiments carried out to examine the feasibility of the process when applied to medium level radioactive wastes. Initially batch experiments were carried out by using a membrane immersed in a well mixed electrolyte with an electrode placed around it. This early experimental set up can be seen in Figure 3.3. The working electrode was either carbon felt or metal grid with an adsorption medium attached to surface of the electrode. Flow cell experiments were also carried out. The main objectives of the study were to investigate materials, fabrication techniques and modes of operation for electrochemical ion exchange cells.

Various materials were selected for electrode, binder and ion exchanger. Physical attributes of electrodes and methods of construction were considered. The performance of the cell was tested in different modes of operation. Materials used for the electrodes included stainless steel, nickel, platinised titanium, carbon and platinum along with plastic mesh spacers to promote turbulence. Of these carbon, platinum and platinised titanium showed the most promise. Some of these materials can be seen in Figure 3.4. PTFE and Kraton were used as binders with PTFE bonded membranes showing poor

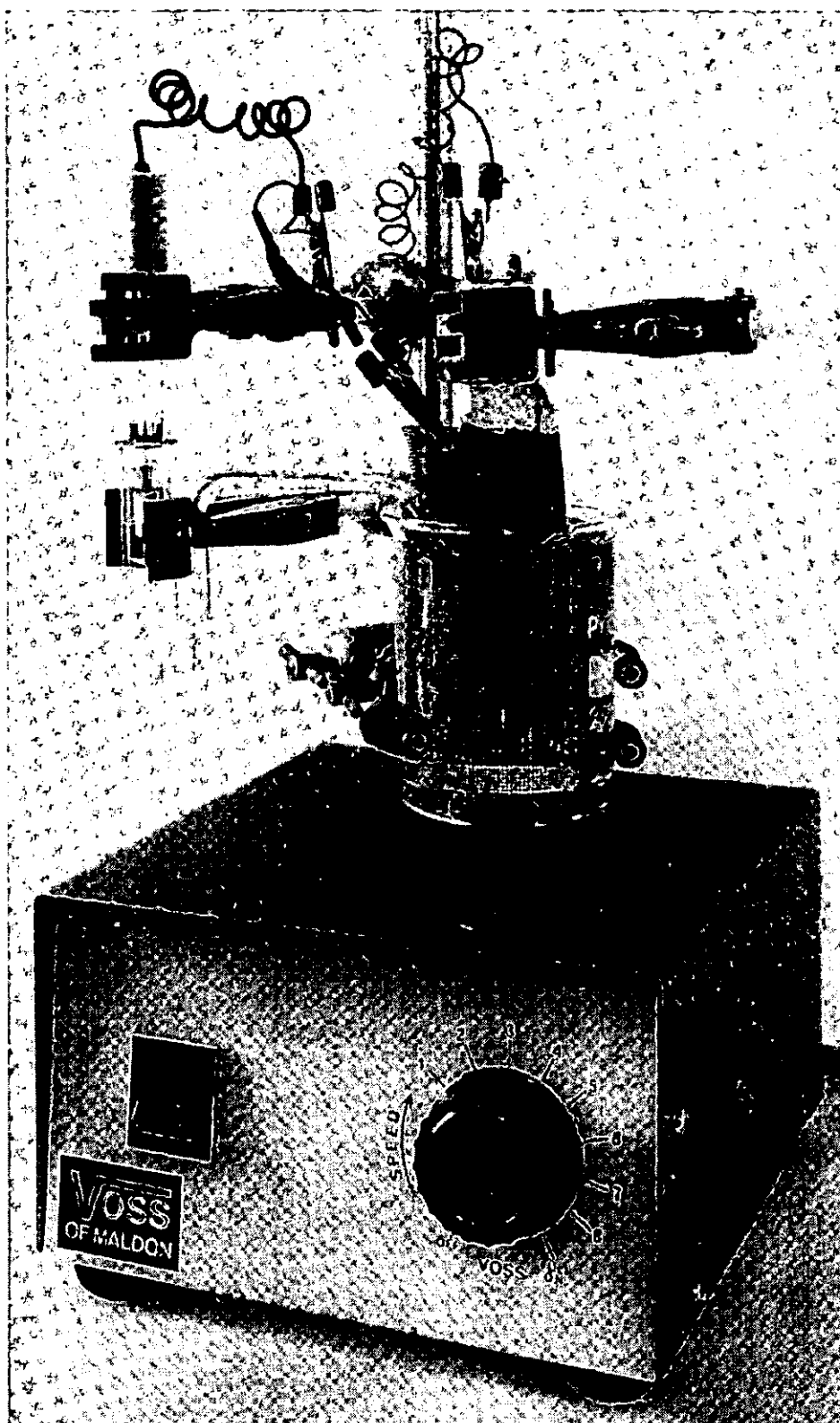


Figure 3.3: A batch Electrochemical Ion Exchange cell

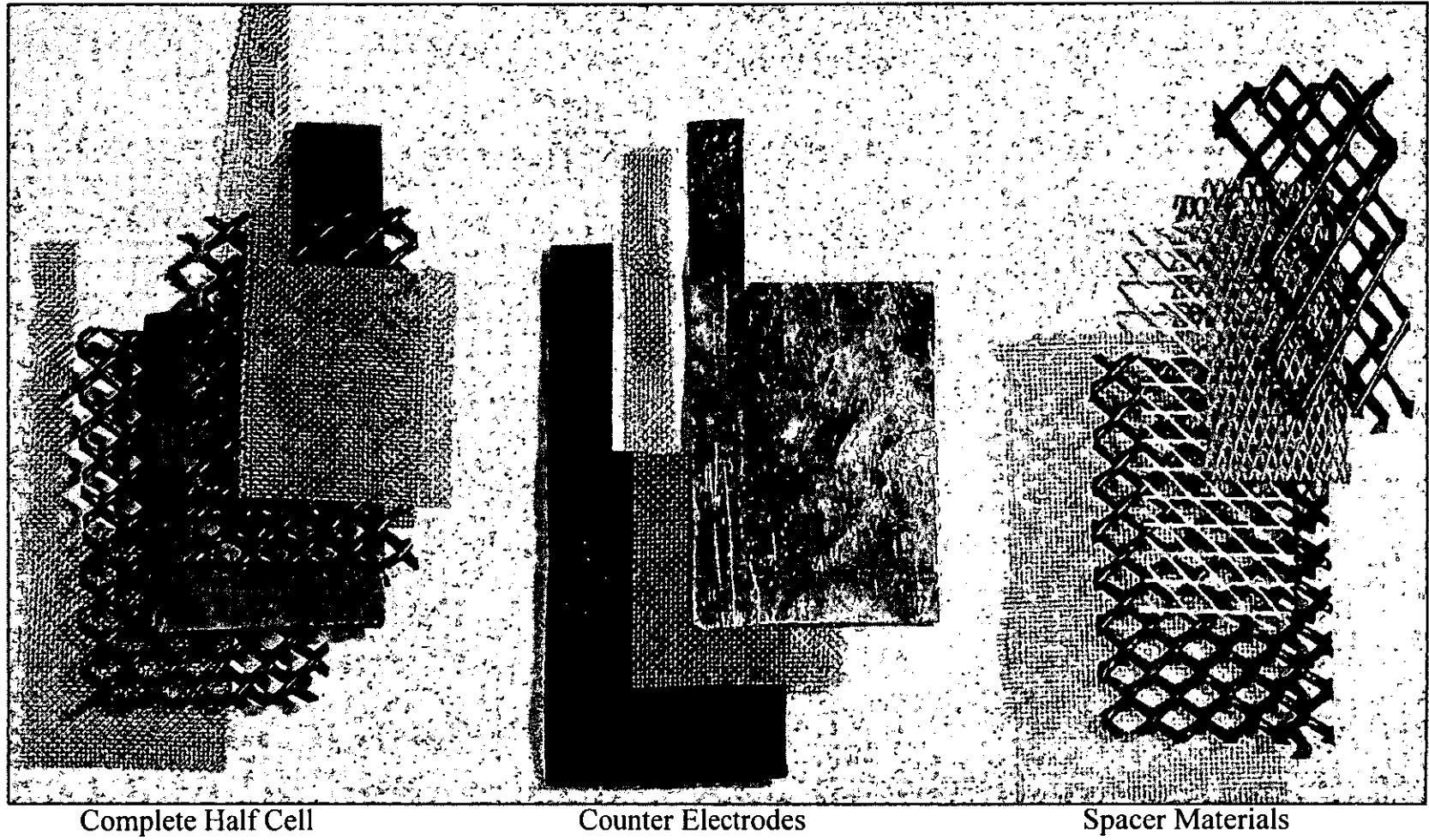


Figure 3.4: A range of materials used for electrodes and spacers

performance. Graphite was used in preparation of electrodes to improve the electrical conductivity of the membrane, and to enhance the adsorption kinetics due to extra ion exchange capacity that carbon offered. Oxidised carbon and weak acid cation exchanger were used as ion adsorbents.

Stainless steel electrodes dissolved when used as anodes and carbon counter electrodes performed well. During elution, carbon re-adsorbed material eluted off the ion responsive electrode with a low but noticeable capacity in dilute solutions. Ion exchange resins with smaller particle size were helpful in the manufacture of mechanically stable electrodes and offered a larger surface area. Comparison of carbon and ion exchangers highlighted the suitability of each material used in the manufacture of the membranes. The wide range of ion exchange resins available had a high capacity. However, carbon was a better conductor of electricity than ion exchange resins but had to be chemically treated before use. Carbon could be burned easily to obtain the radionuclides after removal.

Carbon electrodes seemed to be activated during elution in the neutral or basic pH. This contributed to the adsorption capacity of the membranes. Initially, the electrodes suffered from poor adhesion of the adsorption medium and the current collector. Evans found the same due to the expansion of the ion exchange material particularly at high loading. This was overcome by covering the electrode with Viledon, a cheap polyamide cloth. It did not affect the performance of the cell greatly.

Effects of pH and electrolyte concentration on the performance of the cell were examined. The pH became increasingly acidic as more cations were adsorbed. More cations were removed in a given time from a more concentrated solution into the same amount of resin.

Turner et. al (1983) found graphite free electrodes adsorbed similar quantities of ions but with slower kinetics and considerably larger voltages. The performance of the cell did not alter after repeated cycles. Strong cation exchangers showed good adsorption properties but poor desorption characteristics. Flow cell experiments were conducted with two basic types of membrane, a Swiss roll configuration and parallel plate. A typical parallel plate cell can be seen in Figure 3.5. In the early designs gas entrapment was the major source of problems. The major part of the early work at AEA Harwell was concerned with the design of the cell (Turner et. al. (1985)). It was found that the restrained electrode structure in which the counter electrode and the active electrode were physically in contact improved cell life and improved performance. This electrode can be seen in Figure 3.6.

Turner et. al. (1985) worked on different aspects of electrochemical ion exchange ranging from long term kinetics of sodium and caesium removal to development of the membranes. The physical stability of the electrodes was a major problem. The main loss of performance was due to a breakdown of adhesion between the membrane and the current feeder. By changing the viscosity of the binder solution used in membrane manufacture and application of Viledon cloth mechanically stable electrodes were produced. Although for carbon felt electrodes, loss of electrical and mechanical strength occurred in anodic mode. This was probably due to an oxidation effect. This was supported by discoloration of the electrolyte and an increase in voltage. A range of carbon and graphite materials were used but they all showed varying degrees of mechanical failure with long use. Platinised titanium was found to be the most suitable but expensive option to consider.

The main consideration for a current feeder must be chemical and mechanical stability for a wide range of pH (1-12). The material must also allow gas to

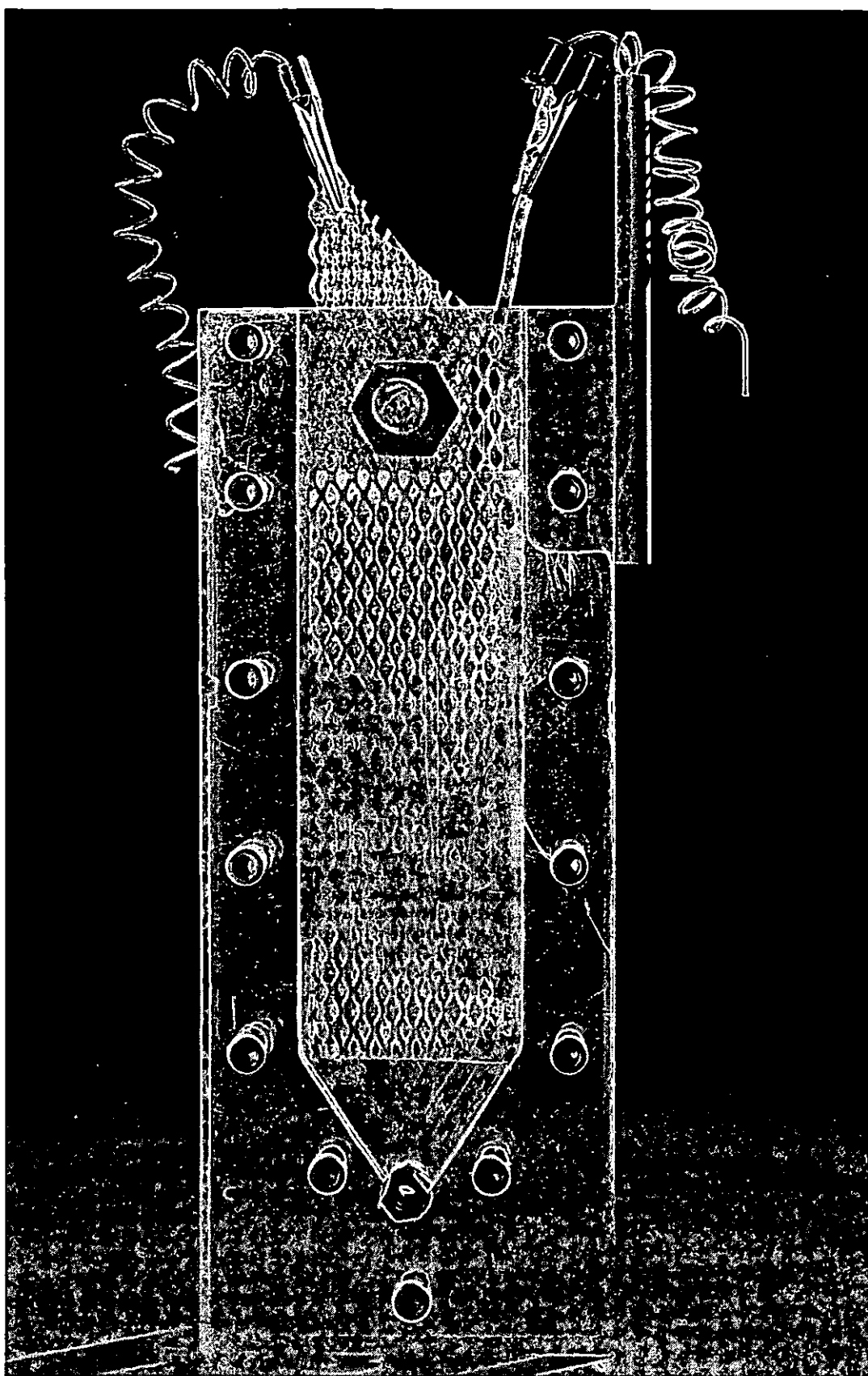


Figure 3.5: An early example of flow cell manufactured at AEA Harwell

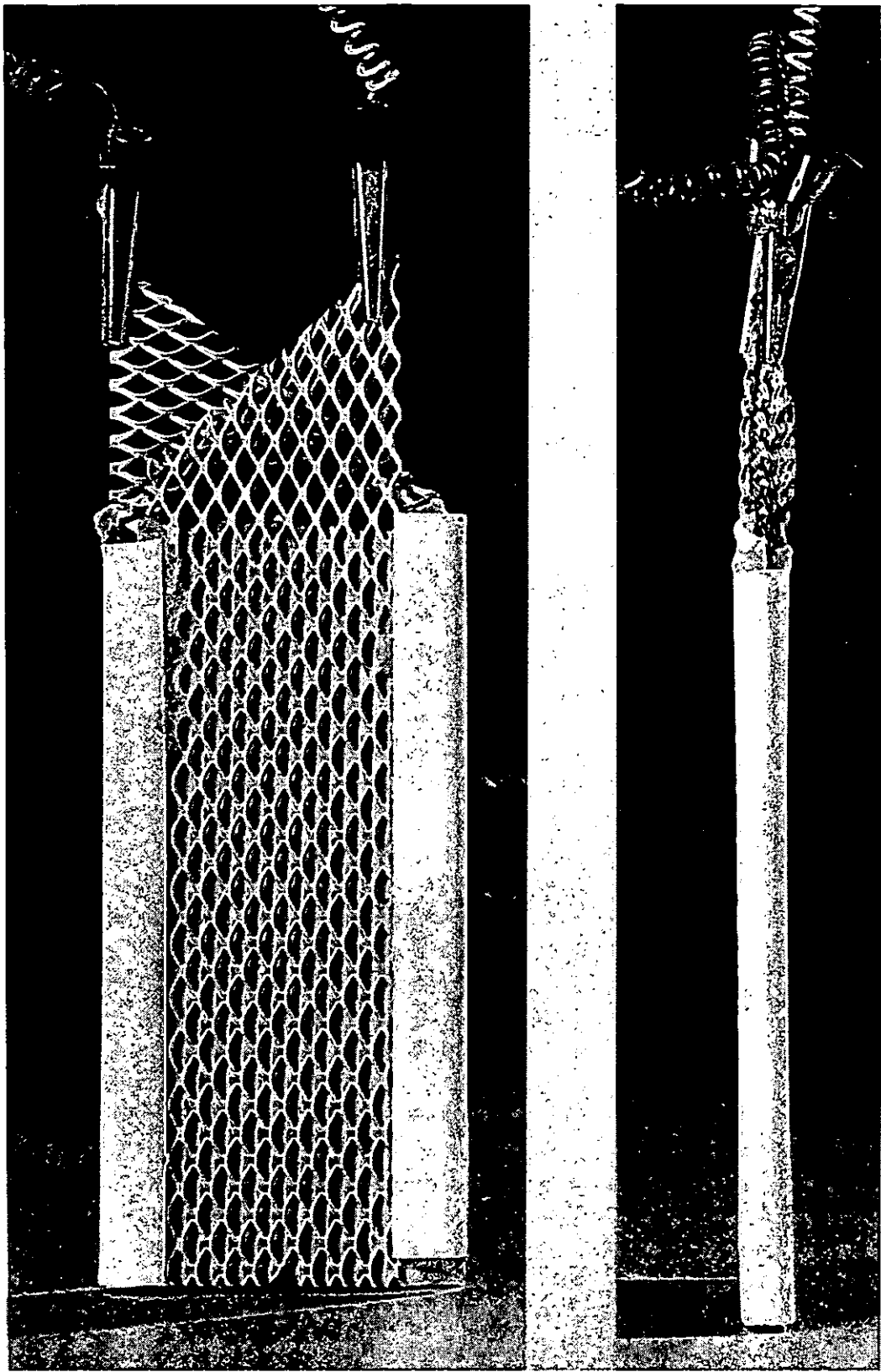


Figure 3.6: Titanium phosphate EIX electrodes manufactured at AEA Harwell

escape produced as result of the water splitting.

It was found that electrodes with graphite had high anodic cell voltages due to the graphite affecting the ion transport through the membrane. It was suggested that this may have been possibly due to reduction of incidence of interparticle contact between resin beads.

Grinding the ion exchange resin to a powder produced electrodes with better kinetics which were also easier to manufacture. It was also found that membranes containing no graphite performed better than those containing graphite. The cells containing graphite had lower cathodic voltages but corrosion of graphite material occurred.

Different cell configurations were also investigated by using a combination of anion and cation responsive membranes, electrodes and spacers. The work produced a robust, corrosion free system capable of withstanding many cycles without degradation in performance. In relation to radioactive application of electrochemical ion exchange, inorganic ion exchange materials were crucial to the process. They offered resistance to damage and kept their performance and structural integrity under radioactive conditions.

A range of inorganic exchangers were screened to be used in the process, these included titanium phosphate and zirconium phosphate. Figure 3.6 shows a titanium phosphate electrode manufactured at AEA Harwell laboratories. The screening usually involved batch experiments with ion exchanger followed by batch and flow cell experiments. Zirconium phosphate was found to hydrolyse to zirconium hydroxide after prolonged exposure to high alkaline solutions. Actual low radioactive materials were tested against weak acid exchanger IRC 84 and zirconium phosphate. Titanium phosphate was not used because of its

high electrical resistance resulting in a high applied voltages to drive the required current.

The development of the flow cell involved a membrane sandwiched between two perspex walls sealed with rubber gaskets. Different configurations were used to test the flow profile and pressure gradient. One of the later flow cell designs can be seen in Figure 3.7 in which stacks of electrodes were combined to produce a cell with multiple active electrodes.

Bridger et. al (1991) summarised the work carried out at AEA, Harwell. Description of the basic EIX cell was given along with a number of experiments conducted for removal of sodium, caesium and cobalt. The conclusion of the work was the development of an electrochemical cell capable of long working life with chemical and mechanical stability.

The overview of the earlier work formed the basis for the studies discussed in the next few chapters with limited initial investigation carried out by Pütz (1991) and a preliminary assessment of electrochemical ion exchange by Cumming (1992). The following were the objectives of the work carried out at Loughborough University described in Chapters 5-10:

- Assessment of the EIX process
- Evaluation of the cell design
- Development of a mathematical model
- Consider different operational strategies
- Examination of the process on pilot plant scale.

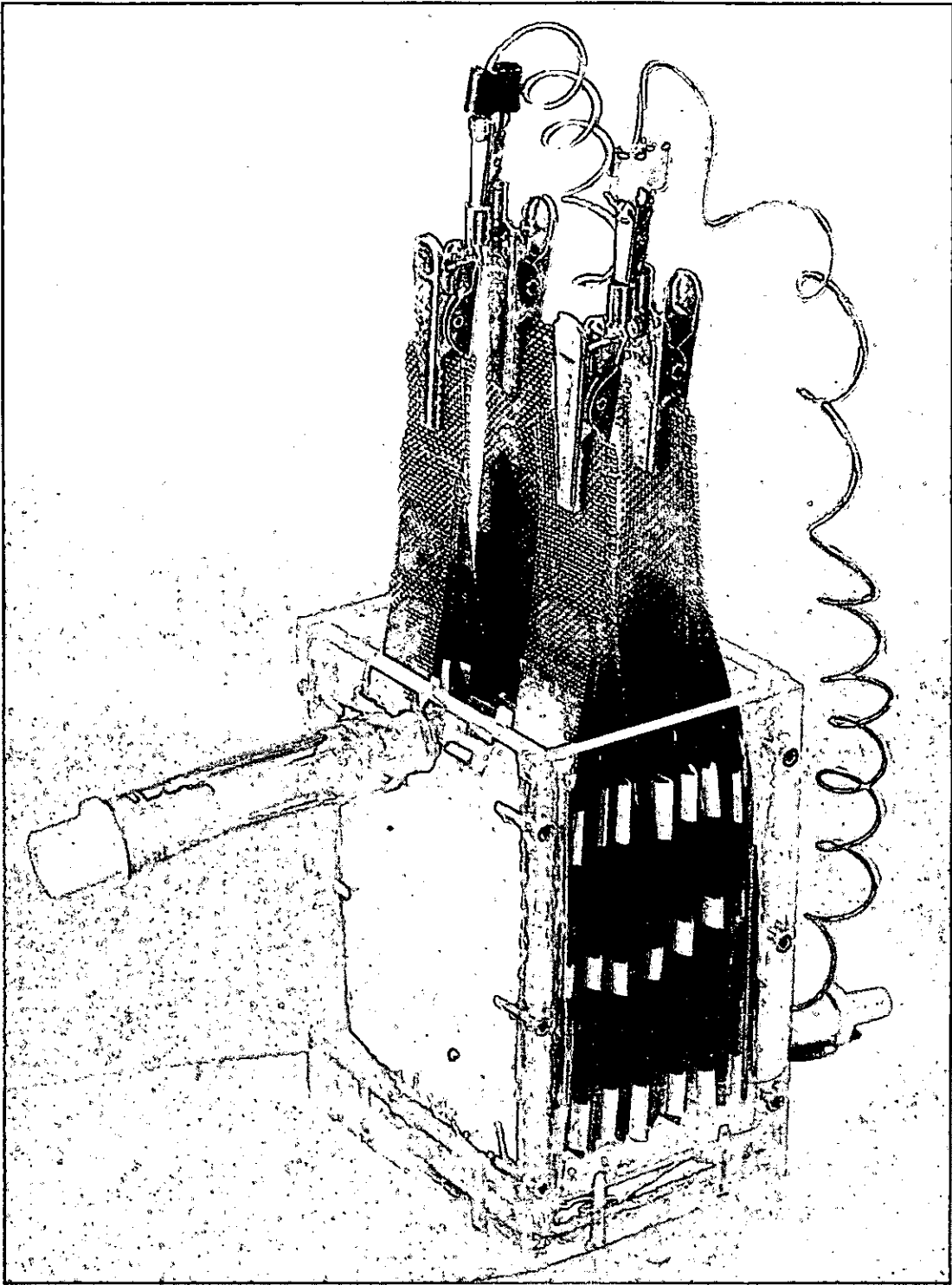


Figure 3.7: Multi membrane flow cell

CHAPTER 4

THEORETICAL BACKGROUND

4. INTRODUCTION

The Electrochemical ion exchange (EIX) cell discussed in the rest of the thesis considers variants on the design described in this chapter. EIX is a two stage process, transport of ionic species to the surface of an ion exchange material and removal of the ions from solution within the membrane by sorption. Both processes are controlled by an applied electric potential. This potential is applied across the membrane by a current feeder electrode embedded in the material and a counter electrode placed on the opposite side of the membrane. The membrane is made of binder and ion-exchanger (weak acid or base) materials. An EIX cell consists of a combination of membranes and electrodes as seen in Figure 4.1. The detailed design of the cell body can be seen in Figure 4.2.

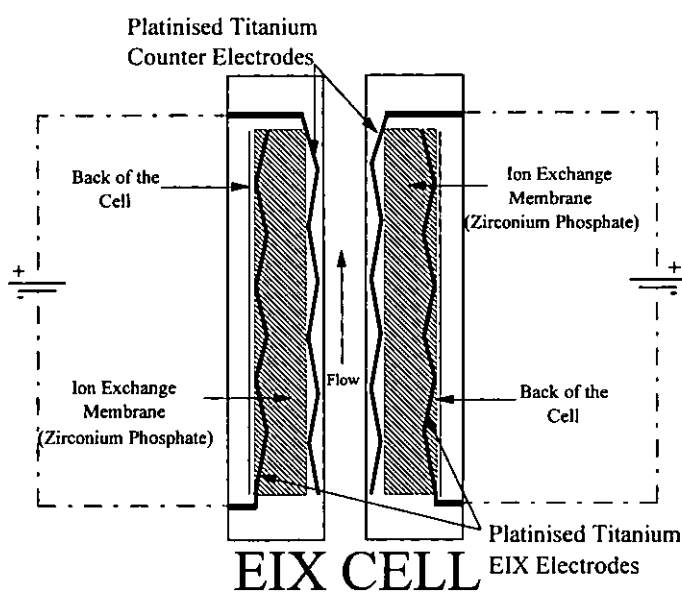


Figure 4.1: An Electrochemical Ion Exchange (EIX) cell

Application of EIX had been mainly focused on the nuclear industry in particular to reducing levels of contaminants to authorised limits and minimisation of overall waste. However, there are other areas of non-nuclear

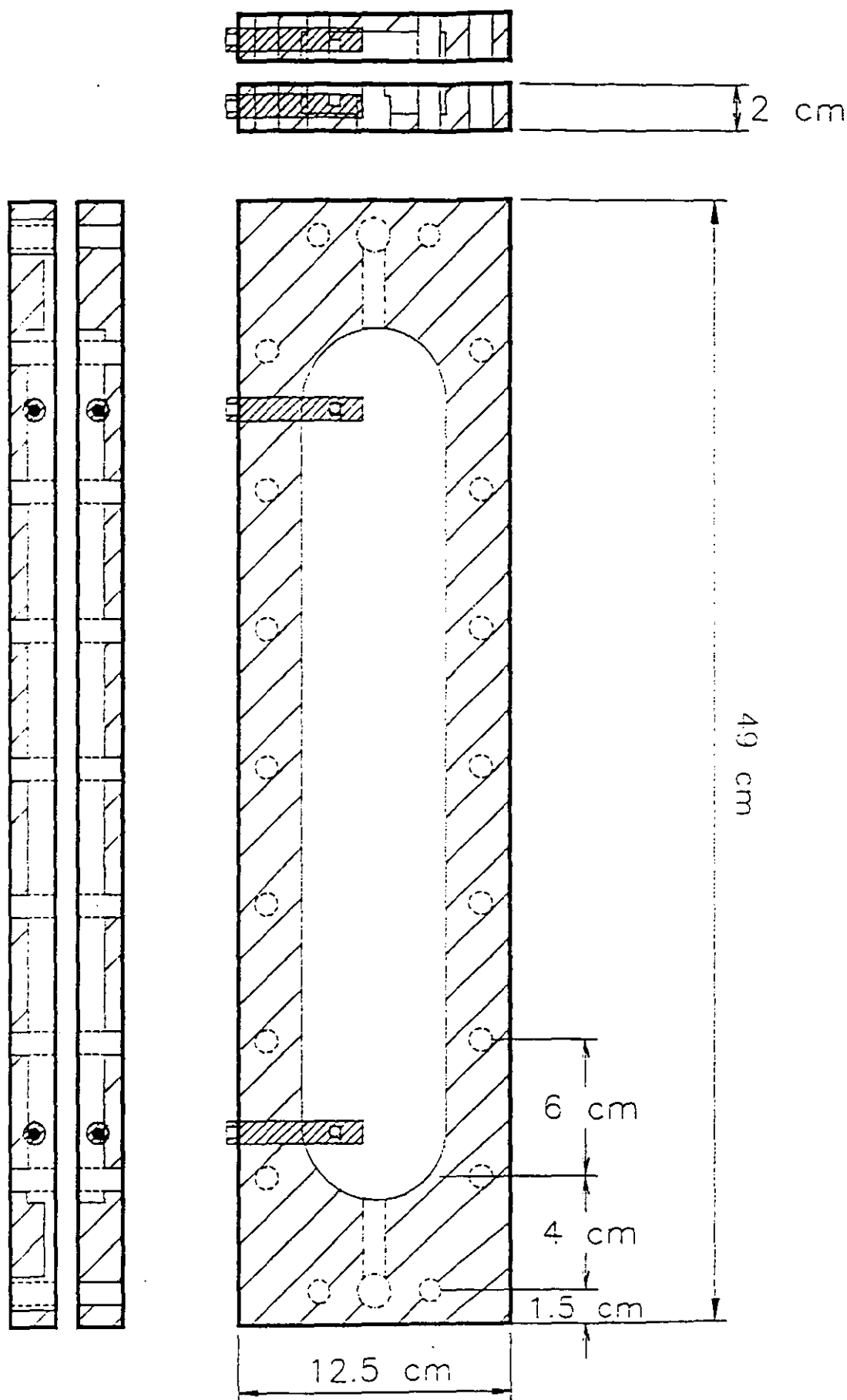


Figure 4.2: Mechanical design of the EIX cell

applications which have been investigated such as water deionisation and corrosive anion removal.

There are two terms that are used extensively in this chapter and need further elaboration, adsorption and absorption. The term absorption is used to indicate the movement of ions from the bulk solution into the membrane which leads to increase in the concentration of these ions. Adsorption is used when the metal ions are actually removed from solution and are fixed onto the surface of the ion exchange resin by sorption.

4.1 Mechanism

Several processes are an inherent part of the EIX process:

- i) Water dissociation
- ii) Ion exchange
- iii) Migration of ionic species.

The overall mechanism of the process can only be described by references to each one of these. The schematic diagram of the processes during cationic absorption can be seen in Figure 4.3.

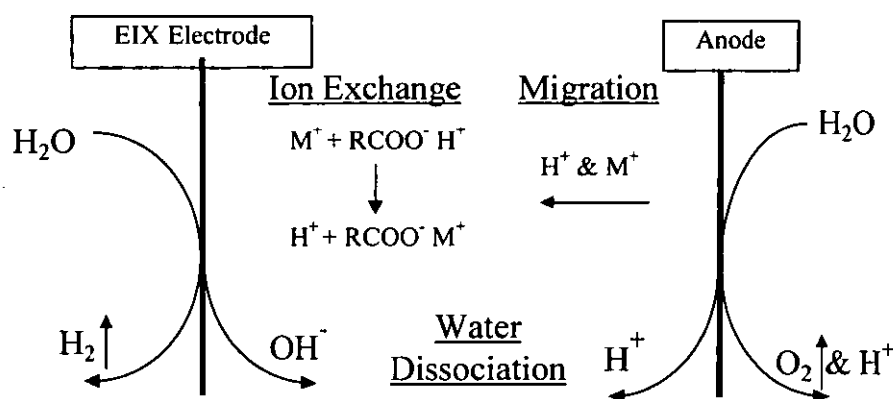
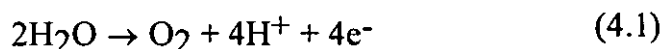


Figure 4.3: Key processes during cationic absorption

4.1.1 Water Dissociation

By applying an applied potential across an aqueous system, water is oxidised at

the anode and reduced at the cathode. Dissociation of water can be represented by Equation 4.1:



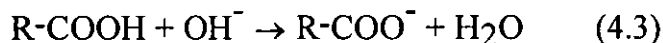
This produces oxygen and lowers the solution pH. The reduction reaction is in the form of:



The above reaction involves hydrogen evolution and an increase in the pH. These two reactions are at the core of the electrochemical process and play a crucial role in the absorption and elution cycles.

4.1.2 Ion-Exchange Activity

Generally, weak acid cation exchangers or basic anion exchangers are used in the construction of EIX electrodes since the process is easily reversed. Cation and anion exchange both consist of two reactions, activation and adsorption. In cationic exchange, the weakly acidic groups present on the resin, such as carboxylic acid groups, lose a proton to obtain an overall negative charge demonstrated by Equation 4.3:



where R is a polymeric chain in the resin. In the solution, there are cations (M^+) that are absorbed on to the resin represented by equation 4.4:



The elution process is the reverse of the above two equations where the

carboxylic group is regenerated.



Corresponding anion exchange reactions occur with the carboxylic group in the resin usually replaced by secondary or tertiary ammonium groups. The activation, adsorption and elution reactions are represented by the following equations.

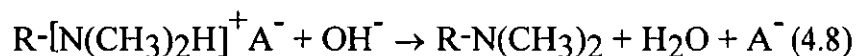
Activation



Adsorption



Elution



4.1.3 Ionic Migration

Ionic species are forced to move towards their respective electrodes under the influence of the potential applied across the cell. During the absorption cycle, the cathode placed within the membrane produces hydroxyl ions which encourages the deprotonation of the resin. The cations (i.e. metal ions) from the bulk of the liquid are transported and adsorbed onto the resin. The circuit is completed by a corresponding reaction occurring at the anode. The pH of the external solution falls due to production of hydrogen ions at the anode.

The reverse is true during anion exchange where hydrogen ions produced at the anode encourage the protonation of the resin. Hydrogen ions competing for active sites on the resin reduce the efficiency of the cell. Similar processes

occur during elution. The influence of these processes is partly dependent on pH and buffer capacity of the feed solution.

4.2 Theoretical Background

The basic principles of ion exchange (Helfferich (1962)) and electrochemical processes (Pickett (1979)) are discussed in the literature. The EIX system is a complex system and difficult to describe mathematically. In an EIX system fluxes of several ionic species are coupled together, fluxes may have several components of diffusion, electrical potential and convection. Further complications may arise due to the selectivity of the ion exchanger, specific interactions between ions in solution, electrolyte sorption and desorption, mass transfer at the electrode surface, mass transfer within the ion exchanger and variation of solution concentrations in the bulk. With so many parameters, the system cannot be described simply. However, it can be approximated by fluxes of the ionic species due to diffusion, migration and convection.

4.2.1 The Flux Equation [Pickett, 1979]

Ionic transfers under applied electrical potential are caused by migration, diffusion and convection. Ionic migration occurs due to differences in chemical potentials of the ions present. The motion of species i is proportional to the chemical potential. The basic equation in one-dimension (x -direction) is given by:

$$v_{ix} = -k_i \frac{d\mu_i}{dx} \quad (4.9)$$

where v_{ix} is the velocity of species i in the x direction, $d\mu_i/dx$ is the chemical potential gradient and k_i is a proportionality constant. The equation can be written in vector form but for presentation purposes it is expressed in one-dimension. This assumes k_i is independent of other ionic species present which holds for dilute solutions. Equation 4.9 can be more properly defined by using

an average velocity of the system v_x , representing a convective velocity component. Therefore, we can write equation 4.9 as:

$$v_{ix} = -k_i \frac{d\mu_i}{dx} + v_x \quad (4.10)$$

In an electrochemical system the chemical potential, μ_i , depends on the electrical state of the system determined by the applied potential. This can be expressed by:

$$\left(\frac{\partial \mu_i}{\partial \Phi_s} \right)_{C_i} = z_i F \quad (4.11)$$

where Φ_s is an arbitrary solution potential, z_i the valency of species i and F Faraday's constant. Equation 4.11 represents the relationship between differences in chemical potentials associated with differences in electrical work at constant concentration C_i . Variation in μ_i can also be represented as:

$$\mu_i = f(C_i, \Phi_s) \quad (4.12)$$

The chemical potential μ_i of species i is related to the activity a_i and standard chemical potential μ_i° by:

$$\mu_i = RT \ln a_i + \mu_i^\circ \quad (4.13)$$

Using equation 4.12 we can obtain the differential form:

$$\frac{d\mu_i}{dx} = \left(\frac{\partial \mu_i}{\partial C_i} \right)_{\Phi_s} \cdot \frac{dC_i}{dx} + \left(\frac{\partial \mu_i}{\partial \Phi_s} \right)_{C_i} \cdot \frac{d\Phi_s}{dx} \quad (4.14)$$

The first partial derivative in equation 4.14 can be obtained by differentiating

equation 4.13 after putting the activity a_i equal to molal concentration C_i .

$$\left(\frac{\partial \mu_i}{\partial C_i} \right)_{\infty} = \frac{\partial(RT \ln a_i + \mu_i^*)}{\partial C_i} = \frac{RT}{C_i} \quad (4.15)$$

Substituting equations 4.11 and 4.15 into 4.14 gives:

$$\frac{d\mu_i}{dx} = \frac{RT}{C_i} \frac{dC_i}{dx} + z_i F \frac{d\Phi_s}{dx} \quad (4.16)$$

By placing equation 4.16 in 4.10 we obtain

$$v_{ix} = -k_i \frac{RT}{C_i} \frac{dC_i}{dx} - k_i z_i F \frac{d\Phi_s}{dx} + v_x \quad (4.17)$$

The flux N_{i_x} of species i in the x direction can be given by:

$$N_{ix} = C_i v_{ix} = -k_i RT \frac{dC_i}{dx} - C_i k_i z_i F \frac{d\Phi_s}{dx} + C_i v_x \quad (4.18)$$

where the flux is the number of moles of i flowing through unit area normal to the x direction per unit time. Equation 4.18 represents the ionic transfer at steady state or at an instant in time. Taking the diffusion coefficient D_i expression:

$$D_i = k_i RT \quad (4.19)$$

and extending it to an ionic species then:

$$N_{ix} = -D_i \frac{dC_i}{dx} - \frac{D_i}{RT} C_i z_i F \frac{d\Phi_s}{dx} + C_i v_x \quad (4.20)$$

where :

N_{ix} Molar flux of the i th species in the x plane through a unit area of membrane per unit time, $[\text{mol.m}^{-2}.\text{s}^{-1}]$

D_i Diffusion coefficient, $[\text{m}^2.\text{s}^{-1}]$

C_i Concentration of i species, $[\text{mol.m}^{-3}]$

z_i Valency of i ,

F Faraday's constant, $[\text{C.mol}^{-1}]$

R Gas constant, $[\text{J.mol}^{-1}.\text{K}^{-1}]$

T Temperature, $[\text{K}]$

$d\Phi/dx$ Potential gradient, $[\text{V.m}^{-1}]$

u_x Velocity, $[\text{m.s}^{-1}]$

x Linear direction

Equation 4.20 is known as the Nernst-Planck equation. The terms of the equation from left to right represent the ionic flux due to diffusion, migration due to potential gradient and convection. The potential gradient term $d\Phi/dx$ has no meaning in any real physical system since the concentration is not uniform throughout the bulk of the system. However, this can be used in simple applications.

4.3 Nernst-Planck Equation

Two main arguments exist against the validity of the Nernst Planck equation and these have been put forward by Buck (1984). The first was based on the macroscopic nature of the derivation averaging over particles and membrane assuming a parallel piped model and ignoring any microscopic inhomogeneity. The second is that assumptions are made that activity coefficients of different charge species are independent of each other which is not true particularly for concentrated solutions. Based on these it is surprising that Nernst-Planck equation has been successfully applied to heterogeneous and homogeneous ion exchange membranes. This is probably due to the equation using spatially averaged parameters obtained by macroscopic methods.

The Nernst-Planck equation is limited in its application particularly when modelling the intrinsic and microscopic aspect of membrane processes. Here the main considerations were overall and averaged transport of charged ionic species from the bulk into the membrane. The equation was suited to the purpose of the work described here. A model was set up to consider the net transport of material from the bulk liquid to an interface and the flux produced by the current is balanced by continually changing concentration in the bulk. This is described in detail in Chapter 8.

4.3.1 Alternatives

There are alternative models that can be applied to the ionic transport in membranes. Irreversible thermodynamics was applied to binary systems by Miller (1966). Bearman and Kirkwood (1958) considered statistical mechanics as a method of obtaining equations of transport in multicomponent systems.

Chemical engineers tend to use the Stefan-Maxwell equation (Cussler (1971), Wesselingh and Krishna (1990)) as an alternative approach. The Stefan-Maxwell equation can also be applied to a host of mass transfer processes ranging from multicomponent separation to ion exchange. However, the presence of multiple charge species in the system which affect the activity of one another complicate the model and renders it difficult to use.

4.4 Other Considerations

The system here can be represented if other fundamental requirements can be defined. There is the electroneutrality condition or charge balance. It can be expressed in the form of:

$$\sum_{i=1}^{i=n} z_i C_i = 0 \quad (4.21)$$

This means that there is no net charge in the system. The change of ionic concentration due to various processes (i.e. formation of hydrogen and hydroxyl ions at the electrodes). These must be accounted for by an overall material balance around the system. These considerations allow the EIX process to be described very simply and a model based on this approach is described in Chapter 8.

CHAPTER 5

EXPERIMENTAL I: Operating Variables

5. INTRODUCTION

The next five chapters will describe the main methods employed to reach these objectives and the main results will be highlighted. This chapter will outline the materials and procedures applied in standard experiments as well as a discussion of results. In any subsequent discussion of experimental methods, only modifications to the basic experimental procedure will be described. Overall conclusions will be stated and discussed in relation to data obtained.

Pütz (1991) conducted early experiments on some aspects of the electrochemical ion exchange cell. Detailed examination of the process and cell were needed for further development. Experiments were conducted in absorption and elution mode to assess the performance of an EIX flow cell in relation to process parameters. These process variables were flow rate, current density, feed pH, feed concentration, gap between electrodes and space between the membrane surface and the counter electrode. Different ion exchange resins were also used to assess their suitability for use in EIX membranes. Their performance was tested under different experimental conditions.

5.1 Experimental

A basic experimental procedure was used to investigate the relationship between process parameters and performance of an EIX cell. The test equipment included a power supply, peristaltic pump, pH meter and an EIX cell. The equipment was set up as shown in Figure 5.1.

5.1.1 Equipment

The power supply was a Thurlby PL320QMD. Two basic Pumps were used. For lower range of flow rates a Watson-Marlow model 101U/R was used. A

Watson-Marlow model 302S/RL was used to generate higher flow rates. The appropriate pump tubing was selected to obtain the desired flow rate. Silicone tubing was supplied by Watson-Marlow. The pH was measured by a Philips PW9420 pH meter.

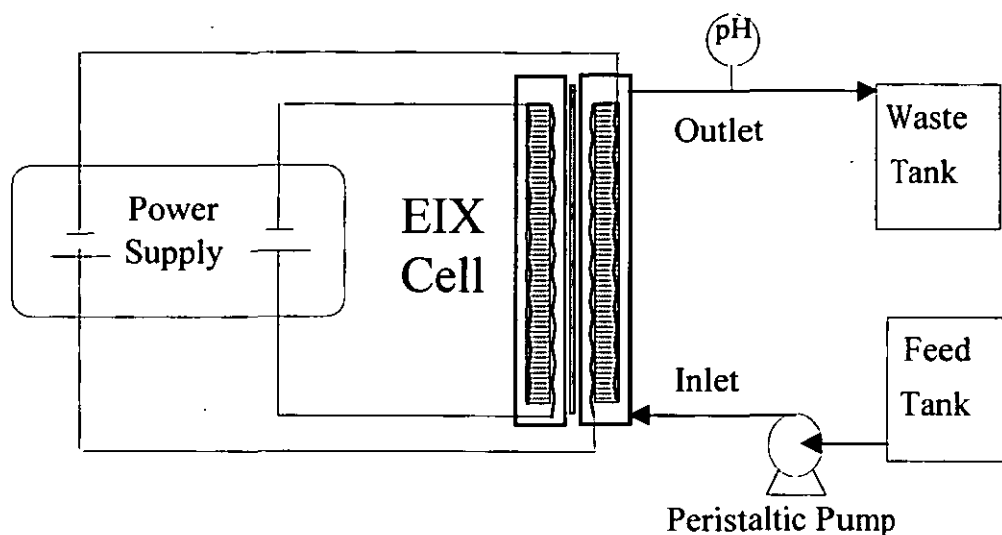


Figure 5.1: Schematic diagram of the process

5.1.2 Method

Feed solutions were prepared by dissolving in distilled water required quantities of laboratory grade metal nitrate salts obtained from Fisher Scientific, UK. The feed pH was adjusted using laboratory grade nitric acid solution or sodium hydroxide solution prepared from laboratory grade pellets. A peristaltic pump was used to pump the solution through the flow cell in a single pass or recycle mode. In single pass mode, the feed solution passed through the cell only once. In recycle mode, the solution was circulated through the cell and back into the feed tank. This was continued until the required outlet concentrations or pH was obtained. A maximum of 32 V and 2 A could be applied across each half cell by the power supply. The flow from the top of the cell was passed through a weir to enable the pH of the outlet solution to be measured. The overflow from the weir was collected in a waste tank. The weir was used to allow easy

collection of samples and for continuous pH measurement. Sample solutions were taken from the outlet stream and the effluent was collected. The total amount of metal removed was calculated by measuring the metal ion concentration in solution leaving the cell and in the waste tank. The feed was gradually decontaminated from the inlet at bottom of the cell through to the outlet at top of the cell. The gases produced during electrolysis left the cell at the top through the outlet.

5.1.3 EIX Cell

The earlier work carried out by AEA Harwell laboratories resulted in a cell described by Turner (1987). This was similar to the cell used during this work but any modifications made to this design are discussed in the following sections. Detailed drawing of the cell can be seen Figure 4.2. The basic cell consisted of two blocks of perspex, each 490 mm by 125 mm and 20 mm thick. Each block supported a half cell made up of an EIX electrode and a counter electrode as seen in Figure 5.2.

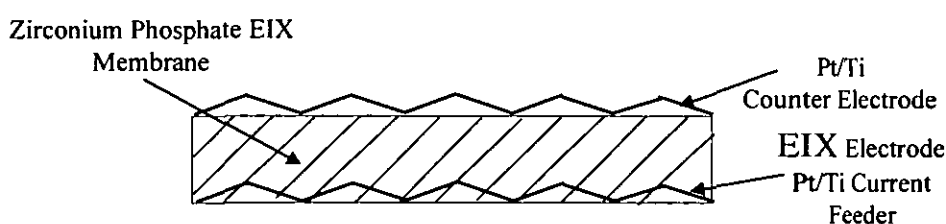


Figure 5.2: Diagram of the EIX half cell

A volume, 280 mm by 63 mm by 5 mm, was cut out of each half block of perspex body to hold the EIX membrane. The EIX electrode consisted of a platinised titanium mesh embedded in an ion exchange membrane. The counter electrode was a platinised titanium mesh placed on the opposite side of the membrane to the current feeder electrode.

The ion exchange membranes were made by AEA by mixing a standard mixture of milled ion exchange material (zirconium phosphate), binder and solvent. The ion exchange material was grounded to about 100 μm in size to

enhance its kinetics performance. The binder material was Kraton, a copolymer of styrene and butadiene, and the solvent used was 1,1,1-trichloroethane. The mixture was then poured into a mould containing a piece of platinised titanium approximately 6.3 cm by 28 cm, with an area of 176.4 cm². It was allowed to stand in a fume cupboard until all the solvent had evaporated and the membrane was dry. The dried membrane was placed in the perspex half cell with an external connection to the power supply.

Cells containing zirconium phosphate membranes were run in absorption mode to ensure that all the excess phosphates were removed from the membrane before being used for actual absorption experiments

The contacts were platinum rods that were placed in holes drilled through the perspex wall. The rods were sealed with a gasket to stop leakage of electrolyte out of the cell. The circuit was completed by a metal mesh counter electrode, with an area of 176.4 cm² which was similarly connected to the external power supply.

The complete cell was made up from two half cells which were sealed by a silicone rubber gasket. The cell arrangement can be seen in Figure 5.3. At the centre of the cell, the two counter electrodes faced each other with a gap to allow the solution to pass between them. The standard gap was 4.7 mm and several tiny non-conducting spacers were used to avoid direct contact between the two counter electrodes.

The inlet and the outlet were openings at the bottom and top of one half cell. The main bulk of the experiments were conducted using zirconium phosphate membranes. However, some experiments were conducted using chelating ion exchange resins manufactured by Purolite International Ltd., UK.

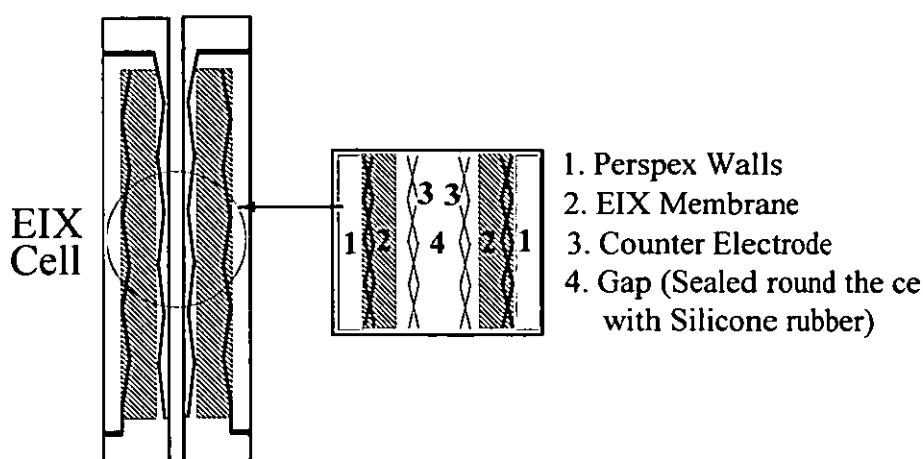


Figure 5.3: The cell set up and expanded view of the cell

5.1.4 Zirconium Phosphate

Zirconium phosphate may be prepared either by precipitation with phosphoric acid from acidic solution of suitable zirconium salts, or by treatment of zirconium oxide with phosphoric acid (Amphlett, 1964). The ion exchange properties of zirconium phosphate were originally demonstrated when columns containing finely divided powder supported on silica wool were used to separate uranium and plutonium from fission products.

In granular form, zirconium phosphate has high physical stability even at 300 °C. In alkaline solutions, the replacement of phosphate by hydroxyl ion is appreciable, particularly at high temperatures. The stability of zirconium phosphate towards hydrolysis at pH greater than 7 appears to vary according to the method of preparation. Zirconium phosphate undergoes hydrolysis in strongly alkaline solutions but can be regenerated by phosphoric acid. The structure of zirconium phosphates crystals was described by Alberti et. al. (1996). Ion exchange and intercalation properties of metal phosphates were also discussed.

Chemical and infra-red spectral evidence suggests that ion exchange in zirconium phosphate involves hydrogen ions in acid phosphate groupings. The

material is also hydrophilic and possesses up to three times as many proton sites as typical sulphonic acid resins. Acidity of the phosphoric acid groups is intermediate between those of fully-ionised sulphonic groups of strong acid resins and of weak acid carboxylic groups in weak acid resins. Zirconium phosphate behaves as an efficient cation exchanger in acidic solutions, whereas weak acid resins such as Amberlite IRC-50 function at or near neutral pH. The saturation capacity of zirconium phosphate increases from 0.5 meq.g⁻¹ in acid solution to as high as 6 in alkaline media. Its selectivity for univalent cations follows a similar pattern to those of strong acid resin:



Rare earth metals are less strongly adsorbed than alkaline earth metals from acidic solutions. Caesium and rubidium are very strongly adsorbed relative to the other alkali metals.

5.1.5 Analysis

Sample solutions were analysed by a Perkin Elmer 1100 atomic absorption spectrometer in flame mode. The following wavelengths were used: 213 nm for zinc, 232 nm for nickel, 324.8 nm for copper, 589 nm for sodium and 852.1 nm for caesium. Analysis was also carried out using a Dionex 4500i ion exchange chromatograph with an IONPAC CS12 column and a conductivity detector. The transition group metals were analysed using an IONPAC CS5 column and reaction with a reagent in conjunction with a Perkin-Elmer Lambda 2 UV/VIS spectrometer. The reagent was made up of 0.4 mM 4-(2-pyridylazo) resorcinol (PAR), 3M Ammonium hydroxide and 1 M Acetic acid. The eluant was 50 mM oxalic acid, 95 mM lithium hydroxide and 5 mM sodium sulphate with a pH of 4.8. The spectrophotometer was Perkin-Elmer UV/VIS spectrometer Lambda 2.

5.1.6 Chemicals

Atomic absorption Standards were made up from analytical grade 1000 ppm standard metal solutions supplied by Fisher Scientific, UK. Nitrate salts of

sodium, zinc, copper and nickel were used as the source of the metal cations for the experiments described unless otherwise stated. These were all laboratory grade chemicals supplied by Fisher Scientific, UK. Caesium chloride was used as the source of caesium cations. Laboratory grade nitric acid (Sp. Gr. 1.42) solution and sodium hydroxide pellets were used to make dilute solutions to adjust the feed pH. Both of these chemicals were supplied by Fisher Scientific, UK. The zirconium phosphate used by AEA, Harwell laboratories was supplied by Magnesium Elektron.

5.2 Operating Variables

The first series of experiments were conducted to obtain a comprehensive set of data over a wide range of operating parameters. Six main variables were selected based on their importance to the cell design. These were flow rate, feed pH, feed concentration, current density, electrode gap and membrane gap.

5.2.1 Electrode Gap

The electrode gap was the distance between two half cells as shown in Figure 5.4a. This was adjusted by placing either several gaskets between each half cell or by sealing the two half cells with a thin strip of silicone rubber, approximately 1 mm thick. The gap was kept constant between the two counter electrodes by introducing small pieces of silicon rubber of different thickness between them.

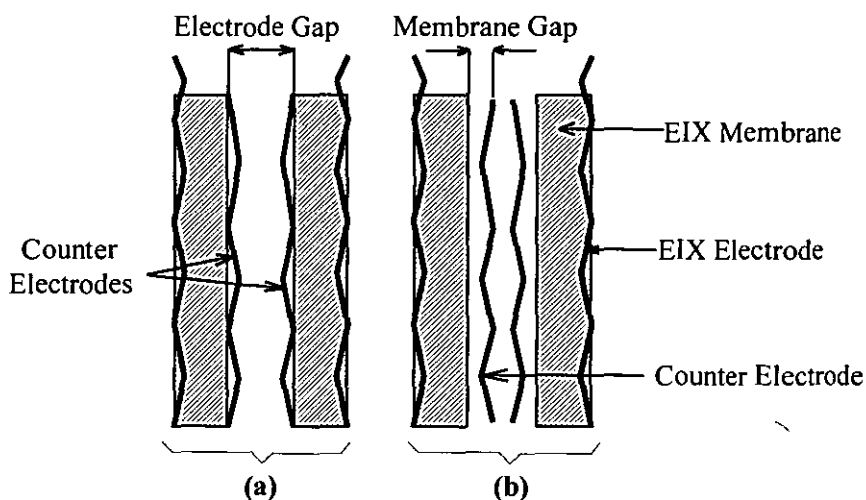


Figure 5.4: a) Electrode Gap b) Membrane Gap

The gap was measured by placing plasticine between the two counter electrodes. The cell was then put together, taken apart and the thickness of the plasticine measured to give both the distances between the counter electrodes and the surface of the membranes. The reported gaps were the average of the two. Experiments were conducted for gaps of 2.8, 4.7, 6.4 and 8.8 mm.

5.2.2 Membrane Gap

A series of experiments were carried out to evaluate the performance of the zirconium phosphate cell with increasing gap between the counter electrode and the membrane. The membrane gap can be seen in Figure 5.4b as the distance between the counter electrode and the surface of the EIX membrane. Experiments were conducted with a feed concentration of about 300 mg.l^{-1} of sodium, feed pH of 3 and 12 and current density of 3 mA.cm^{-1} . The flow rates were between 0.6 and 10 l.h^{-1} .

In a series of experiments, two central counter electrodes were replaced by a single counter electrode with a gap about 5.7 mm from each membrane to the counter electrode. The gaps were between 1 to 3 mm and were measured by placing plasticine between the electrodes and the membranes as discussed in Section 5.2.1.

In a standard half cell, the counter electrode was pressed hard against the outer surface of the membrane with no space between them. Unless stated otherwise, experiments were carried out for an electrode gap of 4.7 mm and a membrane gap of 0 mm.

5.2.3 Flow Rate

The Flow rate referred to here was the rate of the solution passing through the cell. This was changed by altering the pumping rate of the peristaltic pump. The flow rate was calculated based on the volume of solution leaving the cell

over a certain time period. There were variations in the flow rate which were thought to be due to the friction between the pump parts and tubing. These were kept to about 5% by monitoring the flow rate throughout the experiments and adjusting pumping rate accordingly.

By changing the flow rate, the effect of superficial velocity and residence time on the performance of the cell were examined. This series of experiments were also used to estimate a realistic throughput of solution that could be treated by the EIX cell. All the flow rates used were in the low Reynolds numbers range indicating a laminar flow regime. The maximum flow rate was $3.3 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$ corresponded to superficial velocities of $11 \cdot 10^{-3} \text{ m} \cdot \text{s}^{-1}$. A rectangular duct with dimensions $6.3 \cdot 10^{-3} \text{ m}$ by $4.8 \cdot 10^{-3} \text{ m}$ cross section would give a Reynolds numbers of 98 based on a hydraulic mean diameter d_m of $8.9 \cdot 10^{-3} \text{ m}$, where:

$$\text{Reynolds number } Re = u d_m \rho / \mu \quad (5.1)$$

$$\text{Hydraulic mean diameter } d_m = 2 d_a d_b / (d_a + d_b) \quad (5.2)$$

and u is superficial velocity

d_a is length of the flow channel, m

d_b is width of the flow channel, m

Density of water $\rho = 1000 \text{ kg} \cdot \text{m}^{-3}$

Viscosity of water $\mu = 10^{-3} \text{ N} \cdot \text{s} \cdot \text{m}^{-2}$

5.2.4 Feed pH

The feed pH was adjusted by using nitric acid or sodium hydroxide solutions. This gave an indication of the level of interference caused by hydrogen ions. The limits of the process were examined under extreme pH conditions when using sodium. All experiments using copper, nickel and zinc were carried out under acidic conditions to avoid precipitation. In the event of precipitation occurring, the overall removal would be enhanced but it would not be a true measure of metals removed by ion exchange. The precipitation of heavy metals in the bulk solution was assumed to be negligible in this series of experiments.

5.2.5 Feed Concentration

The affects of altering the metal ion concentrations on the process were also examined. The cation concentration in the feed solution ranged between 0.02 and 6 g.l⁻¹. The effect of changes on the process were examined and the concentration limits of electrochemical ion exchange established.

Some experiments were carried out to test selectivity of the ion exchange membranes by combining two or mores metal ions such as sodium, caesium, copper, nickel and zinc in the feed. Experiments were carried out on membranes both in hydrogen form and sodium form. Membranes were repeatedly loaded and unloaded with metal ions and their performance evaluated after each absorption and elution cycles.

5.2.6 Current Density

There were two ways of operating the electrochemical cell, either under constant current or constant voltage. Under constant current conditions, the applied voltage changed to keep the current steady. At constant voltage, the current was varied to meet system requirements. It was decided to conduct experiments under constant currents so the electrical efficiency of the process could be more easily related to the amount of ions removed by the process. Current density was the applied current per unit area of membrane.

The range of values used for these parameters can be seen in Table 5.1.

Table 5.1: Lower and Upper limits of parameters

Parameters	Minimum	Maximum
Flow rate [l h ⁻¹]	0.2	12
Feed pH	1	12
Cation feed concentrations [g l ⁻¹]	0	6
Current density [mA cm ⁻²]	0.5	15
Electrode gap [mm]	2.8	8
Membrane gap [mm]	0	5.7

Only one variable was changed at a time to eliminate any interference from other parameters.

Percentage removal was used to interpret data and for presentation purposes. It is defined by:

$$\text{Percentage Removal} = \frac{(\text{Inlet Concentration} - \text{Outlet Concentration})}{\text{Inlet Concentration}} \cdot 100$$

the electrical efficiency is defined by:

$$\text{Electrical efficiency} = \frac{\text{Current carried by target ion}}{\text{Total current}} \cdot 100$$

5.3 Purolite Membranes

Experiments were carried out using ion exchange resin other than zirconium phosphate. The other ion exchange membranes used were Purolite S930 and Purolite S950, both cationic chelating resins.

Purolite S930 is a polystyrene based resin with iminodiacetic base groups used for removal of heavy metals from solution containing high concentration of univalent and divalent cations. The pH operating range in the hydrogen form is 2 to 6 and in the sodium form is 6 to 11.

Purolite S950 is a aminophosphonic acid chelating resin designed to remove cations of toxic metals such as lead, copper, zinc from effluents at low pH. Purolite S950 is selective for a range of both heavy metals and divalent ions depending on the conditions it is operated under. It has similar pH operating range to the Purolite S930.

All Purolite membranes contained non-ionic surfactant used in their manufacture and these were removed before use. The cells were rinsed with distilled water at low flow rates until there was no sign of any froth leaving the cell. In all, the cells were rinsed with 40 l of distilled water.

All Purolite membranes were received in sodium form, the cells were run in absorption mode without any metal cations present in the feed solution. A feed pH of 3 and a current density of 3 mA.cm^{-2} were used. This was to examine the leakage of sodium from the membranes during absorption mode. The current density of 3 mA.cm^{-2} was the maximum the power supply could provide. The applied voltage was not sufficient to drive any higher current across the electrodes, particularly at higher flow rates.

Experiments were continued to assess the performance of the Purolite membranes in the sodium form. Flow rates between 0.6 and 10 l.h^{-1} were used to investigate the removal of caesium by the Purolite membranes. It had been previously found that precipitates were forming during absorption experiments of the transition metals copper, zinc and nickel. Caesium was used because it did not precipitate at high pH. So the concentration build up of material could be detected without interference from precipitation.

After several early experiments, the back of the cell was sealed and the bare parts of the EIX membranes exposed at the bottom of both half cells covered as shown in Figure 5.5. It was thought that the large amount of precipitation was due to easy access of the hydroxyl ions produced at the EIX electrode to the bulk solution. The cell was sealed by applying a silicone sealant round the edges between the membrane and the cell wall. The bare part of the EIX electrode were covered with binding material containing solvent and rubber

mixture but no ion exchange resin. Experiments were conducted to compare the performance of the cell before and after modifications.

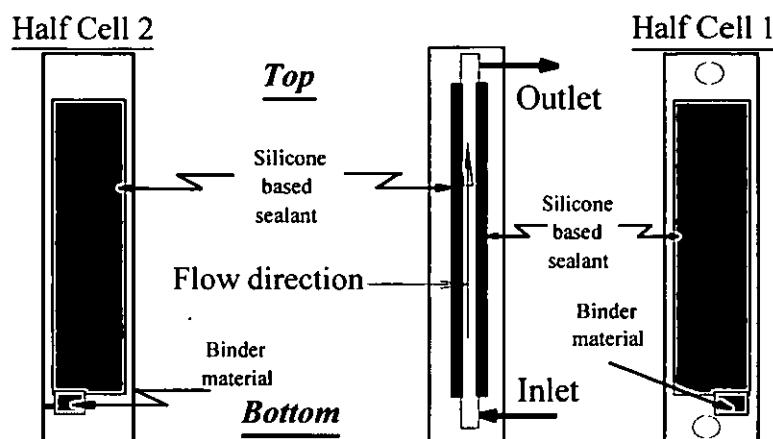


Figure 5.5: Points of application of sealant

Several experiments were carried out to examine the removal of zinc by the S950 and S930 membranes. The experiments were conducted with a feed concentration of about 30 mg.l^{-1} zinc, feed pH of 3.5 and current density of 3 mA.cm^{-2} . The cells were then eluted until there was no change in the outlet concentration or pH. It was assumed that the membranes were then in hydrogen form.

Experiments were conducted to study the performance of the Purolite membranes in the hydrogen form. Initially, the absorption of Caesium was examined followed by experiments conducted to test the absorption of zinc. These were carried out for a current density of 3 mA.cm^{-2} , feed pH of 3 and feed concentration of 30 mg.l^{-1} of zinc. The flow rates used were between 1 and 10 l.h^{-1} .

5.4 Operating Variables: Results

Initially a series of tests were carried out to determine the time to reach pseudo equilibrium i.e. constant outlet conditions. These were followed by over one

thousand experiments to examine the relationship between individual parameters and process performance. Only one parameter was changed at a time, after each change, it was necessary to wait until steady state was reached to take samples and readings. The condition of membranes was continuously changing as the ion exchange resins were loaded and unloaded. Parameters were changed in a random way to avoid any discrepancy between the experimental results and the order in which experiments were conducted.

As shown Figure 5.6 the time needed to reach steady state was between 10 and 20 minutes, for a current density of 1 to 5 mA.cm⁻² and flow rate of 0.9 l.h⁻¹. The average volume of solution contained in each cell was about 130 ml. In terms of bed volume (BV), this meant that 2 to 3 BVs had to pass through the cell for it to reach pseudo steady state. This agreed well with the value of 5 BV recommended by AEA Harwell. At lower flow rates and current densities, longer time would be required to reach pseudo steady state due to longer residence time of solution and less mixing within the cell.

5.4.1 Flow Rate

Early experiments were carried out using zirconium phosphate membranes. These indicated a reduction in removal of sodium ions with increasing flow rate. The results can be seen in Figure 5.7 for current density of 6 mA.cm⁻² and in Figure 5.8 for current density of 1 mA.cm⁻². In the earlier experiments, the flow rates were limited by the size of the peristaltic pump, a larger pump was used to obtain a wider range of flow rates.

Experiments were carried out on using new membranes termed membrane 1 as represented by triangular symbols in Figures 5.7 and 5.8. These were repeated

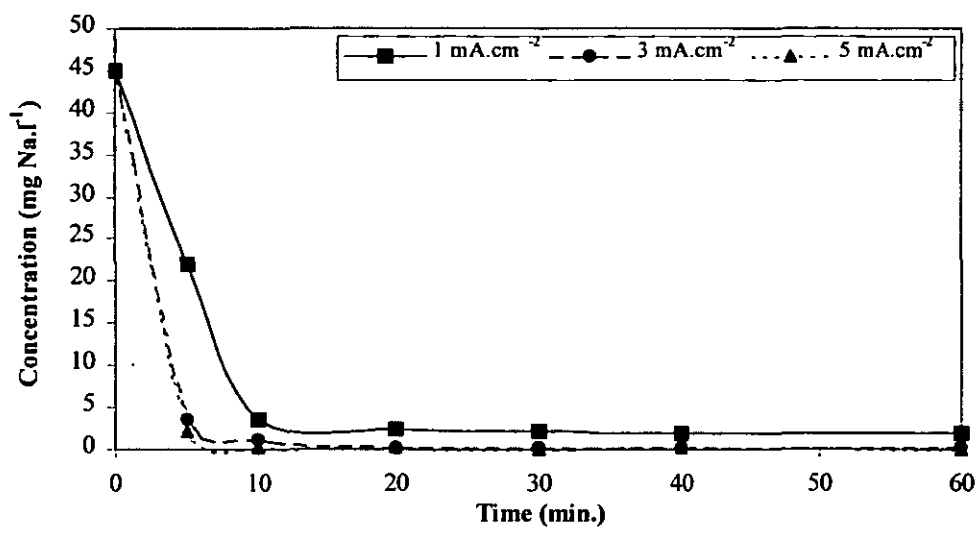


Figure 5.6: Time required to reach steady state for different current densities
Feed Concentration = 45 mg $\text{Na.I}^- \text{ l}^{-1}$, Flow rate = 0.9 l.h^{-1} , Feed pH = 9.8

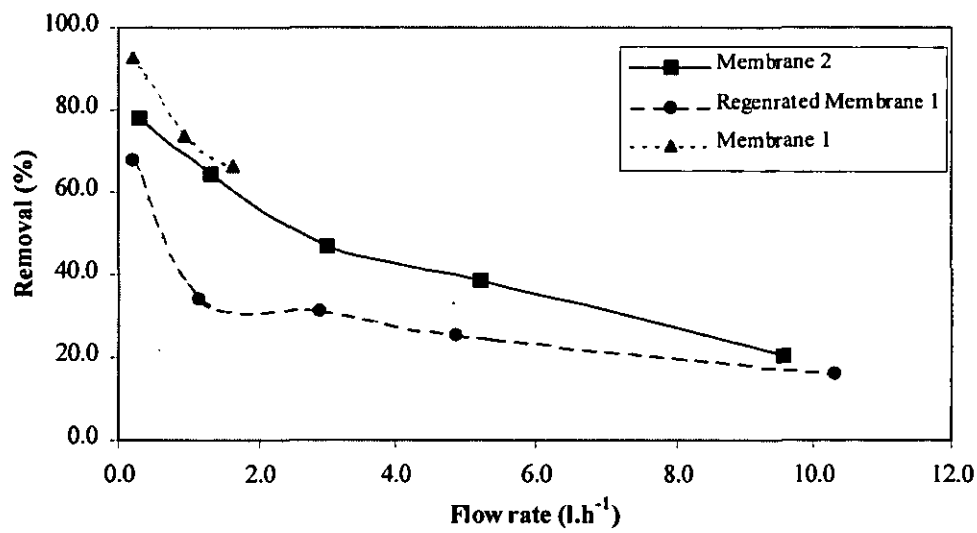


Figure 5.7: Removal of sodium by New and Regenerated membranes over a range of flow rates
Feed Concentration = 300 mg $\text{Na.I}^- \text{ l}^{-1}$, Current density = 6 mA.cm^{-2} , Feed pH = 2.9

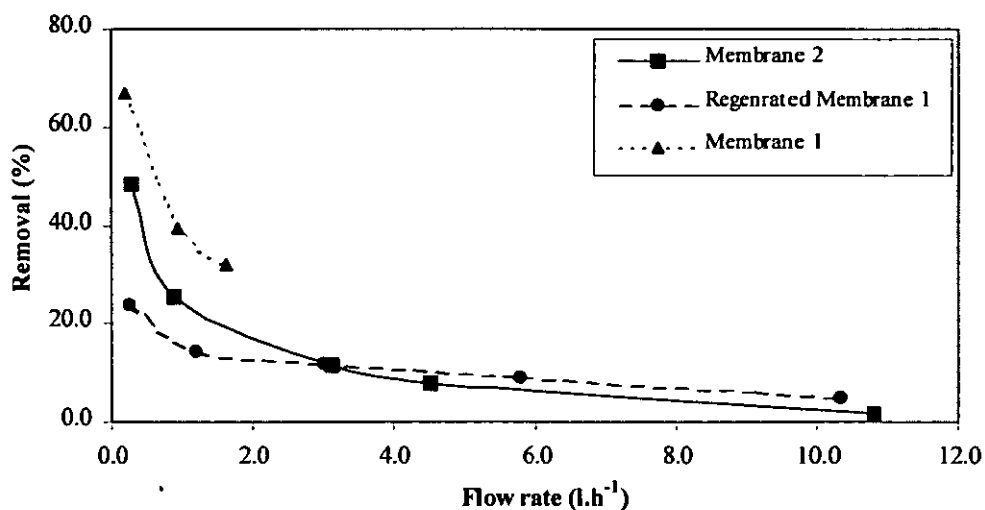


Figure 5.8: Removal of sodium by New and Regenerated membranes at a current density of 1 mA.cm^{-2}

Feed Concentration = 300 mg Na.l^{-1} , Current density = 1 mA.cm^{-2} , Feed pH = 2.9

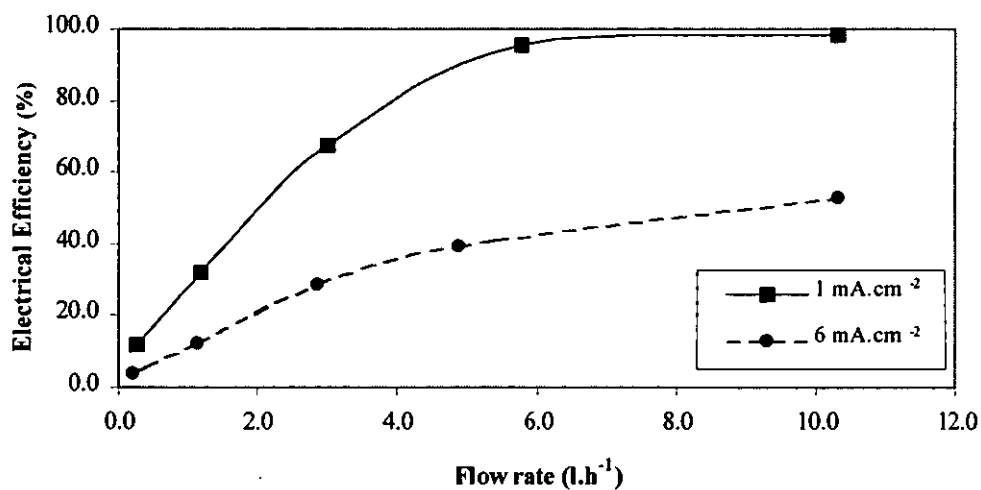


Figure 5.9: Electrical efficiency over a wide range of flow rates and current densities of 1 and 6 mA.cm^{-2}

Feed Concentration = 300 mg Na.l^{-1} , Feed pH = 2.9

over a wider range of flow rates using a cell which had been used extensively for other experiments. Results for the repeated experiments indicated that removals were lower than tests carried out with the cell containing new membranes. In order to improve the performance of the membranes used, these were treated with a 20 mM phosphoric acid solution in elution mode for 24 hours.

Experiments were repeated with the regenerated membranes the result of which can be seen in Figures 5.7 and 5.8, represented by the circular symbols. The results clearly show the capacity of zirconium phosphate for sodium was drastically reduced. This was due to the deterioration of the membranes when used for prolonged period and exposed to highly alkaline conditions. The membranes were regenerated further with 1 M phosphoric acid solution with little improvement in their performance. These results showed the crucial nature that ion exchange plays in EIX process. It also demonstrates that only chemically resistant ion exchange materials are suitable for EIX application.

New sets of membranes were obtained to conduct a third series of experiments at a low pH of 2.9. Flow rates ranged between 0.6 and 10 l.h⁻¹ and feed concentrations were about 300 mg.l⁻¹ of sodium. The results for membrane 2 can be seen in Figures 5.7 and 5.8, represented by square symbols. The removal of sodium was not as good as membrane 1 but were much closer to the original results than experiments carried out using regenerated membranes. The difference between the two sets of data may be due to the way that membranes were fabricated. This would suggest the manufacture of membrane is an important factor in producing membranes with good ion exchange capacities and mass transfer properties.

Overall, it was found that by increasing the flow rate the removal steadily declined due to shorter solution residence time of within the cell. Although in

absolute terms, more sodium ions were removed at higher flow rate of 9.5 l.h^{-1} (582 mg Na.h^{-1}) than at the flow rate of 0.3 l.h^{-1} (86 mg Na.h^{-1}) for a current density of 6 mA.cm^{-2} . This was due to less interference from hydrogen ions as discussed in Section 5.4.2.

The electrical efficiency of the process improved by increasing the flow rate which can be seen in Figure 5.9. At higher flow rates, the pH change from the inlet to outlet was not as great and hence current was predominantly carried by the sodium ions rather than hydrogen ions.

5.4.2 Feed pH

Hydrogen ion concentration is an important factor in the EIX process and its presence in the feed interferes with removal of target metal ions. Feed pH greatly influences the performance of the EIX cell. The hydrogen ions are more mobile than metal ions and are likely to carry most of the current when present in high concentrations. In absorption mode, the hydrogen ion concentration within the membrane is lower than the bulk due to the production of hydroxyl ions at the EIX electrode acting as the cathode. This is the reason for the process working well even when the bulk pH is lower than the optimum for a particular ion exchange resin which is a major advantage of EIX.

The effect of changing the feed pH on the removal of sodium can be seen in Figure 5.10. The results show that increasing acidic conditions reduced the removal of sodium ions. The large difference in the results between pH 1 and 2 in comparison to pH 2 and 3 is due to the logarithmic nature of the pH scale. Figure 5.11 shows the removal of sodium at feed pH of 3 and 12 and for current densities of 1 and 10 mA.cm^{-2} . High levels of removal were achieved at pH 12 compared to pH 3 even at the low current density of 1 mA.cm^{-2} .

The electrical efficiency of the process is a measure of the amount of current carried by target ions in this case sodium. The efficiency was better at a feed

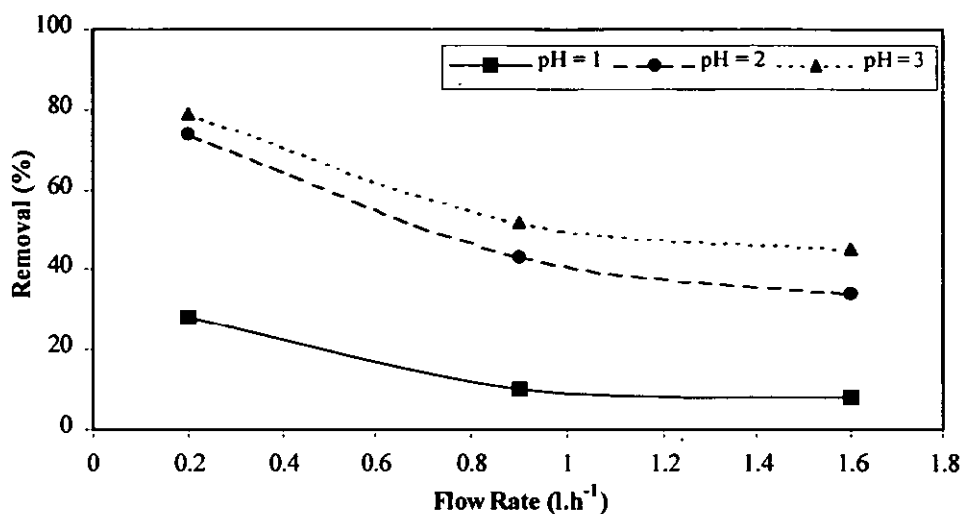


Figure 5.10: Removal of sodium at three different feed pH
Feed Concentration = 470 mg Na.l⁻¹, Current Density = 6 mA.cm⁻²

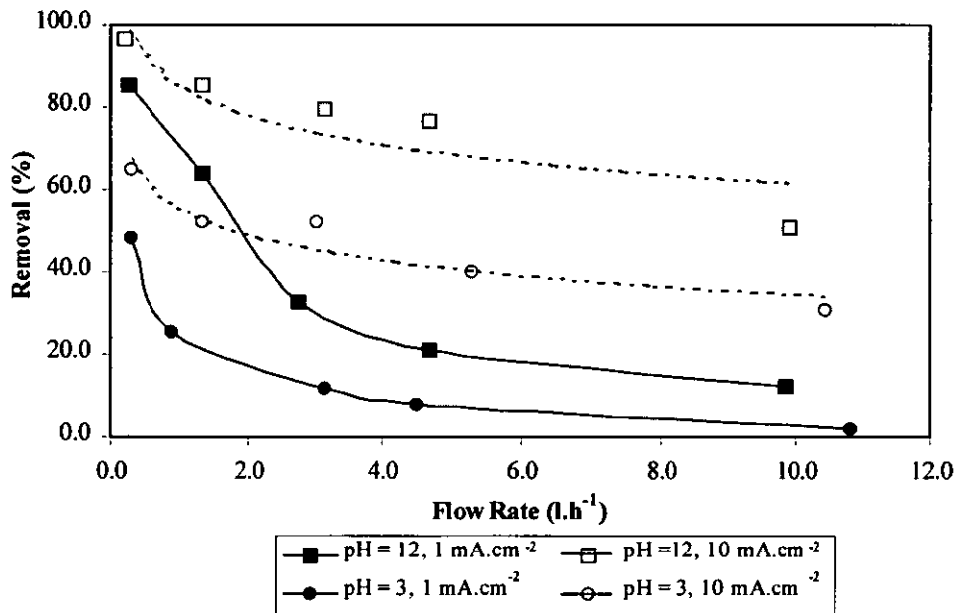


Figure 5.11: Removal of sodium at feed pH of 3 and 12 for current densities of 1 and 10 mA.cm⁻²

Feed Concentration = 220 mg Na.l⁻¹ at pH=12, Feed Concentration = 300 mg Na.l⁻¹ at pH=3

pH of 12 than at a feed pH of 3 as shown in Figure 5.12. Increasing flow rate and decreasing current density also improved the electrical efficiency. This was because more sodium ions were carrying the current at feed pH of 12. For a feed pH of 3, the results show that there was little difference between efficiencies at current densities of 3 and 10 mA.cm⁻² particularly at flow rates less than 4 l.h⁻¹. This was due to the system being saturated with hydrogen ions at these conditions.

5.4.3 Feed Concentration

A series of experiments were carried out with sodium feed concentration ranging between 0.02 and 6 g.l⁻¹. A limited number of experiments were conducted with other cations such as Zn, Cu, Ni and Cs present in the feed. The percentage removal of sodium decreased with increase in feed concentration. Experiments conducted with feed concentration of 20 mg.l⁻¹ showed that the EIX process was particularly good at removing trace quantities of metal ions as seen in Figure 5.13. This is another advantage of the EIX process; it can be used at low concentrations where other methods such as electroplating are not economically viable.

The relationship between process performance and presence of ions in high concentration was investigated by using a model system of sodium and zinc. Removal of zinc was examined at a feed concentration of 30 mg.l⁻¹ and the results can be seen Figure 5.14. Almost all the zinc was removed when the feed contained only 30 mg.l⁻¹ of zinc only. Sodium removal was examined using a feed containing 300 mg.l⁻¹ of sodium only. Then, a feed solution bearing 300 mg.l⁻¹ of sodium and 30 mg.l⁻¹ zinc was treated by the EIX process. Removal of zinc was reduced to the same level as sodium e.g. 40 % removal at the highest flow rate of 1.6 l.h⁻¹. The experiments were all conducted for a feed pH of 5 to reduce the interference from hydrogen ions and

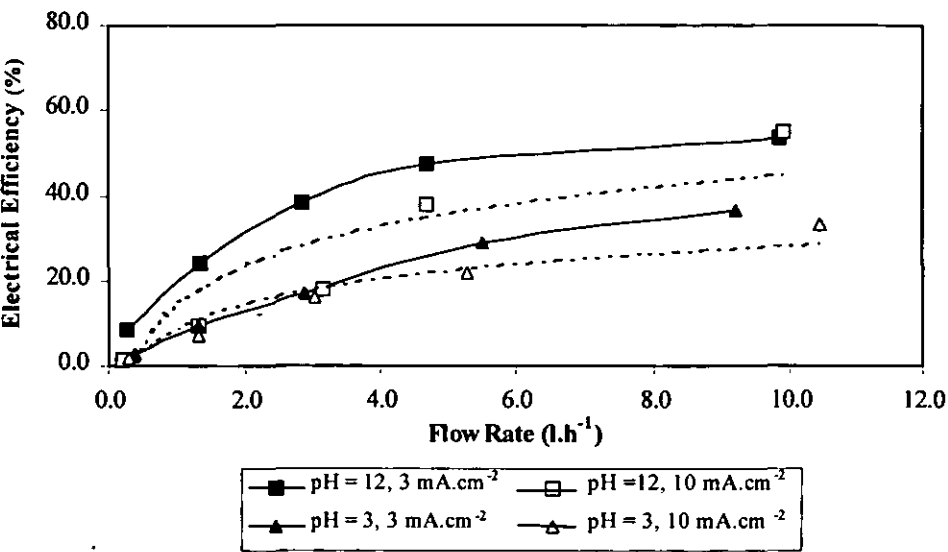


Figure 5.12: Electrical efficiency at feed pH of 3 and 12 for current densities of 3 and 10 mA.cm⁻²
Feed Concentration = 220 mg Na.l⁻¹ at pH=12, Feed Concentration = 300 mg Na.l⁻¹ at pH=3

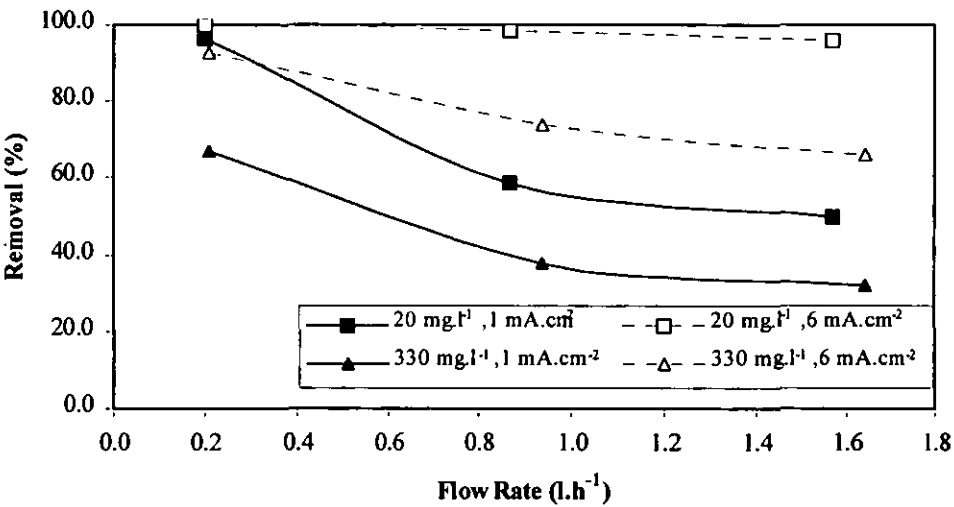


Figure 5.13: Removal for two feed concentrations at current densities of 1 and 6 mA.cm⁻²
Feed pH = 3

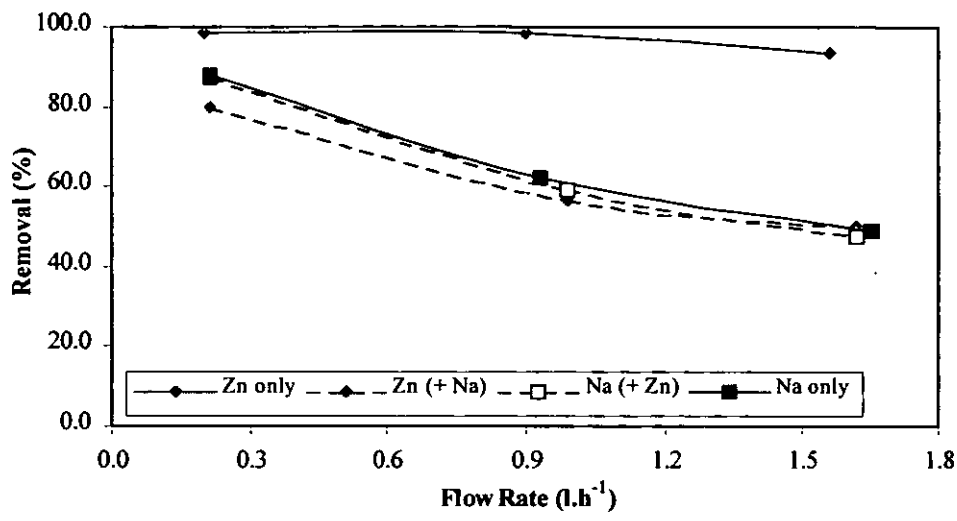


Figure 5.14: Effect of excess concentration of interfering ions on the removal of target cation
Feed Concentration Zn = 30 mg.l⁻¹ Na = 300 mg.l⁻¹; Current Density = 3 mA.cm⁻², Feed pH =5

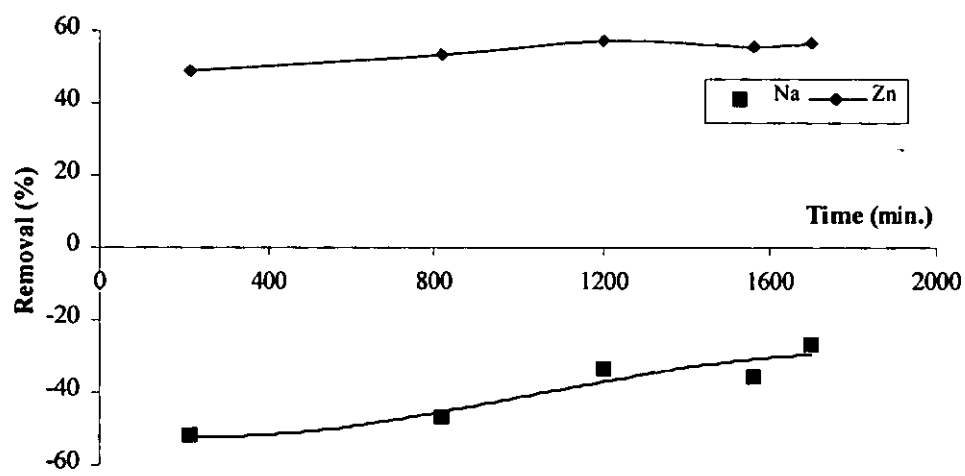


Figure 5.15: Removal of zinc by the sodium form of zirconium phosphate
Feed Concentration Zn = 31 mg.l⁻¹ Na = 320 mg.l⁻¹; Current Density = 3 mA.cm⁻²,
Flow Rate = 0.6 l.h⁻¹, Feed pH =3

minimise the risk of zinc precipitation. As expected, the results indicated that the removal of metals was influenced by total ionic concentration in the feed.

Zirconium phosphate membranes were converted to the sodium form by running in absorption mode with a feed solution containing about 5 g.l⁻¹ of sodium. The experiment was conducted for over 72 h until there was no change in sodium ion concentration leaving the cell. During the experiment sodium removal decreased steadily until there was no change from inlet to outlet concentration.

The cell was not eluted but used for further two tests. In the first experiment, the feed contained 5.2 g.l⁻¹ of sodium and 30 mg.l⁻¹ of zinc and feed pH was 3 and the flow rate 0.65 l.h⁻¹. The second experiment was carried out using a lower feed concentration of sodium, 320 mg.l⁻¹ and 31 mg.l⁻¹ of zinc. The feed pH was 2.9 and the flow rate was 0.63 l.h⁻¹. Each feed was passed through the cell for approximately twenty nine hours. For high sodium feed concentration, the average removals were -0.4% of sodium and 16% for zinc.

In the first experiment, a precipitate of zinc was forming near the inlet section of the cell, most likely some form of zinc hydroxide. Although this may have enhanced the removal of zinc, the results indicate a selectivity of the sodium form of zirconium phosphate towards the zinc ions. The precipitation of transition group metals may improve the performance of the process but it can only be useful if it is retained and reversed during elution. The sodium form of the membrane would allow the passage of co-ions such as hydroxyl ions. The pH within the membrane would increase until it would breakthrough into the centre of the cell. There may have also been material leaking from the back of the cell into the bulk solution. The solution exposed to these alkaline conditions would result in precipitation of zinc. There may have also been

solid formation due to salting out of zinc nitrate out of solution in presence of a high sodium concentration.

In the second part of the experiment, the feed was changed over without rinsing or emptying the cell. The current was also kept on at all times and the feed was switched from high a sodium feed concentration to a low sodium feed concentration. The solids disappeared from within the cell when the feed was changed. The results for the second experiment can be seen in Figure 5.15. The results indicate the removal of zinc to be fairly constant. The negative removal of sodium indicates that the outlet concentration of sodium was much higher than the feed.

As sodium leaked from the membrane into the bulk solution, the membrane was partially converted to hydrogen form. The average percentage removals were 56 % for zinc and -27 % for sodium at the end of the experiment. These corresponded to outlet concentrations of 407 mg.l^{-1} of sodium and 13.5 mg.l^{-1} of zinc. This showed that the sodium form of the zirconium phosphate would be better suited to removing base metals from solution in the presence of high concentrations of sodium ions. The removal of zinc was similar to the experiment carried out using the hydrogen form of zirconium phosphate membranes discussed in this section. The disadvantage is the instability of zirconium phosphate in sodium form as it undergoes hydrolysis at high pH.

After twenty eight hours the system had not reached steady state. This was demonstrated by the slowly changing sodium outlet concentration. It was also difficult to assess the quantity of sodium ions exchanged with zinc, as there was an excess of sodium ions present in the solution.

5.4.4 Current Density

The applied current can be used to control the electrochemical ion exchange process. It can be easily adjusted by varying the voltage applied across the electrodes.

Current densities of between 1 and 20 mA.cm⁻² were used to examine the relationship between applied current and performance of the process. At maximum current densities of 15 and 20 mA.cm⁻², the solution temperature leaving the cell rose by over 20 °C particularly when the feed pH was 12 and at low flow rates. For other current densities the temperature increased by up to 5 °C. The results were unpredictable at these higher current densities and the performance of the process deteriorated with time. Hence, only a limited number of experiments were carried out at current densities of 15 and 20 mA.cm⁻². The temperature increase was due to the high applied voltage required to maintain these currents.

Figures 5.16 and 5.17 show respectively removal of sodium for a range of current densities and feed pH 3 and 12. The applied voltage is the driving force that facilitates the ionic transfer across the membrane. The current density is characteristic of the amount of ions transferred across the electrodes. As expected, the removal of sodium increased with increasing current density. The relationship between applied voltage and current can be seen in Figures 5.18 and 5.19.

The voltage readings were taken at the end of experiments when pseudo steady state had been reached. The current value was the total current for each half cell with in an EIX process unit. At low flow rate of 0.3 l.h⁻¹, The voltage needed to drive the same current was similar for both feed pH of 3 and 12. The same was not the case at the higher flow rate of 10 l.h⁻¹. At a feed pH of 3,

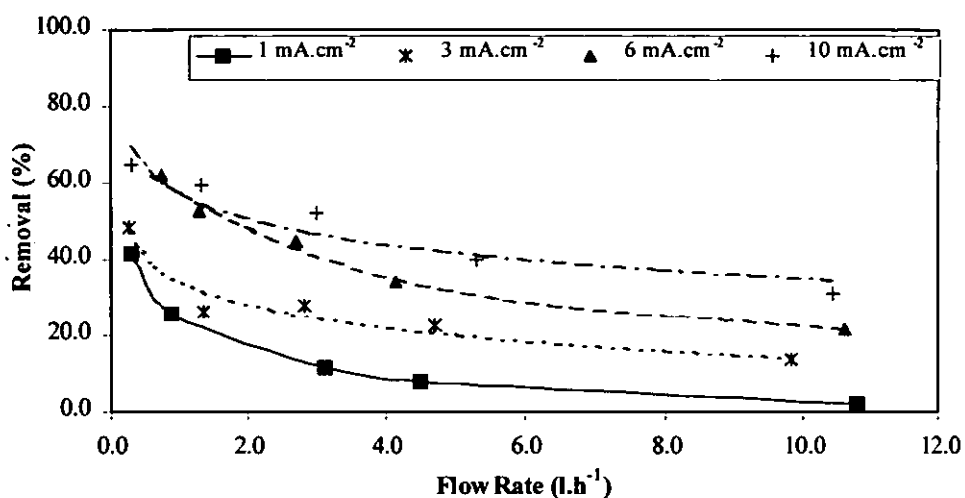


Figure 5.16: Sodium removal for a wide range of current densities and flow rates in acidic conditions

Feed Concentration Na = 290 mg.l⁻¹, Feed pH = 3

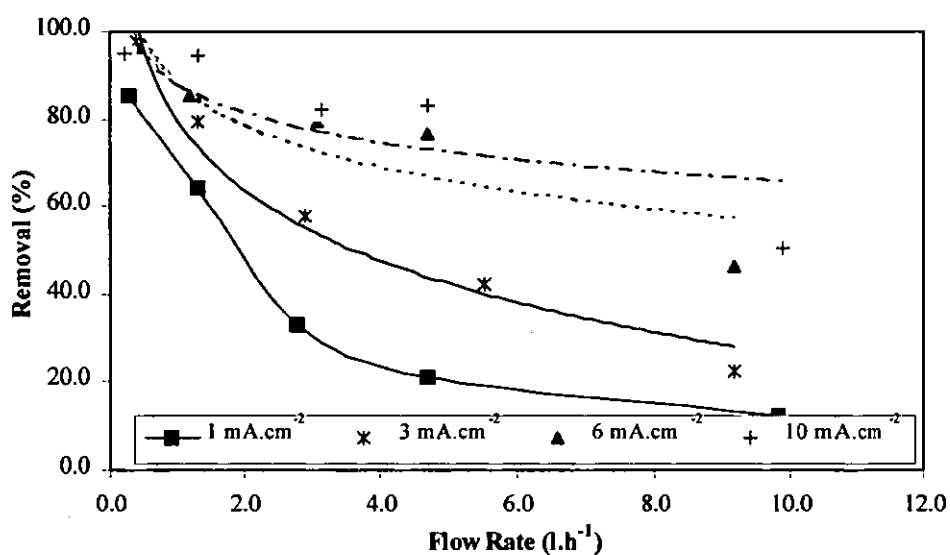


Figure 5.17: Sodium removal for a range of current densities and flow rates in alkaline conditions

Feed Concentration Na = 220 mg.l⁻¹, Feed pH = 12

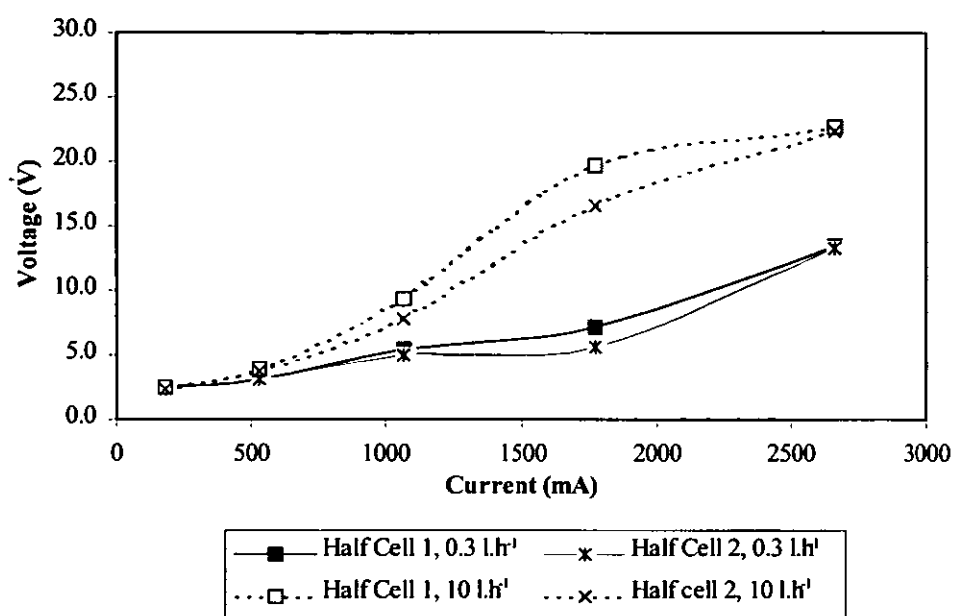


Figure 5.18: Applied voltage versus supplied current for both half cells at a feed pH of 3

Feed Concentration = 300 mg Na.l⁻¹, Flow rate = 0.3 and 10 l.h⁻¹, Feed pH = 3

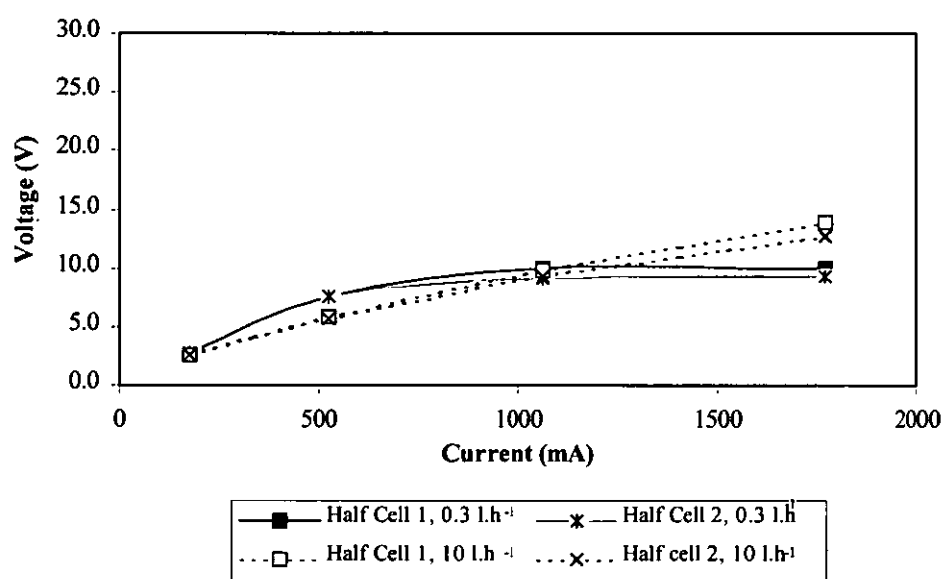


Figure 5.19: Relationship between applied voltage and supplied current for both half-cells at a feed pH of 12

Feed Concentration = 220 mg Na.l⁻¹, Flow rate = 0.3 and 10 l.h⁻¹, Feed pH = 12

much higher voltages were needed to drive a current of 1770 mA through both half cells. This could have been due to the conditions the membranes were in during that experiment. At a current of 1770 mA and flow rate of 10 l.h^{-1} , the applied voltage was higher than at the low flow rate of 0.3 l.h^{-1} in both alkaline and acidic conditions. This was because of the lower pH swing across the cell as result of the higher flow rate. There were less mobile hydrogen ions that could carry the current.

None of the relationships were ohmic and factors such as feed pH, feed concentration and flow rate were important. The type of resin and its form are also important in determining the voltage required to drive a particular current through each half cell. The economic considerations of the process are crucial if the process is to be used commercially. The power requirements need to be optimised in relation to operating conditions to attain the lowest power consumption for maximum removal. An important indicator for this would be the electrical efficiency.

5.4.5 Electrode Gap

The difference between electrode gap and membrane gap was outlined in Sections 5.2.5 and 5.2.6. Tests were carried out for four different electrode gaps of between 2.8 and 8.8 mm at different flow rates, feed pH and current densities. Typical results for flow rates of 0.2 and 1.6 l.h^{-1} and a current density of 1 and 6 mA.cm^{-2} can be seen in Figures 5.20 and 5.21.

These results indicate that sodium removal improved with decreasing electrode gap which may have been partly due to better mixing within the cell. This brought the two half cells closer together leaving a smaller gap for the bulk solution to flow through. This in turn enhanced the mixing effect of the bubbles generated at the counter electrode.

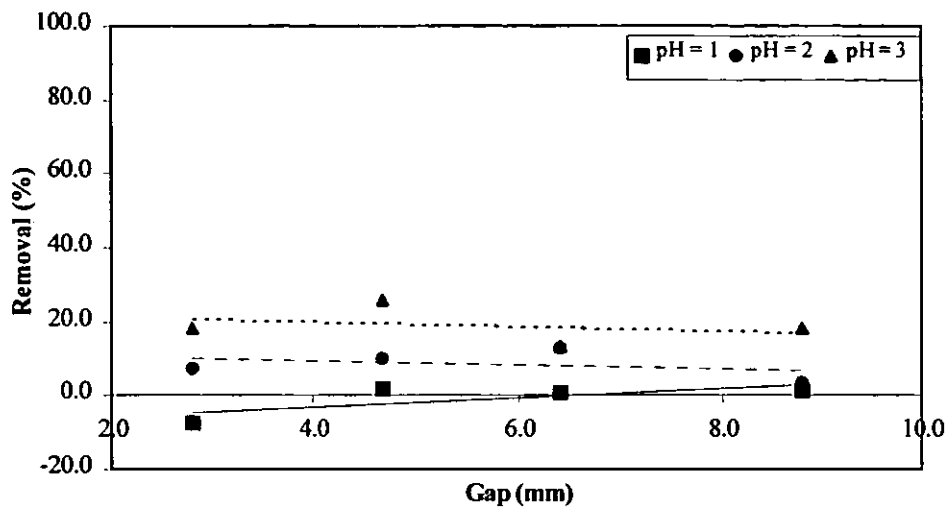


Figure 5.20: Removal experiments carried out for different electrode and current density of 1 mA.cm^{-2}
Feed Concentration = 330 mg Na.l^{-1} , Current Density = 1 mA.cm^{-2} , Flow rate = 1.6 l.h^{-1}

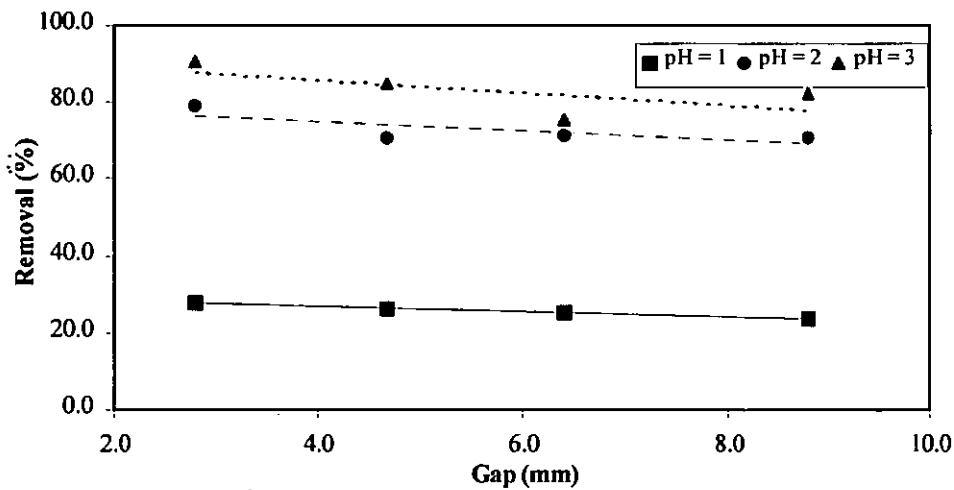


Figure 5.21: Sodium removal for current density of 6 mA.cm^{-2} and electrode gaps between 2.8 and 8.8 mm
Feed Concentration = 330 mg Na.l^{-1} , Current Density = 6 mA.cm^{-2} , Flow rate = 0.2 l.h^{-1}

Figure 5.20 shows results of experiments carried out at a current density of 1 mA.cm^{-2} . Sodium was removed from solution except for the smallest gaps at a feed pH of 1. Under these conditions, sodium was eluted off the membrane. This was probably due to high concentration of hydrogen ions in the bulk solution creating extremely acidic conditions partly because of the low feed pH and a narrow gap of 2.8 mm resulting in a low cell volume.

The reason why this did not occur at higher current densities was two fold. The mixing in the bulk solution was better at a current density of 6 mA.cm^{-2} compared to a current density of 1 mA.cm^{-2} . At high current densities there was much greater generation of gas bubbles. Secondly, at higher current densities, the cations experience a greater potential gradient driving ions from the bulk solution in to the membrane.

Figure 5.21 shows the results of experiments conducted at a flow rate of 0.2 l.h^{-1} and current density of 6 mA.cm^{-2} . There were improvements in sodium removal by decreasing the gap. This was mainly due to the better mixing effect of bubbles generated at the higher current density of 6 mA.cm^{-2} . The improved removal was more marked at a feed pH of 2 and 3 than a pH of 1 where the effect was not as great due to high concentration of hydrogen ions in the system.

Overall, there was an improvement in sodium removal with a decreasing electrode gap. This was more evident at higher feed pH and current densities.

5.4.6 Membrane Gap

In the original electrochemical ion exchange cell, the counter electrode was pressed against the membrane so that it touched the membrane with no space between the two. In order to improve the performance of the cell at low feed pH's, a gap was introduced between the counter electrode and the membrane.

It was thought this would reduce the local hydrogen ion concentration occurring where the counter electrode touched the EIX membrane. This would then increase the possibility of the target ion entering the membrane by allowing the solution to pass between the counter electrode and the membrane. Experiments were carried out to examine the effect of changing the membrane gap.

Experiments were conducted for membrane gaps between 0 and 3 mm for a feed pH of 5. The results in Figure 5.22 indicate that sodium removal was better at low flow rates and membrane gaps. This may have been due to better mixing close to the surface of the membrane by bubbles generated at the counter electrodes. As the flow rate was increased, the results show that there was hardly any difference between the results generated with different membrane gaps.

The current efficiency was also better when there was no gap between the membrane as shown in Figure 5.23. The results obtained from these experiments carried out at near neutral pH of 5 suggest that the best removal occurs when the counter electrodes are in direct contact with the surface of the EIX membranes.

Experiments were carried out to examine the influence of the membrane gap on the performance of the EIX cell, under both alkaline and acidic conditions. Two extreme cell configurations were used; the first experiments were conducted using a standard EIX cell with a membrane gap of 0 mm i.e. no space between two counter electrodes and the EIX membranes. Secondly, one common counter electrode was placed in the centre away from each membrane to give a maximum membrane gap of 5.7 mm. Feed pH of 3 and 12 were used with current densities ranging between 1 and 15 mA.cm⁻².

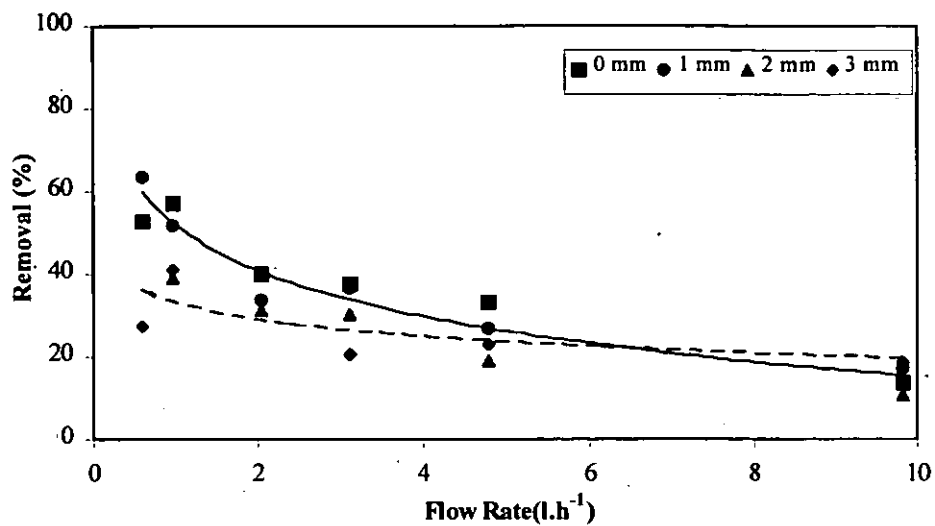


Figure 5.22: Removal for different gap experiments
 Feed Concentration = 250 mg Na.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 5

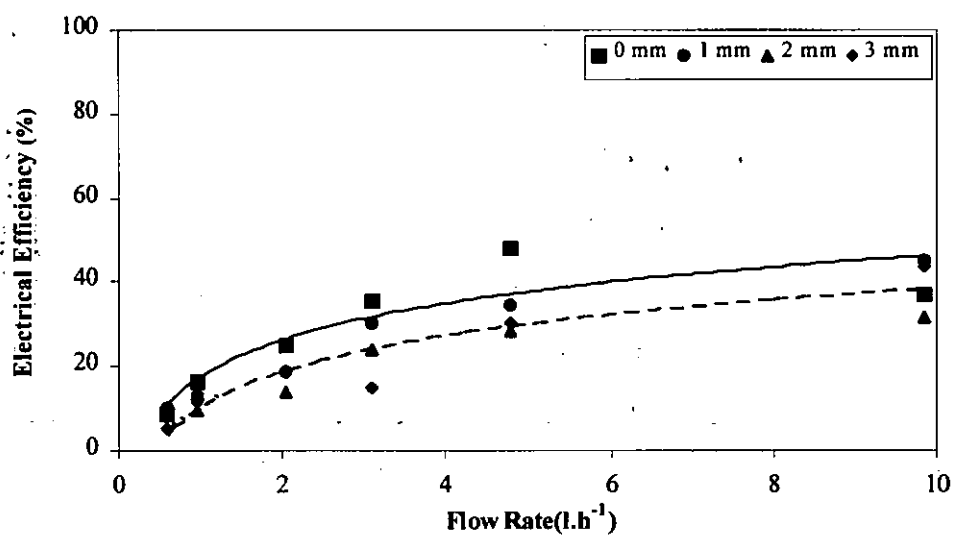


Figure 5.23: Electrical efficiency for different gap experiments
 Feed Concentration = 250 mg Na.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 5

Results of some experiments are shown in Figures 5.24 to 5.25. In Figure 5.24, it can be seen that sodium removal was only better for the case when one central electrode was used at feed pH of 12 and current density of 10 mA.cm^{-2} . This may be explained by considering the competition between the hydrogen and sodium ions to carry the current. At high feed pH, the hydrogen ion concentration is insignificant compared to the hydroxyl ions. Sodium ions would then carry bulk of the current. If the counter electrode is close to the membrane then the likelihood of hydrogen ions passing into the membrane and carrying the current is greater than if there was a gap between the counter electrode and the membrane. There were not any significant differences between the results obtained for feed pH of 3 with both cell configurations. The results indicated that only under extreme alkaline conditions and high current densities was there a significant improvement in sodium removal. This would suggest that the design of the cell was already optimised with respect to the membrane gap. Since it is unlikely that the cell would be used under such extreme pH conditions. Adequate mixing existed within the cell enhanced by bubbles generated at the counter electrodes for all other experiments.

The voltages for the pH 12 experiments can be seen in Figure 5.25. The applied voltages were generally higher for experiments conducted with one central counter electrode. This was mainly to the increased distance between the counter electrode and the EIX electrode. The increase in distance meant extra resistance due to solution between the counter electrode and the EIX membrane. This would indicate that any improvement in performance is offset by higher operating cost due to higher voltages.

5.5 Purolite Membranes

Purolite S930 and Purolite S950 membranes were used to generate considerable amount of experimental data to compare with results obtained using zirconium phosphate membranes. These gave important indications to factors governing

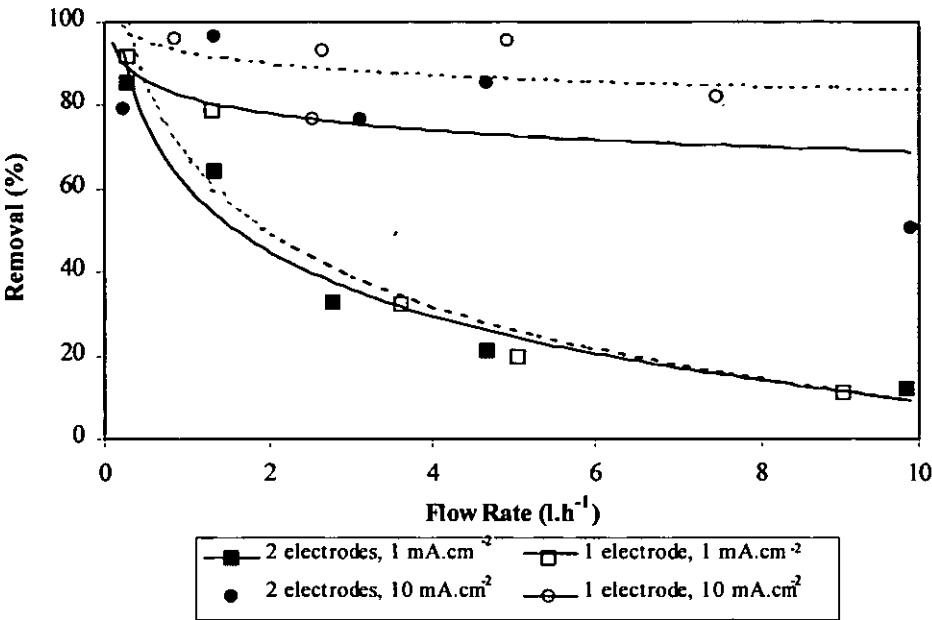
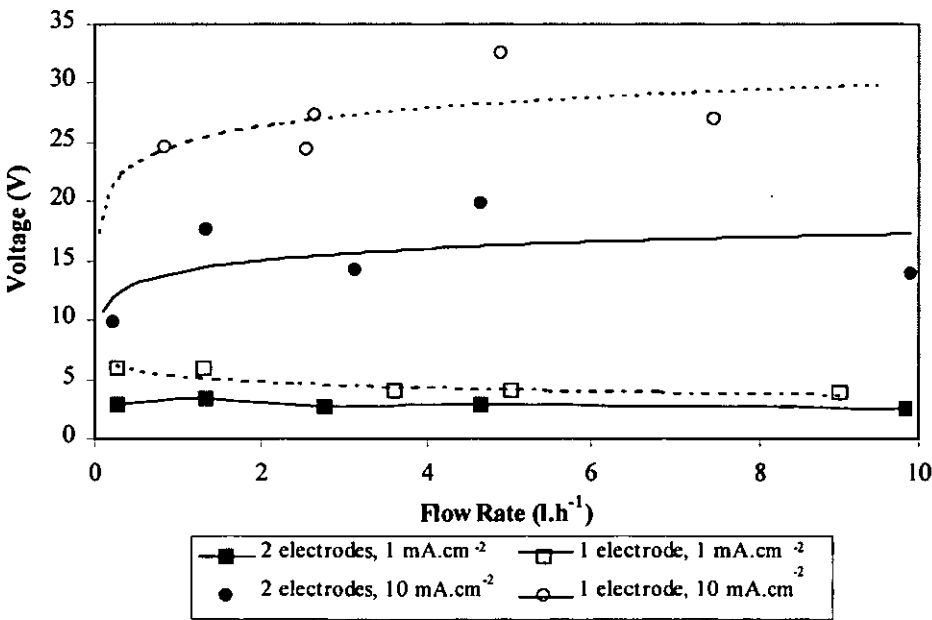


Figure 5.24: Sodium removal at feed pH of 12 using two or one counter electrode
Feed Concentration Na = 220 mg.l⁻¹, Feed pH =12



Feed Concentration Na = 220 mg.l⁻¹, Feed pH =12
Figure 5.25: Applied voltages at feed pH of 12 using two or one counter electrode

the flow cell design and development. The experiments were carried out with both the sodium and hydrogen form of Purolite membranes. Purolite membranes were found to perform well over a wide range of experimental conditions and were suitable for EIX application.

5.5.1 Sodium Form

Early experiments using S930 and S950 ion exchange membranes showed signs of sodium leaking out from the membrane during absorption cycles. A current density of 3 mA.cm^{-2} was used with a feed pH of 3.7, flow rate of 2.9 l.h^{-1} and without any metal cation present in the feed. The results can be seen in Figure 5.26. The level of sodium leakage steadily increased during the experiments. The outlet pH indicates that the sodium was lost in the hydroxyl form with hydrogen exchanging for sodium, as there were no other cations present.

Following these experiments, a series of tests were carried out to examine the adsorption performance of the Purolite membranes. As caesium would not precipitate in alkaline solution, it was selected to examine the removal of cations by ion exchange only. The results can be seen in Figure 5.27. Both membranes showed unstable performance which was mainly due to the form of each exchanger changing from sodium to hydrogen. This can be clearly seen since the outlet concentration and pH follow the same pattern. Earlier experiments had higher outlet pH indicating the presence of sodium. The outlet pH was more acidic for latter experiments. Experiments were conducted in random order and the adsorption of the resin deteriorated with each experiment. However, S950 proved to be better at removing caesium than S930 which was expected given the nature of each resin.

Zinc absorption experiments were carried out using the sodium form of the Purolite membranes, the results can be seen in Figure 5.28. Removal of zinc was similar for both the S950 and S930 membranes over a wide range of flow

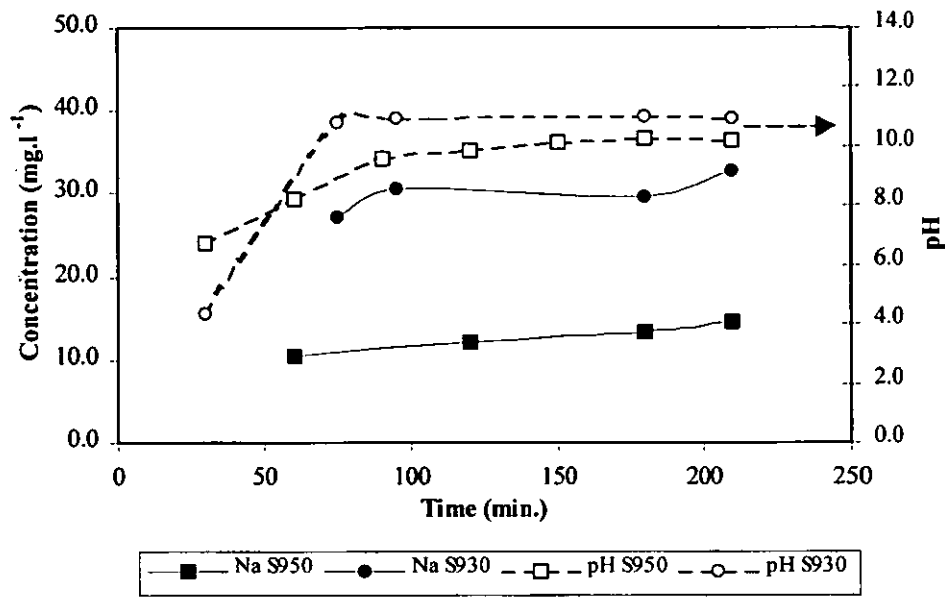


Figure 5.26: Leakage of sodium from Purolite membranes during an absorption cycle

Feed Concentration = 0.1 mg Na.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 3.6

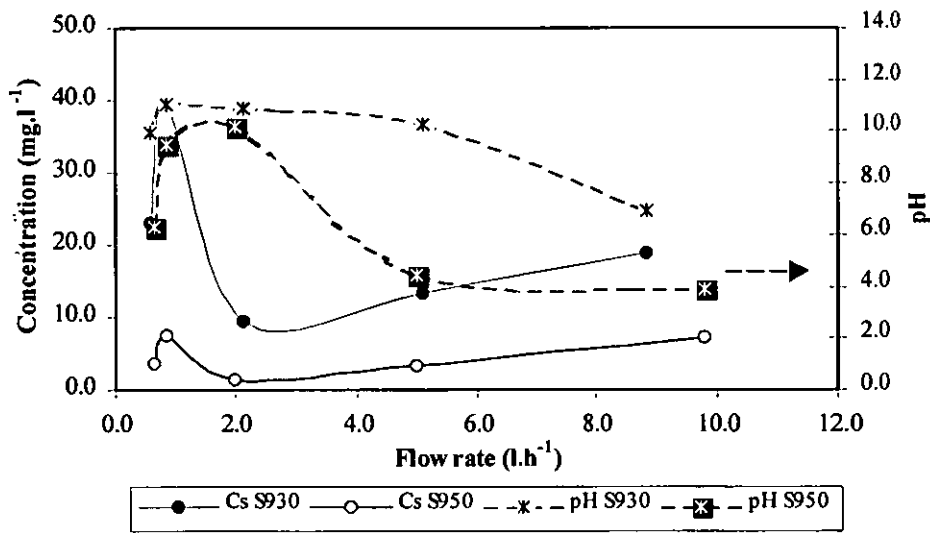


Figure 5.27: Caesium absorption experiments carried out using sodium form of Purolite membranes

Feed Concentration = 30 mg Cs.l⁻¹, Current Density = 3 mA.cm⁻²,
Flow Rate = 2.1 l.h⁻¹, Feed pH = 3.1

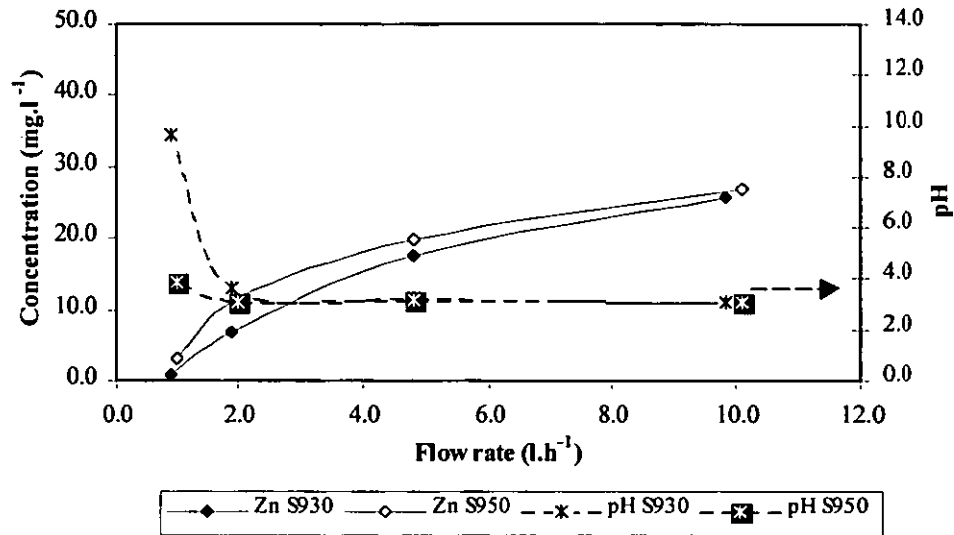


Figure 5.28: removal of zinc by sodium form of S950 and S930
Feed Concentration = 30 mg Zn.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 3.1



Figure 5.29: Solids forming at the cathode during zinc absorption experiments

rates. The outlet pH was similar for both except at the lowest flow rate, the outlet pH of the S930 cell was much higher. The corresponding sodium and caesium outlet concentrations were also higher for the cell containing S930 membranes.

Overall, the sodium form of the Purolite S950 membrane removed caesium better than the sodium form of the S930. The results indicated that the sodium form of S930 and S950 membranes performance were similar for removal of zinc. This is as expected since, S930 chelating resin was designed to remove base metals in the presence of high concentration of univalent and divalent ions. Whereas S950 resin was designed for removing divalent ions and base metal cations in presence of univalent ions only.

During the zinc removal experiments, solid formation and precipitation occurred where the bulk solution was in direct contact with the bare metal mesh of the EIX electrode, acting as the cathode. The dendrite type solids were greyish black in colour and can be seen in Figures 5.29. The solids may have been zinc metal electroplating out of the solution. Precipitates collected at the bottom of the cell near the inlet. These were white in colour and may have been zinc hydroxide.

Two types of solids were formed one on the bare metal mesh and another settling at the bottom of the cell. The reasons for the formation solids seem to have been exposed areas of cathodes and highly alkaline solution leaking from the back of the cell. The bare metal was covered to reduce the exposed area of the metal electrodes. Alkaline solution collected at the back of each half cell. A small amount of solution escaping from the back of the cell would result in higher pH near the vicinity of the leakage which would subsequently cause precipitation. The membranes were sealed to reduce the leakage of material

from the back of the cell to the bulk solution. Detailed discussion on the change in performance of the EIX cell following the sealing is given in Section 6.6.1.

Experiments were conducted to examine the relationship between sodium ion concentration and zinc removal. The removal of zinc and sodium for these experiments can be seen in Figure 5.30 at different flow rates. Feed sodium concentrations of 138 mg.l^{-1} or 300 mg.l^{-1} were used with a solution containing about 30 mg.l^{-1} of zinc. The experiments were carried out at constant current density of 3 mA.cm^{-1} and feed pH of 3. The removal of sodium decreased by increasing the sodium feed concentration. At a flow rate of 5 l.h^{-1} , the removal of zinc was lower by as much as 15 % for sodium feed concentration of 300 mg.l^{-1} compared to feed concentration of 138 mg.l^{-1} . As in the case of the zirconium phosphate membranes, the results suggest that increasing sodium concentration reduces the removal of target ions because of interference from the sodium ions when the membranes are not completely in the sodium form.

The S930 and S950 membranes were then eluted with 0.1 M nitric acid solution until the pH leaving the cells were constant. It was assumed that the membranes were then in the hydrogen form. A series of experiments were conducted to assess the performance of the hydrogen form of these resins.

5.5.2 Hydrogen Form

Removal of various cations was examined by using hydrogen form of Purolite membranes. Initially, the caesium removal was examined and the results can be seen in Figure 5.31. Both membranes performed well but Purolite S950 was better at removing caesium than Purolite S930. The outlet caesium concentration of S950 was constant through out the experiment. The S930 showed slower kinetic properties as the concentration of caesium gradually

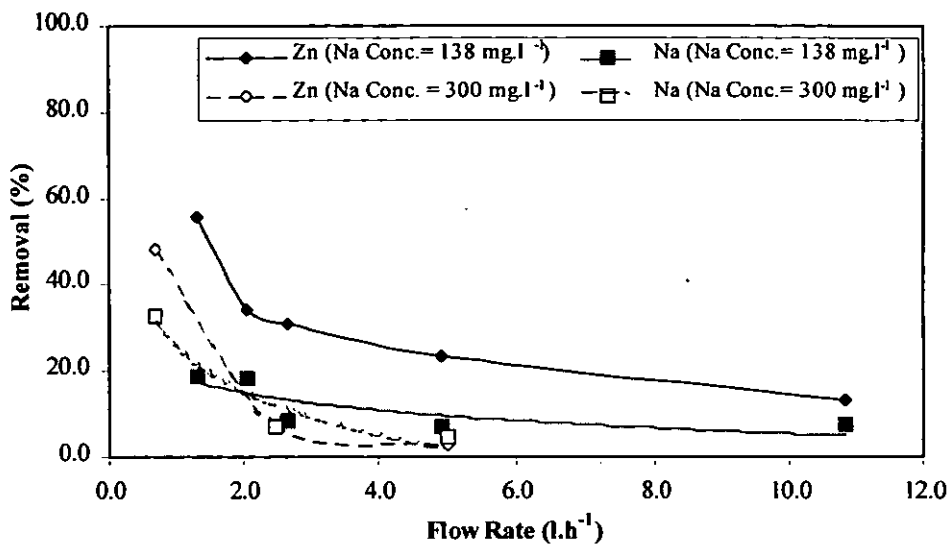


Figure 5.30: Concentration limit of Purolite S930 membranes for a current density of 3 mA.cm⁻²
Feed Concentration = 29 mg Zn.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 3

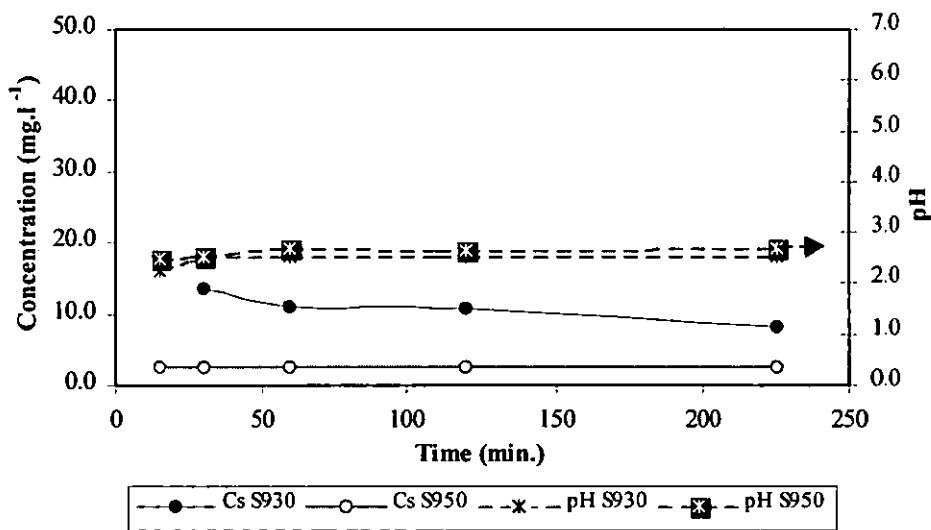


Figure 5.31: Caesium removal by hydrogen form of Purolite membranes
Feed Concentration = 30 mg Cs.l⁻¹, Current Density = 3 mA.cm⁻²
Flow Rate = 2.1 l.h⁻¹, Feed pH = 3.1

decreased from the beginning of the experiment to the end. Both cells had been operated under the same experimental conditions prior to these tests.

Zinc removal experiments carried out by the hydrogen form of Purolite membranes gave mixed results. At low flow rates, S950 removed zinc slightly better than S930 as shown in Figure 5.32. At higher flow rates, the results indicated no significant difference between the performance of these membranes. The difference between the result at lower flow rates could be due to the selectivity of S930. Overall, the performance of the two resins were similar except for better removal of zinc by the hydrogen form and better removal of caesium by both forms of S950. S930 membranes were selected to continue with further experiments as these performed better for zinc removal and showed better selectivity.

A combined feed of sodium, copper, nickel and zinc was used to examine the selectivity of the hydrogen form of S930 membrane. The result for this experiment can be seen in Figure 5.33. The removal of all cations was similar after the initial period. The removal levelled off at about 75% once the system had reached steady state. Although the removal was generally high, there was no indication of any selectivity. Similar results were obtained when using the sodium form of S930.

5.6 Discussion

Electrochemical Ion Exchange (EIX) processes offer a high ratio of surface area to volume, since the ion exchange beads embedded in the membrane offer a large reaction surface which compares well with the electrolyte volume. The results from the experiments discussed in this chapter indicated that the system configuration was almost optimised. All aspects of the cell were well designed to remove trace quantities of metal ions from solution. Only small

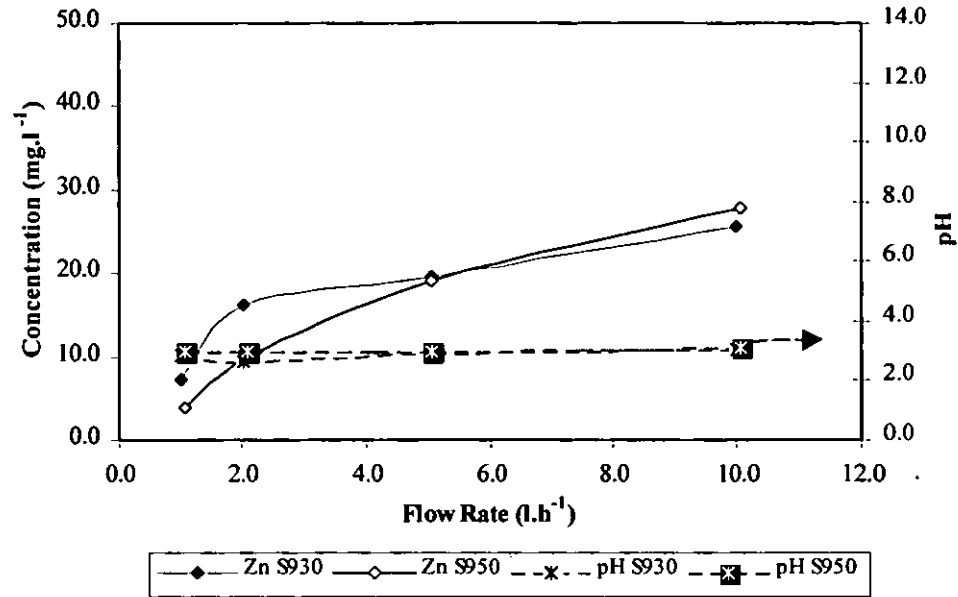


Figure 5.32: Removal of zinc by hydrogen form of Purolite S950 and S930 membranes

Feed Concentration = 30 mg Zn.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 3.1

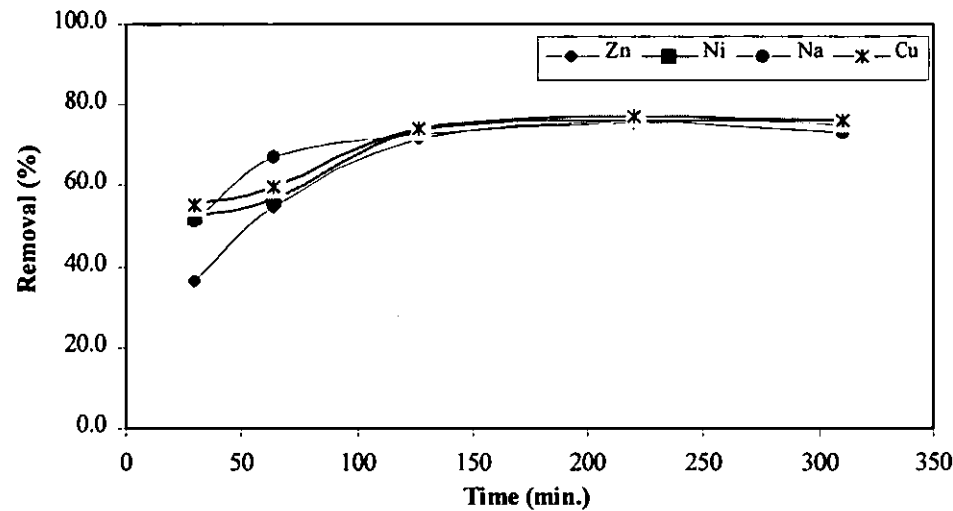


Figure 5.33: Experiment carried out with a combined feed of Cu, Ni, Zn and Na using hydrogen form of S930

Feed Concentration Cu, Ni and Zn = 10 mg.l⁻¹ Na = 130 mg.l⁻¹; Current Density = 3 mA.cm⁻², Flow Rate = 1 l.h⁻¹, Feed pH = 3.1

improvements could be obtained in the cell performance by changing any cell configurations.

The reason for the good performance of the EIX process was partly due to gas bubbles generated at the counter electrode which flow up the cell mixing the bulk solution in the centre of the cell. The effect of gas evolution (Wu and Rangaiah (1993) and Ben Youssef (1994)) and sparging (Sigrist et. al. (1979)) on mass transfer in electrochemical reactors have been presented. In general, an enhancement of mass transfer was obtained by gas flows across the surface of the electrodes.

Increasing the flow rate in an electrochemical cell could also enhance mass transfer in some cases. The disadvantage of increasing the superficial velocity would be higher energy consumption which increases by square of the velocity.

A series of experiments were conducted to examine if any further enhancement in the mass transfer can be obtained within the EIX cell. These are not reported as there were no significant improvements obtained by gas sparging, obstructing the path of the flow or by the use of plastic mesh spacers. The effects of changing the flow rate and reducing the gap have already been discussed. There was indication that characteristics of the original system promoted very efficient mass transfer within the system. This was mainly due to the following:

- a) Mixing by gases evolving at the counter electrodes
- b) The gauze like electrodes have a rough surface which promotes turbulence which has been discussed in the literature by Bisang (1992)

Major indications of good mass transfer were that no limiting current was encountered in any experiments even at the low concentrations and the lowest

efficiencies were better than those obtained in normal electrochemical processes at similar concentrations. Many aspects of the EIX process were examined and the main findings are summarised in the next section.

5.7 Conclusions

Considerable amount of data was generated while examining the performance of the EIX cell under different experimental conditions. The following are the main findings:

- Zirconium phosphate membranes deteriorated with time and could only be partially restored using phosphoric acid.
- An increase in flow rate resulted in higher outlet concentration but increase the electrical efficiency.
- The hydrogen ion concentration greatly affected the performance of the EIX process, the removal decreased with reduction in feed pH.
- Increasing the concentration of interfering ions such as sodium reduced the removal of target ions such as zinc to the same level as the interfering ions.
- The form of the membrane was important in the selectivity of the process.
- The loading of the membrane also affected the removal of ionic species from the bulk solution in the case of the chelating resin.
- Increase in current density improved the removal but also increased the power requirements of the process particularly at high pH.
- Decreasing the electrode gap improved the removal of sodium due to better mixing particularly at low flow rates.
- At high pH, replacing two counter electrodes with one improved the removal of sodium but there was also a large increase in applied voltage.
- Of the two chelating resins, the hydrogen form of the S930 showed better performance for the removal of zinc.

CHAPTER 6

EXPERIMENTAL II: Profiles

6. INTRODUCTION

In most electrochemical systems, the current distribution along the length of the cell is a criterion by which cells can be characterised. The position of highest and lowest currents is crucial to the design and operation of an efficient electrochemical cell. It can give an indication of cell modifications required to enhance its performance. In most chemical engineering systems, the flow patterns can be used to understand the behaviour of the system. Both current and flow profiles were studied in a series of experiments conducted under different process conditions.

An objective of the research was to obtain an overall understanding of the EIX process. Therefore, a systematic study of the cell was conducted to obtain concentration and pH profiles. In Chapter 5, aspects of process design were evaluated to understand the behaviour of the system during basic operation using a standard EIX cell, described in Section 5.1.3. An EIX cell was modified to obtain samples from different parts of the cell as well as allowing the current distribution and flow patterns within the cell to be examined. The cell was divided into five main sections with sampling points along the length of the cell to measure concentration, pH and the electric current. During the experiments, sample solutions were taken from all over the cell including the centre and inside the membranes. Flow patterns were examined by use of a tracer, nigrosine dye.

6.1 Experimental Modifications

The main experimental details were described in Section 5.1. These remained the same with absorption and elution cycles being carried out in exactly the same way as before. The only changes that were made to the equipment was

the alterations made to the cell. The discussion in the next section includes the modifications made to experimental materials.

6.1.1 Concentration and pH Profiles

The modifications made to the EIX cell to obtain the concentration and pH profiles can be seen in Figure 6.1. In Figure 6.1 points HC10 to HC15 and HC21 to HC25 represent points where samples were taken from the back of the half cells. Points M1 to M5 were the position of syringes used to obtain samples from the centre of the cell. The samples were taken opposite to the direction of the flow, from top M5 to bottom M1, to avoid any discrepancy caused by changes in the solution concentration and pH caused by flow disturbance as the samples were drawn.

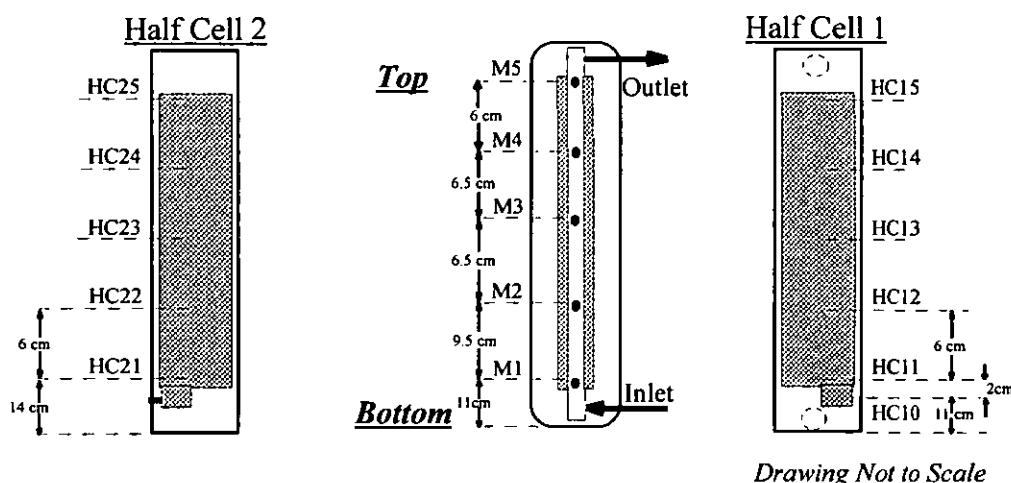


Figure 6.1: Sample points for the determination of concentration and pH

Figure 6.2 shows the small portholes made in the cell, to allow the intrusion of syringe needles to draw sample solutions from back of the cell. These were sealed with rubber discs which allowed the insertion of needles in and out of the holes. Needles were inserted into the centre of the cell through the gasket and were covered with inert material to avoid direct contact with the counter electrodes.

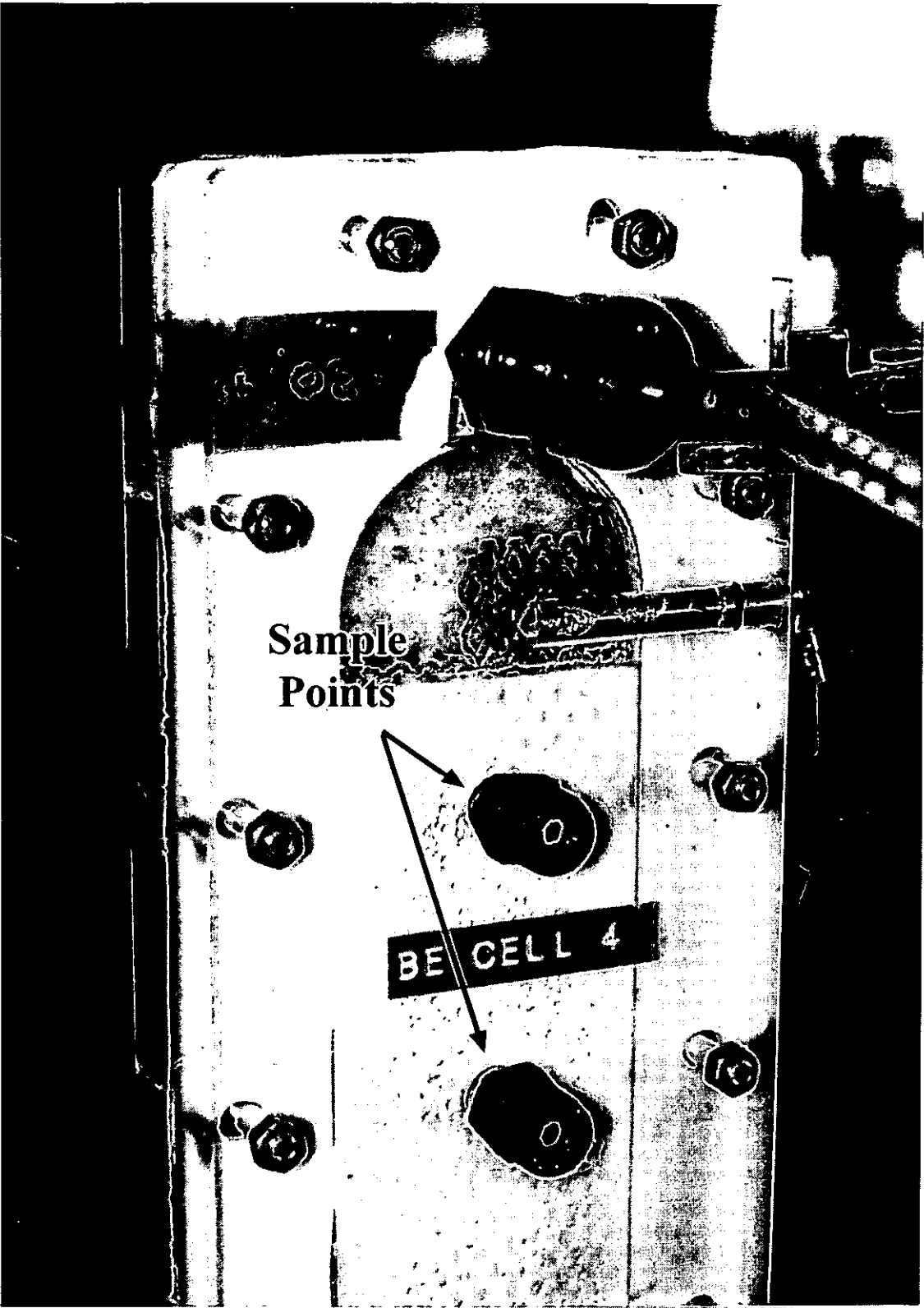


Figure 6.2: Sample Points at top of the cell

Samples collected from the centre and the back of the cell were used to measure the pH and concentration profiles along the length of the cell. The volume of the samples drawn out of the cell was 2 ml. The bulk of the work was conducted using zirconium phosphate membranes. However, Several experiments were carried out using the Purolite S930 and S950 membranes.

6.2 Current distribution

Two methods were used to obtain the current distribution. The first was the current follower (CF) technique which employed an operational amplifier to convert the registered current to an output voltage. The second method involved direct measurement of the current flowing through particular sections of the cell by an ammeter.

6.2.1 Current Follower Measuring Device

Initial experiments on the modified cell were primarily to evaluate the Current Follower (CF) technique in-situ. Other modifications were made to allow samples to be taken from within the cell as previously discussed in section 6.1.1. Samples were needed close to the point of the current measurements since early experiments indicated a relationship between concentration and output voltage particularly at concentrations less than 200 mg.l^{-1} . The electrodes 1 to 5 were equally spaced going from the bottom of the cell to the top. These correspond to the sample points HC21 to HC25 in Figure 6.1.

The current follower circuit is shown in Figure 6.3. Point 8 corresponds to a flattened end of a platinum wire acting as a measuring electrode. There were five of these electrodes. The end of each was flattened and held within the gaps of a standard electrode. The measuring electrodes were all electrically insulated except the flattened ends. A circuit was set up between the metal mesh electrode and a counter electrode. It was assumed the current density was evenly distributed around the area where the measuring electrodes were placed.

The Current Follower (CF) device then measured the current passing between the EIX and counter electrodes.

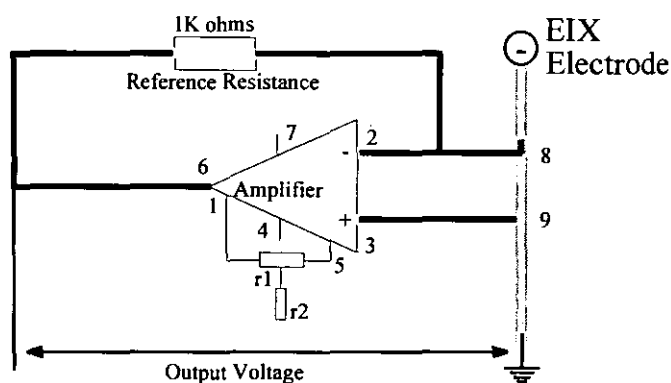


Figure 6.3: The current follower circuit

The device operated by balancing the potential difference between the platinum wires and the common earth. The output voltage corresponded to the current flowing through the electrolyte and membrane.

The CF was tested on metal mesh electrodes immersed in a beaker of sodium nitrate solution. Several trials were also carried out using a zirconium phosphate EIX electrode. These experiments were conducted for different concentrations of sodium nitrate in stirred and unstirred beakers. The device was installed in an EIX cell and a number of experiments were carried out to evaluate the viability of the method.

6.2.2 Direct measurement

The current follower technique was eventually found to be unsuitable. The cell was modified to measure currents directly along the length of the membrane and to obtain sample solutions from the centre and back of the cell.

Current distributions in electrochemical cells have been determined directly by multi-segmented electrodes by Bisang (1991) and Janssen and Visser (1991). In each case the electrodes were separated into segments electrically insulated

from each other. The overall current distribution was obtained by measuring the current flowing through each individual section.

The modifications for direct current measurements were in the form of small portholes made in the perspex walls and are shown in Figure 6.4. This was to allow the intrusion of electrodes into the membrane and syringe needles to draw sample solutions from the centre and the back of the cell.

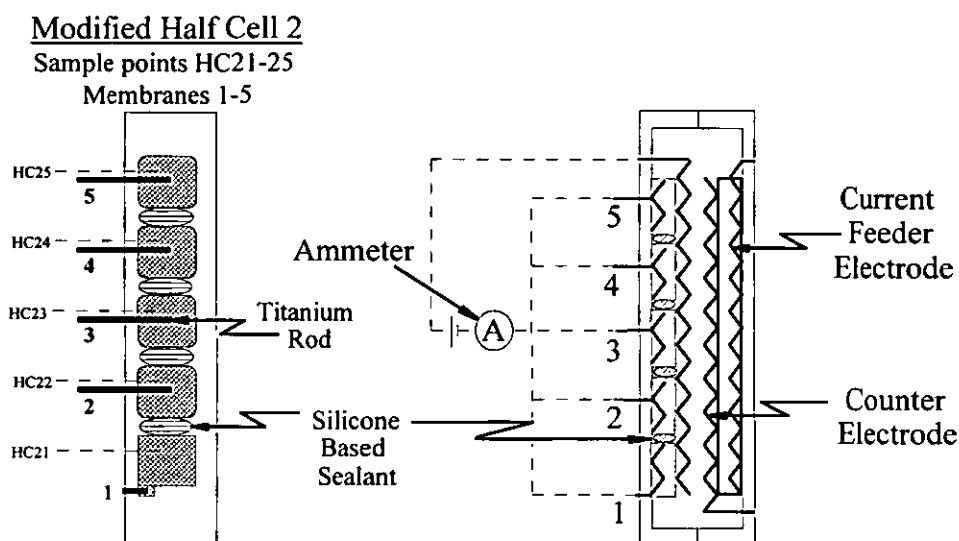


Figure 6.4: Modified EIX cell

One half of the cell, half cell two HC2, was taken out and replaced by a new membrane in five separate but electrically insulated parts. These sections were made to the same specification as the AEA membranes. The correct mixture of milled ion exchanger (zirconium phosphate), binder and solvent material was made. It was then poured into a mould containing five separate pieces of ordinary metal mesh electrode, all with the same area (5 cm by 6.3 cm). The liquid mixture was contained by perspex blocks and was placed in a fume cupboard to allow the solvent to evaporate. The mould was lined with grease proof paper to avoid the resin sticking to perspex. Once the electrodes were completely dry they were placed into an EIX cell.

Prior to casting, titanium wires were spot welded onto the electrodes to allow for connections to the external power supply. The contact to each individual electrode was made by titanium wires of 5 mm diameter to avoid large potential drops across the connection. The five EIX electrodes '1' to '5' were placed in the cell isolated from each other by silicone based sealant. It needs to be stated that the electrodes were equally spaced going from bottom of the cell to the top. The counter electrode was a single piece of metal mesh. Using an ammeter to measure the currents flowing through each section completed the circuit.

The current was measured by an ITT MX545 metrix multimeter. The ammeter was connected between the titanium wires and the power supply. The relationship between a number of parameters and the current profile was examined under different process conditions. Feed pH was changed to observe the effect on the current profile. Different current densities and flow rates were also used.

6.3 Flow patterns

The EIX cell was used to study the flow patterns within the system. Nigrosine dye was injected into the cell through the portholes and samples were taken from outlet of the cell. These were analysed optically to obtain concentration of dye. The samples were analysed on a Lambda 2 Perkin-Elmer UV/VIS spectrometer. After scanning the visible spectrum, 500 nm was found to be the optimum wavelength for the Nigrosine dye.

Two basic types of tests were conducted. Firstly, experiments were carried out to determine the nature of the flow through the centre of the cell. Concentrated solutions ($1000\text{--}2500\text{ mg.l}^{-1}$) of the dye were injected through point M1 shown in Figure 6.1. Samples were taken from the outlet at regular intervals. The second set of experiments was to observe the flow patterns in the back of the

cell. Solutions were withdrawn from the outlet with the nigrosine solution introduced through the sampling points at the back of the half cells.

6.4 Profiles: Results & Discussion

The series of experiments discussed in this chapter were aimed at obtaining concentration, pH, current and flow pattern profiles. Results indicated that there was a direct relationship between these parameters discussed in chapter 5 and process performance. Removal of cations was a measure of the cell performance in relation to the cell design and efficiency. This criterion could only be examined in relation to the concentration, pH and current distribution during operation cycles. The concentration and pH results were also used to assess cation removal and leakage of zirconium phosphate and Purolite membranes.

Samples of up to 2 ml were drawn from inside of the cell which were taken to be representative of the solution around the sampling point. The concentration and pH values were determined using these solutions. At times, it was difficult to collect samples because there was very little dead volume at the back of the cell. At high current densities, samples were often less than 1 ml due to the gas generated at EIX electrode being trapped at the back of the cell, making analysis very difficult.

6.4.1 Concentration and pH profiles

Some concentration and pH profiles obtained by taking samples along the length of the whole cell can be seen in Figures 6.5 and 6.6. These show the concentration and pH measurements made in the centre of the cell, back of half cell 1 and half cell 2 respectively denoted by HC1 and HC2. The distance

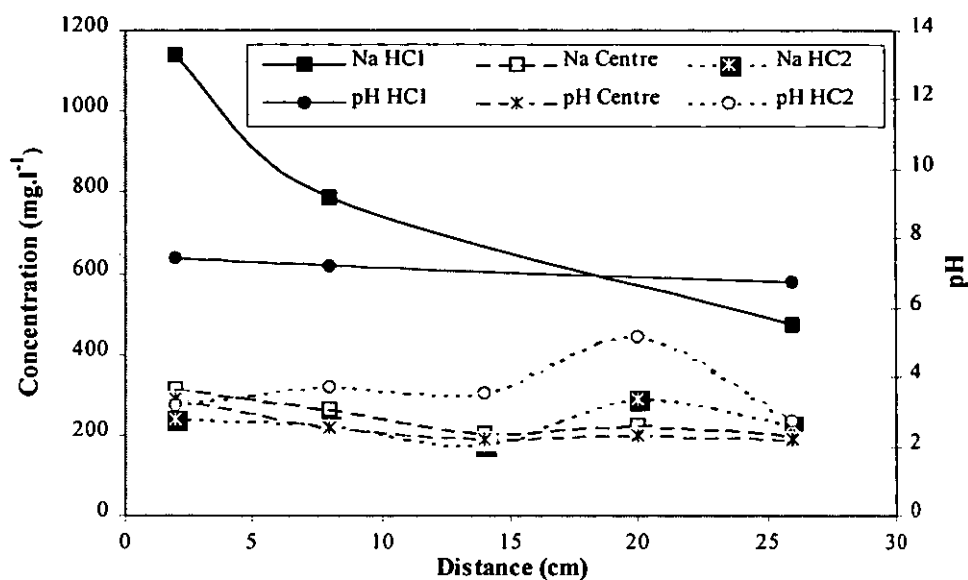


Figure 6.5: Concentration and pH values at centre and back of the cell

Feed Concentration = 300 mg Na.l^{-1} , Current Density = 4.5 mA.cm^{-2} ,
Flow rate = 2 l.h^{-1} , Feed pH = 10

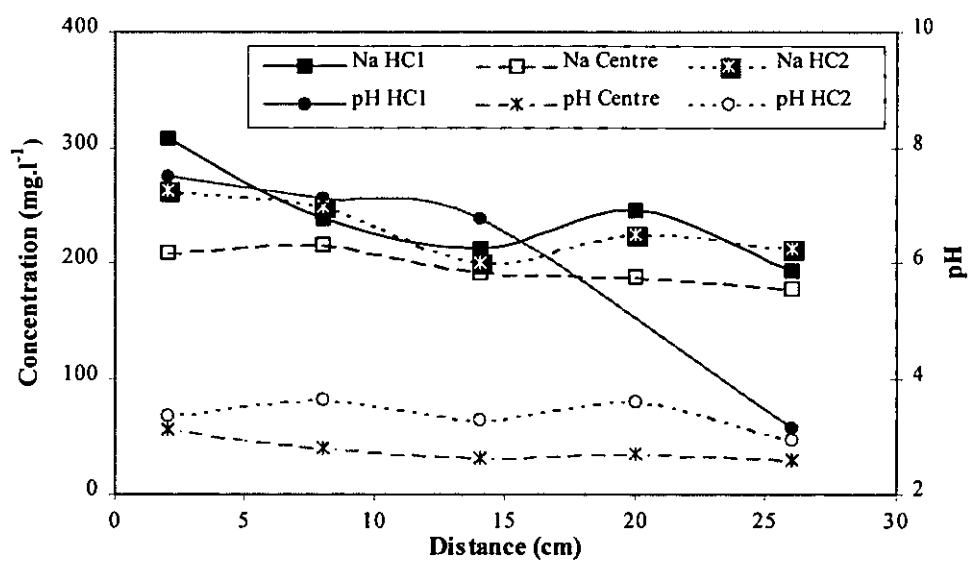


Figure 6.6: pH and concentration profiles at the back of both half cells and centre of the cell

Feed Concentration = 300 mg Na.l^{-1} , Current Density = 1 mA.cm^{-2} ,
Flow rate = 2 l.h^{-1} , Feed pH = 3

corresponds to the point where samples were drawn starting at 0 cm from the bottom edge of EIX membranes. These are the results of experiments carried out at a flow rate of 2 l.h^{-1} . The results for the higher and lower flow rates showed similar trends.

Feed pH of 3 and 10 were used to examine the performance of the cell under extreme acidic and alkaline conditions. Higher feed pH than 10 were not used because of the detrimental effect of high pH on zirconium phosphate membranes. The lowest pH was 3 because in more acidic conditions the pH swing across the cell would have been small and the change could not easily be measured for the purpose of these series of experiments. However, it was deemed that feed pH of 3 was sufficiently acidic to test the performance of the cell under acidic conditions. Current density of 4.5 mA.cm^{-2} was the maximum current density that could be supplied using the available power supply. The lowest current density used was 1 mA.cm^{-2} .

Figure 6.5 shows the results for concentration and pH profiles along the length of the cell for current densities 4.5 mA.cm^{-2} and a feed pH of 10. The concentration and pH in the centre decreased gradually along the length of the cell. The concentration of sodium measured at top of the membrane was 197 mg.l^{-1} while in the outlet it was 210 mg.l^{-1} , with a feed concentration of 300 mg.l^{-1} of sodium. The results were for the samples taken after one and a half hours of the experiment.

The results indicated that there was contamination of the outlet stream. The contamination was due to leakage of material from the back of the cell where the sodium concentration was four times that of the feed. The corresponding pH at the back of the cell was also high compared to the centre of the cell. The pH in the centre of the cell was almost immediately acidic while the pH at back of half cell 2 was near neutral but still higher than the centre. The reason for

the higher concentration and pH at only the back of half cell 1 was because half cell 2 was modified to obtain the current distribution. In the modified half cell, there were gaps between each section that allowed leakage of material from the back of the cell to the bulk solution.

Similar results were obtained for a feed pH of 3 as shown in Figure 6.6. At the back of the cell, sodium concentrations were not as high when compared to results conducted at a feed pH of 10 tests. The sodium ion concentration were still significantly higher than at the centre of the cell.

At the back of the cell, the concentration and pH profiles changed significantly with time. The longer the experiments were carried out, the higher the concentration and pH. The results shown in Figures 6.7 to 6.8 are for experiments conducted for 5 hours with current density of 4.5 mA.cm^{-2} and a feed pH of 10. Similar results were obtained for other tests conducted under different process conditions. There was evidence of an increase in pH and sodium concentration at the back of both half cells.

After five hours, the maximum sodium concentration at the back of half cell 1 was forty times greater than the feed concentration of 300 mg.l^{-1} as shown in Figure 6.7. The corresponding pH profiles can be seen in Figure 6.8. The pH values were about 12 at the back of half cell 1 after five hours. The sodium concentration was only three times greater than the feed at the back of half cell 2. This indicated that a substantial amount of the metal removed during the absorption cycle was accumulating at the back of the cell. It also showed that there was a slow and steady leakage of material to the bulk solution decreasing the level of removal by the process.

Similar results were obtained for the feed pH of 3 with a build-up of material at the back of the cell and a corresponding increase in pH. The concentration and

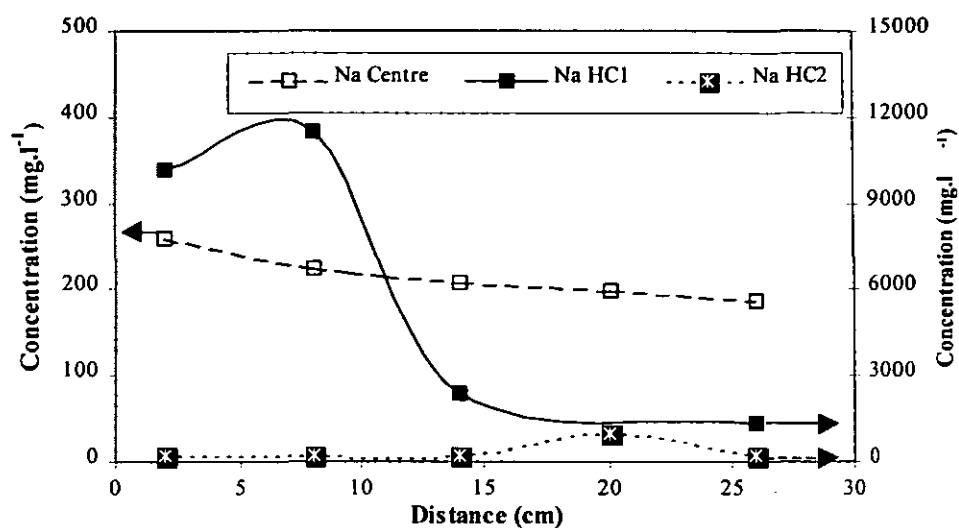


Figure 6.7: Sodium concentrations in EIX cell after 5 hours of absorption cycle
 Feed Concentration = 300 mg Na.l⁻¹, Current Density = 4.5 mA.cm⁻²,
 Flow rate = 2 l.h⁻¹, Feed pH = 10

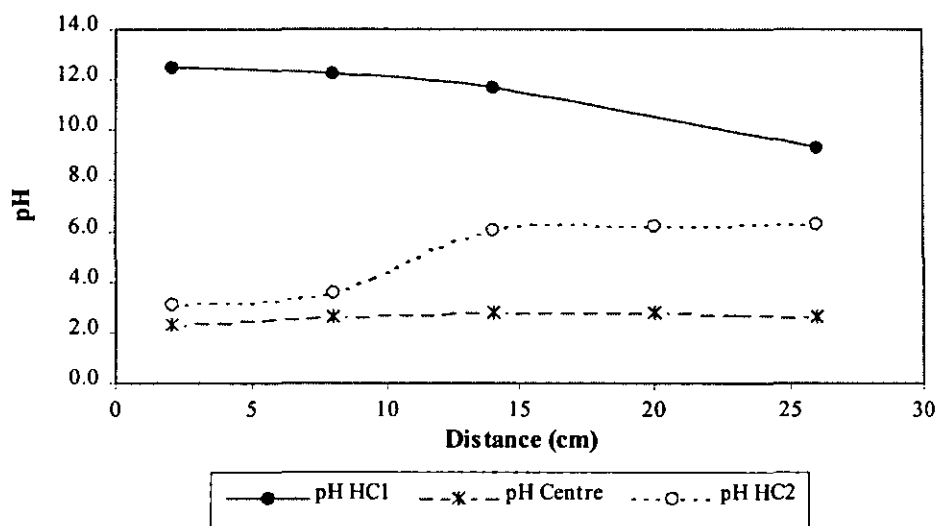


Figure 6.8: pH values in EIX cell after 5 hours of absorption cycle
 Feed Concentration = 300 mg Na.l⁻¹, Current Density = 4.5 mA.cm⁻²,
 Flow rate = 2 l.h⁻¹, Feed pH = 10

pH in the centre of the cell also increased with time. The outlet concentration increased with time indicating that there was also a gradual leakage of material from the back of the cell to the bulk solution. After 1 hour of operation, the sodium concentration measured at the top of the cell was 139 mg.l^{-1} and the outlet was 164 mg.l^{-1} . The difference between the concentration at the top of the cell and the outlet was less after five hours. This was thought to be due to leakage occurring from the bottom of the cell where the concentration increased by 76 mg.l^{-1} in four hours.

The pH and concentration profiles matched each other so when there was high concentration of sodium the pH was also high. This indicated that the species present was sodium hydroxide and not sodium nitrate which further suggested the leakage was from the back of the cell.

6.4.2 Current distribution

The current profile along the cell was obtained by direct measurement. Initially, a method was developed to measure the current in a particular part of the cell by using an operational amplifier. The current follower method involved the measurement of the current by platinum electrodes. The results for one such electrode can be seen in Figure 6.9. A voltage was induced across the circuitry to balance a measured current. This voltage represented the current flowing in that section of the membrane. The current follower method was calibrated in several ways. Experiments were conducted with five individual electrodes placed to give a representative current measurement of all parts of the system.

Firstly, the electrodes were installed on a bare metal mesh electrode to assess the viability of the current follower technique. The metal mesh electrode was then placed in a beaker containing sodium nitrate solution. On successful completion of these trials, the method was applied by using an EIX membrane

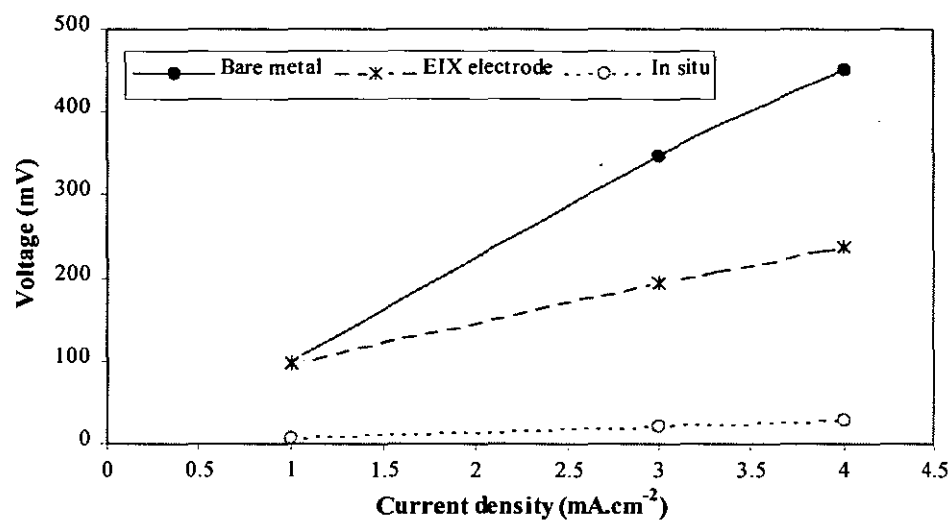


Figure 6.9: Calibration curves using the current follower technique
Feed Concentration = 50 mg Na.l^{-1} , Flow rate = 2 l.h^{-1} , Feed pH = 5

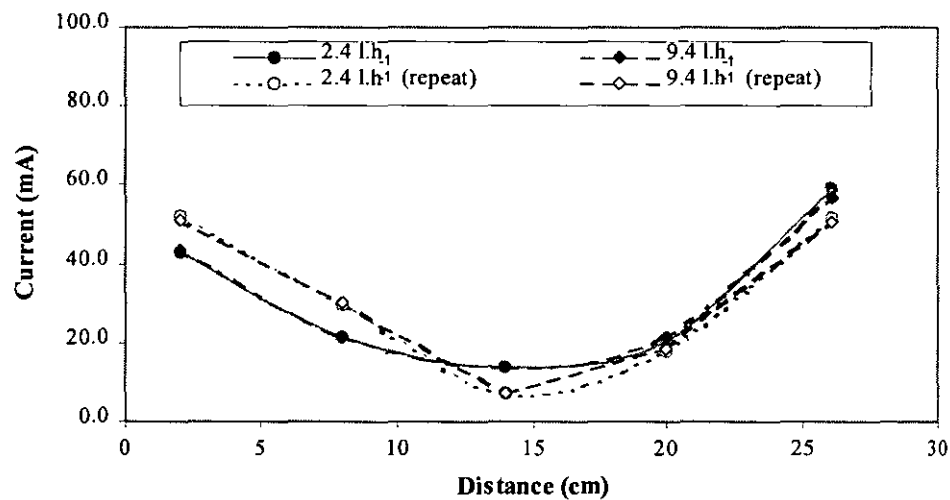


Figure 6.10: Current distribution along the length of cell at two different flow rates
Feed Concentration = 280 mg Na.l^{-1} , Current Density = $1 \text{ mA}\cdot\text{cm}^{-2}$, Feed pH = 3

instead of a metal mesh electrode. These results produced a lower voltage reading for the same conditions as shown in Figure 6.9. This was due to the surface of the electrode being partially shielded from the current by the membrane. The calibrations were still linear and the change in voltage reading with current acceptable with a 46 unit change in voltage corresponding to one unit change in current density. This would allow the current to be measured with reasonable resolution.

The current follower method was next used in-situ. Five platinum electrodes were placed within the membrane through portholes described in Section 6.2.1. Experimental conditions were the same as those for other tests. The results were very different with voltage readings drastically reduced. The change in output voltage was very small for a large change in current density as shown in Figure 6.9. The voltage increased by only 20 mV for a change in current density of 3 mA.cm^{-2} . For the same change in current density, the voltage change was over 300 mV for the calibration using the bare metal mesh electrode.

The difference in calibration curve obtained by tests in beaker and in-situ when using an EIX membranes could have been due to two reasons. The results shown here were for those with the lowest ratio of change in voltage to current density. The electrode was placed in the centre of the cell, the results in Section 6.4.3 show this was the position of the lowest current. Overall, the calibration curves were worse when the EIX cell was used. This would suggest that there was another reason for the difference. This was most probably due to the difficulty in introducing the platinum electrodes into the membrane when using the EIX cell. This may have resulted in part of the electrode area being masked from the current since it was difficult to determine the angle of the electrode facing the current. Due to the poor calibration curves obtained

in-situ, it was decided that the direct current method should be used to obtain the current distribution.

6.4.3 Direct Current Measurements

The direct measurement method was described in Section 6.2.2. One half of the cell was divided into five sections and an ammeter then measured the current flowing through each section. Different experiments were conducted to study the effect of changing process parameters on the current profile. The results can be seen in Figure 6.10. The current readings were found to be highest at the top and the bottom of the cell. The minimum current reading was in the middle section of the cell. The current distribution was unchanged over wide range of flow rates between 2.4 l.h^{-1} and 9.4 l.h^{-1} .

6.4.4 Order of membranes

The sequence of membranes was changed to ensure that the current distribution was independent of individual membranes. Figure 6.11 shows the electrode sequence before and after the order of membranes was altered.

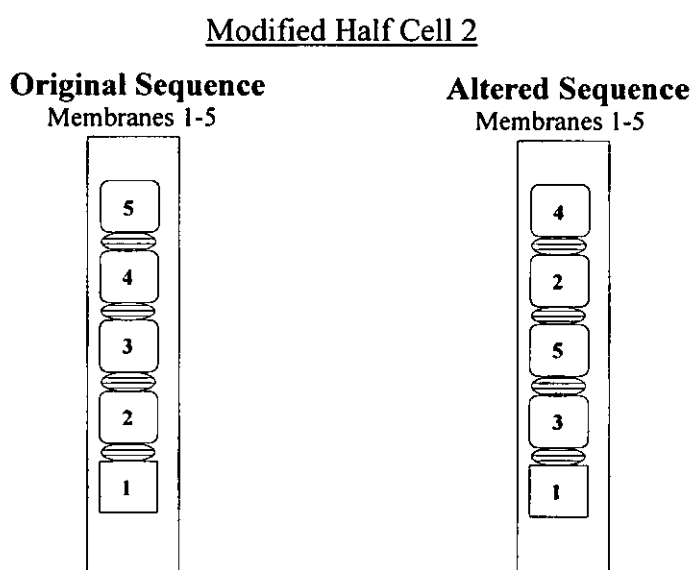


Figure 6.11: Modified membrane sequence

The results for experiments carried out after the alterations can be seen in Figure 6.10, denoted by repeat lines. The experiments were repeated under the

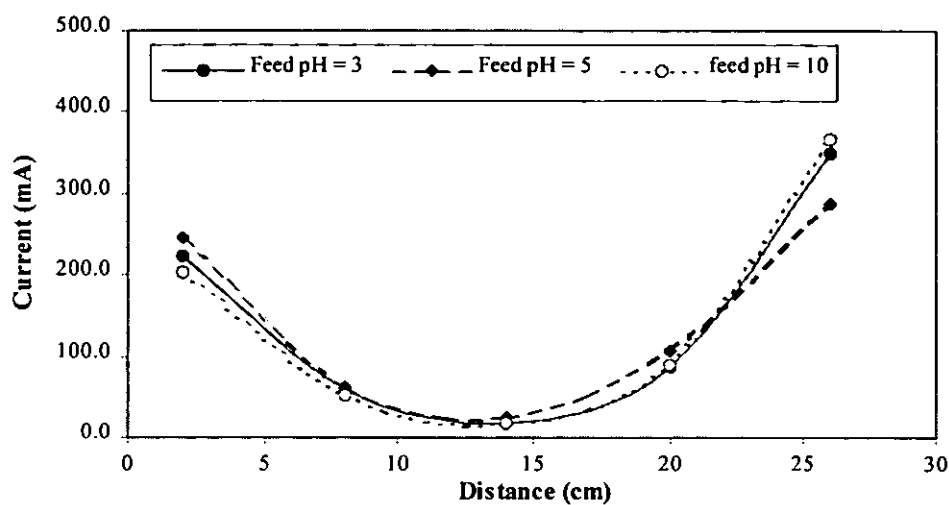


Figure 6.12: Current profile at different feed pH

Feed Concentration = 280 mg Na.l^{-1} , Current Density = 4.5 mA.cm^{-2} , Flow rate = 2.4 l.h^{-1}

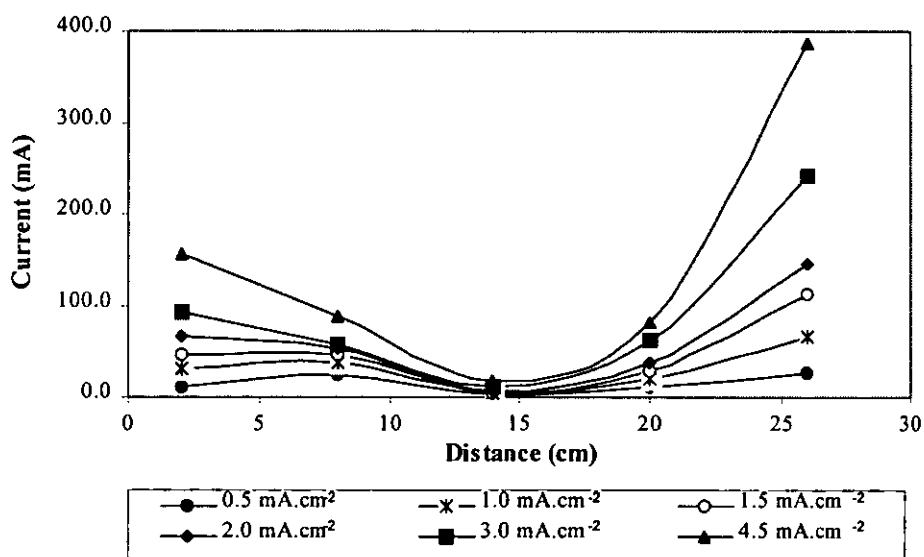


Figure 6.13: Current distributions for different current densities and pH of 10

Feed Concentration = 300 mg Na.l^{-1} , Flow rate = 2 l.h^{-1} , Feed pH = 10

same experimental conditions, the current distributions were found to be similar to the original profiles. This indicated that profile was not dependent on the properties of the membrane sections.

A number of experiments were conducted to determine the reason for the meniscus shape of the current distribution. Different feed pH and current density were used to examine the effect of changes in these parameters on the current profile. The relationship between the current density and the current profile at feed pH of 3, 5 and 10 are shown in Figure 6.12.

It can be seen that the current profile had a curved shape with the minimum current reading in the centre section of the cell and maximum readings at the inlet and outlet. This basic shape of the current distribution was obtained over a wide range of flow rates, current densities, electrode gaps, feed pH and feed concentration. The back and centre of the cell was sparged with air to examine the effect of better mixing within the cell on the current distribution. The cell used to obtain the current profile was taken apart several times for alterations. During one of the modification, one of the 5 mm titanium rod, providing the connection to the external power supply, became disconnected from the membrane. This gave an opportunity to study the relationship between thickness of the membrane and the current profile.

6.4.5 Thickness of membrane

The EIX electrode was cleaned of all the original membrane material. The titanium rod was then spot welded back onto the platinised titanium metal mesh. The membrane was recast with fresh solvent, ion exchanger and binder. Half the amount of material was used compared to the original membrane. The final membrane was thinner, 5.9 mm wet compared to the thickness of the original membrane 8.7 mm wet. However, the ratio of ion exchanger to binder to solvent was kept constant. The new membrane was placed within the cell in

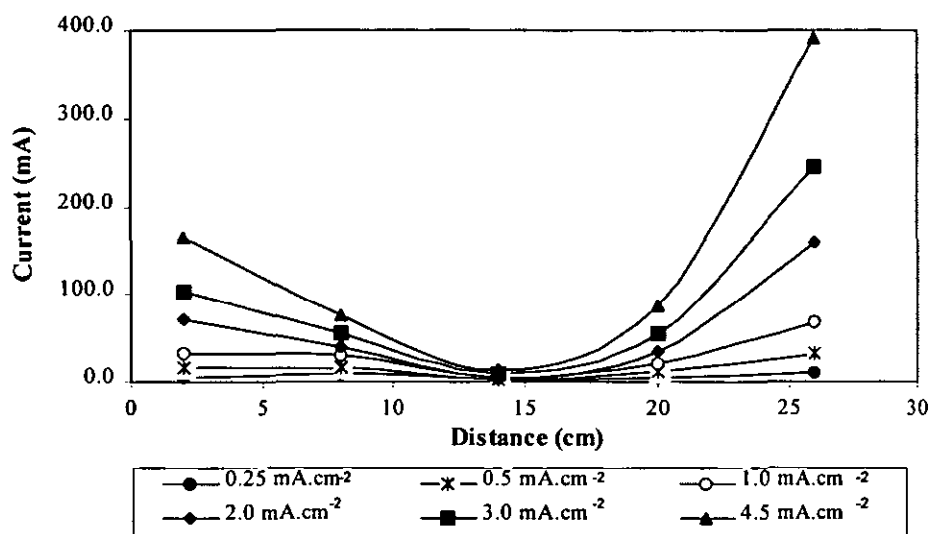


Figure 6.14: Current distributions for different current densities and pH of 3
 Feed Concentration = 300 mg Na.I⁻¹, Flow rate = 2 l.h⁻¹, Feed pH = 3

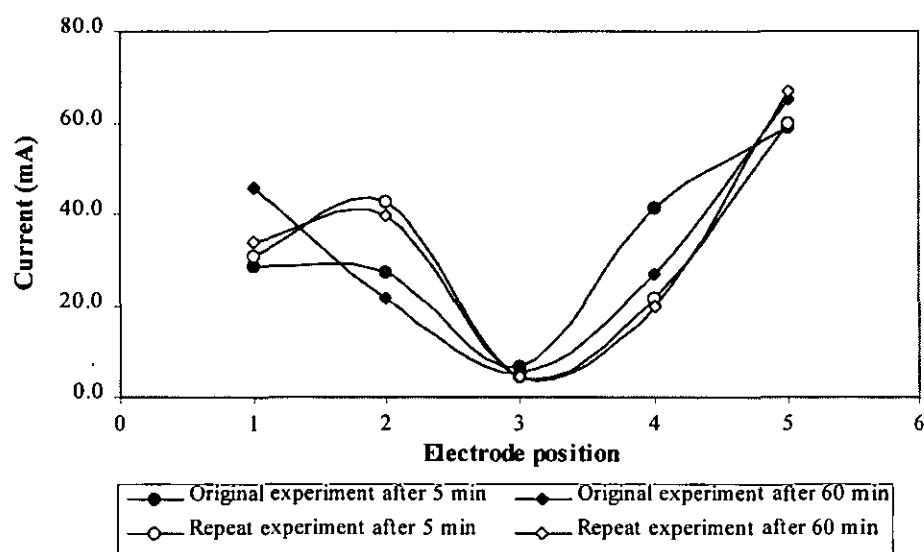


Figure 6.15: Current profile before and after replacing the second electrode and for a current density of 1 mA.cm⁻²
 Feed Concentration = 300 mg Na.I⁻¹, Flow rate = 2 l.h⁻¹, Feed pH = 10,
 Current Density = 1 mA.cm⁻²

the second position that is the second membrane from the inlet as seen in Figure 6.3. The new membrane was conditioned by conducting a series of absorption and elution cycles.

Table 6.1 contains the thickness of original and new sets of membranes, both dry and wet. Previously, the membranes had been moved around to ensure the current profile obtained was independent of the membranes used and their thickness. It can be seen that there was a range of membrane thickness. The thickness of each membrane had also changed between measurements. The reason for this anomaly could be due to different loading of the ion exchange membranes at time of the measurements. Another possibility was uneven surface of the membrane, although, three different measurements were taken and the average has been reported here.

Table 6.1: Thickness of the membranes before and after the addition of the new membrane

Electrode	Thickness (mm)			
	Dry after	Wet after	Dry before	Wet before
1	8.7	9.5	8.7	9.1
2	5.5	<u>5.9</u>	6.7	<u>8.7</u>
3	6.9	8.5	6.2	8.7
4	8.2	9.3	6.8	9.1
5	7.5	8.2	6.0	9.0

6.4.6 Other parameters

Further experiments were carried out at feed pH of 3 and 10 with the new membrane installed in the cell. The results can be seen in Figures 6.13 and 6.14. The figures show that the current readings for the second electrode were greater than the first electrode at lower current density, particularly under alkaline conditions. All readings were taken after one and a half hours to ensure that the system had reached pseudo steady state. It can be seen that as

the current density increased the new membrane behaved more like the older thicker membrane, that is, the current reading for the second electrode fell between the first and third membrane.

There are several possible reasons for the change in the current profile when using a thinner second membrane. The change in current readings could be partly explained by the thinner membrane offering a lower resistance to the passage of a current through it. The current profile experiments were carried out at random to avoid the results being affected by the order experiments were conducted. Therefore, the form or loading of the membrane did not influence the results.

The difference in experimental results were more marked between the new membrane and the original membrane at lower current densities and high feed pH. In both cases, the hydrogen ion concentration was lower. At low current densities, more of the current was carried by sodium ions as less hydrogen ions were present in the liquid.

At high feed pH, some hydrogen ions produced at the counter electrode were neutralised and sodium ions contributed more to carry the current. The results indicated that when sodium ions were responsible for carrying the bulk of the current the thickness of the membrane was more important than when hydrogen ions were present in excess. This would suggest that when sodium ions were present in the membrane the subsequent hydroxyl ion concentration in the membrane would have been also high. Hydroxyl ions would have contributed to the transport the current especially when total the amount of ion exchanger was less and exchange between sodium and hydrogen less likely.

6.4.7 Change with time

The changing behaviour of the membranes with time was examined using both sets of membranes. The experiments were repeated after the addition of the new membranes under the same conditions as the original tests. The results can be seen in Figures 6.15 and 6.16. Figure 6.15 shows the current profiles for a current density of 1 mA.cm^{-2} and feed pH of 10. The higher current reading through the second section was unchanged after sixty minutes in the repeated experiments.

In the original experiment, current flowing through the first membrane was initially lower after five minutes compared to sixty minutes. Conversely, The current flowing through fourth membrane was reduced after sixty minutes when compared to current after five minutes. At the beginning of the experiment, the concentrations outside and inside the membrane were not fully established. In the bottom section of the cell, the first membrane was in alkaline conditions and most of the sodium ions were removed by ion exchange. Therefore, there were not less ions to carry the current. Higher up the cell the conditions were more acidic and more hydrogen ions contributed to carry the current. At high current densities and low pH, the current profiles were similar as the membranes were all in more acidic conditions and there was always sufficient number of ions to transport the current as seen in Figure 6.16. The experiments were carried out at a feed pH of 3 and a current density of 1 mA.cm^{-2} .

6.4.8 Current distribution at high feed concentration

During the selectivity experiments discussed in Section 5.4.3, the current distribution across the cell was also determined. The results for one of these experiments can be seen in Figure 6.17. These indicate a slow but definite increase in the current in the middle section. There was an equivalent drop in the current readings at top of the cell. As expected, this would suggest that the current distribution is partly related to concentration and pH profiles within the

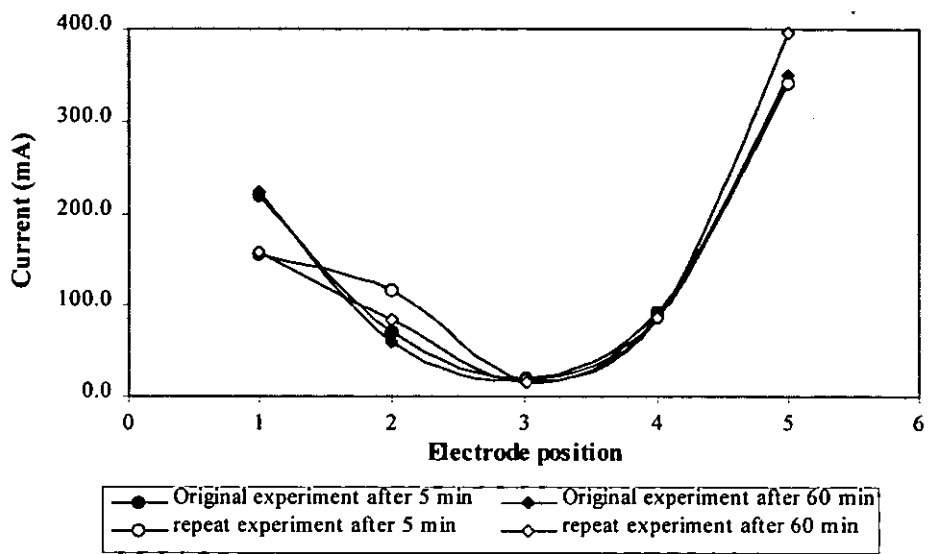


Figure 6.16: Current profile before and after replacing the second electrode in acidic condition, for a current density of $1\text{ mA}\cdot\text{cm}^{-2}$
Feed Concentration = 300 mg Na.l^{-1} , Flow rate = 2 l.h^{-1} , Feed pH = 3

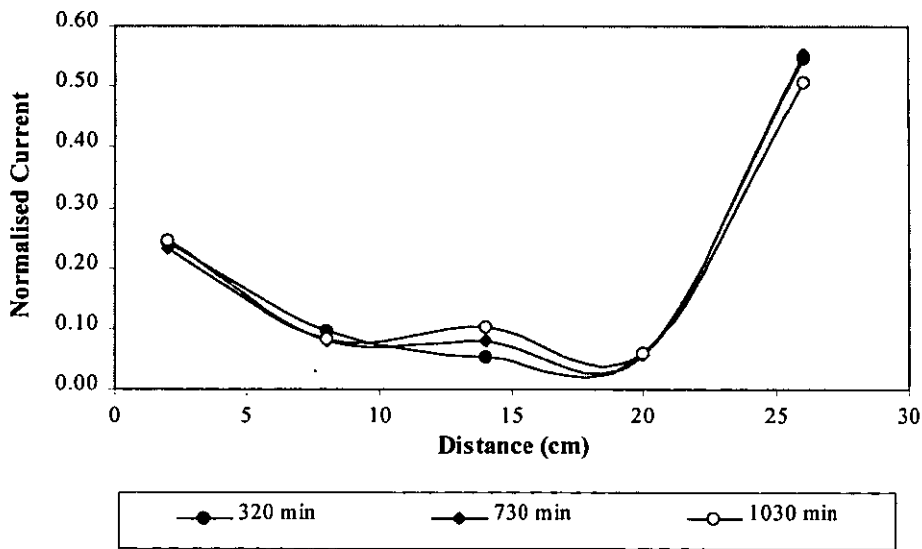


Figure 6.17: Change in current profile during absorption cycle with high sodium feed concentration
Feed Concentration = 5300 mg Na.l^{-1} , Current Density = $4\text{ mA}\cdot\text{cm}^{-2}$
Flow rate = 1 l.h^{-1} , Feed pH = 5.6

membrane. During absorption cycles, concentrations and pH were measured in all parts of the cell including inside the membranes. It was difficult to determine any significant differences between the concentration inside the membranes and the back of the cell. This was partly due to the high sodium concentration and high pH experienced in all parts of the cell.

The volume of samples was between 1 and 2 ml which were comparable to the total volume present within the membrane and back of the cell. Any samples drawn out of the membrane with these volumes would have meant that the solution was partly contaminated by the solution from nearby areas. Smaller samples would have been difficult to analyse and larger volumes could not be exactly representative of the position samples were drawn from.

6.4.9 Effect of Mixing and Electrode Gap

Better mixing was promoted in the bulk liquid to examine the relationship between external mass transfer and current profile. This was carried out by injection of air at the bottom of the cell to observe the change in the current distribution. It was also decided to establish whether mixing at the back of the cell had any effect on the performance of the membrane.

Air was introduced into the cell by placing a plastic tube at the bottom part of the cell pierced at regular intervals along its length. The tube was connected via a rotameter to the air supply. Once the air supply was opened the bubbles flowed up the cell. The effect of changing the air flow rate at different feed pH and current densities were examined.

A gap was also introduced at the back of the cell by placing small pieces of silicon rubber between the membranes and the perspex wall. This allowed process solution easier access and greater flow of material passed the back of the membrane. The current was measured to detect any changes in the

distribution. Air bubbles were also introduced at the back of the cell to promote better mixing. Air was injected into the cell the same as before by placing pierced plastic tubes at the bottom of the cell. Introduction of gaps and air bubbles had no effect on the current readings.

One possible explanation for the current distribution could have been stray or bypass currents at the top and bottom of the cell. Since there were large volumes of solution at the top and bottom of the cell comparable with the volume of solution passing between the counter electrodes. This was considered early on in this series of experiments and efforts were made to cover bare electrodes at either end and stop any short circuits. The results showed current distribution was unchanged and the same profile was obtained. However, it would seem reasonable to suggest that the shape of the current profile was partly due to stray currents at the top and bottom sections of the membranes. Overall, The results indicated that conditions outside the membrane did not affect the current distribution.

Another reason for the meniscus shape of the current profile could be due to conditions within the EIX membrane. In the centre section, the solution was probably more alkaline than any lower or higher section in the cell. The centre of the cell was not directly in contact with a large volume of solution. Both top and bottom sections were in contact with large volumes of solution held in the inlet and outlet sections of the cell. This meant that both these sections may have been in less alkaline conditions with transfer of alkaline solution from the membrane into the bulk solution. This could result in higher concentration gradient across the centre section. Low currents through this section might have arisen because the applied voltage allowed only a limited current to be supported, most of potential being used to maintain the concentration difference across the membrane.

The concentration profile within the bulk solution did not change a great deal. The removal of sodium from the bulk solution continued because there was still ion exchange taking place in the membrane reducing the concentration within the membrane. Sodium was also being pumped to the back of the cell and leaking into the bulk solution at the top and leaving the cell. This might explain the shape of the current profile once the concentration of sodium in the membranes was high. It does not explain the shape of the current profile at the beginning of the experiment when most of the resin would have been in the hydrogen form. However, results shown in Figure 6.15 indicate that current readings were more evenly distributed at the beginning of the experiments than after 60 minutes.

6.5 Flow patterns

Nigrosine dye was used to examine the leakage of material from the back of the cell to the bulk solution. The flow profiles in the centre of the cell were determined under different process conditions using the same technique. Initially, tests were carried out in batch mode to test nigrosine dye for inertness. An EIX half cell was placed in a beaker filled with 500 mg.l⁻¹ of nigrosine dye solution. Current was passed through the half cell for an hour with no change in the measured dye concentration.

6.5.1 Leakage from the back of the cell

Samples of dye, 2 ml in volume, were injected into the back of the cell at three different positions. The concentration of nigrosine dye was 2500 mg.l⁻¹ and the injections were at the top, bottom and centre of the cell corresponding to points HC25, HC23 and HC21 in Figure 6.1. The samples were taken from the outlet of the cell at regular intervals. The response of the cell can be seen in Figure 6.18. These showed that there was little but steady leakage from the back to the rest of the cell. There was a steady leakage from the sides, top and bottom of the membrane. Sample drawn from the injection point showed that most of the

dye solutions seemed to remain near the injection point. The final concentrations were about 500 mg.l^{-1} at these points. Points at the back of the both half cells were used to determine if the leakage was the same from them. It was found that concentration of dye leaving the cell was independent of which half of the cell was used.

The leakage when the dye was injected into the top of the cell was immediate, after the initial peak, the concentration of dye leaving the cell became constant. The amount of material leaking when dye was injected near the bottom of the cell was similar but the peak was much broader. This was probably due to the dispersion effect within the cell. The material from the bottom would enter the bulk near the inlet and pass through the main channel before leaving the cell, it would be affected by the mixing in centre of the cell.

Samples were also injected through the porthole HC23, the leakage from the back of the cell was different in this case. There was a peak after 10 minutes and another after 40 minutes. The second leakage was probably due to the bubbles escaping from the back of the cell and dislodging some concentrated dye solution from the back to the bulk solution. In absolute terms, the leakage was least when dye was injected through point HC23 in the centre of the cell.

6.5.2 Central channel

Dye experiments were carried out to obtain flow patterns within the centre of the cell. These were conducted for a range of flow rates and current densities. A sample of nigrosine dye was injected through point M1 shown in Figure 6.1. Samples were then taken from the outlet at regular intervals to obtain the concentration of dye leaving the cell.

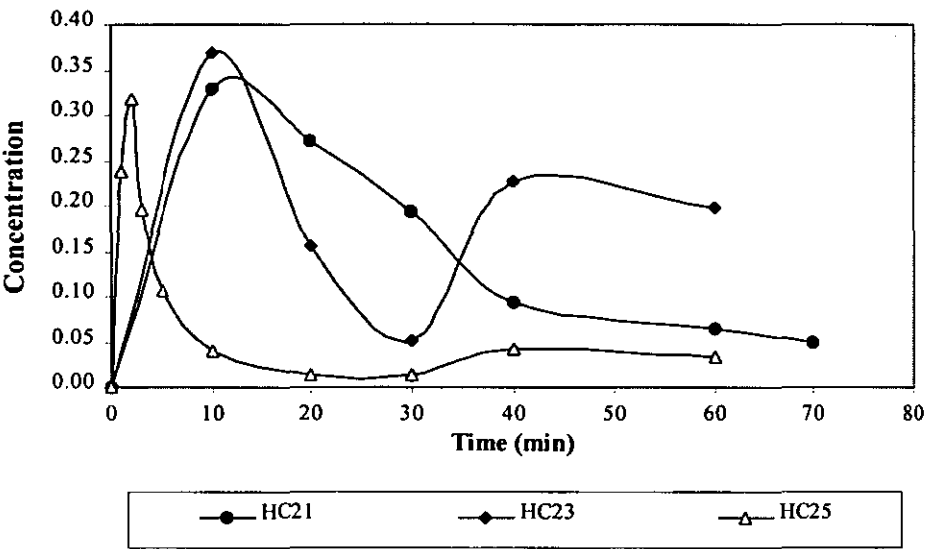


Figure 6.18: Leakage of material from back of the cell with dye injected into the cell at different points
Feed Concentration = 300 mg Na.l⁻¹, Current Density = 1 mA.cm⁻²
Flow rate = 0.2 l.h⁻¹, Feed pH = 3

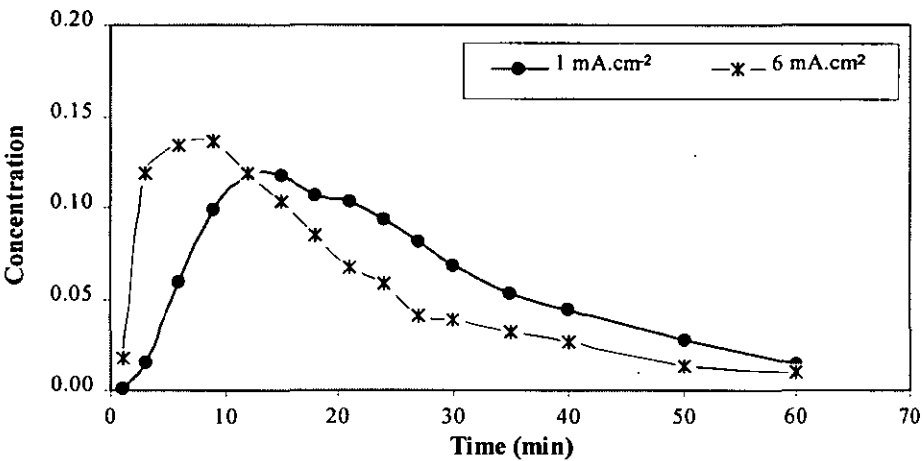


Figure 6.19: Normalised Nigrosine dye concentration at a low flow rate of 0.2 l.h⁻¹
Feed Concentration = 300 mg Na.l⁻¹, Flow rate = 0.2 l.h⁻¹, Feed pH = 3

The results of some experiments can be seen in Figures 6.19 to 6.21 with plots of normalised concentration versus time. Normalised concentration on the vertical axis was used in order to compare the results of all experiments on the same basis. In this way, small variations in the amount solution injected can be ignored. The results indicate two main factors governing the flow patterns within the centre of the cell were current density and flow rate.

The Figures show that at a higher current density of 6 mA.cm^{-2} the concentration peaks appear earlier than for current density of 1 mA.cm^{-2} . This indicates that the mixing in the cell is improved by the generation of gas. At high flow rates, the peaks are sharper than at lower flow rates. This means that at the higher flow rate the cell may behave more like a plug flow reactor with less back mixing.

Mixing processes due to flow rate and bubbles generated as result of electrochemical reactions at the electrodes were working in parallel during normal operation of an EIX cell. At high flow rates, the process was dominated by the action of the flow. As the flow rate decreased, the mixing effect of bubbles was more important. The peak at the lowest flow rate appears well before the predetermined time of twenty seven minutes but there is a long drawn out tail which indicates that there was significant back mixing. At higher flow rates, the peak appears at the predicted time of one and a half and six minutes.

6.6 Purolite Membranes

The concentration and pH profile experiments were also carried out using Purolite S930 and S950 membranes. The cell containing the S950 membrane was only modified to obtain samples from the centre of the cell. The results for some experiments can be seen in Figures 6.22 to 6.27.

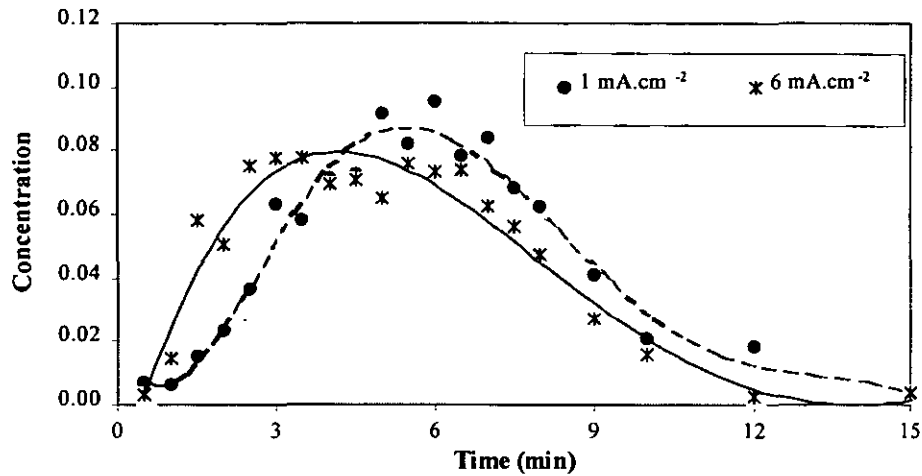


Figure 6.20: Profile of outlet concentration of dye at a flow rate of 0.7 l.h⁻¹
Feed Concentration = 300 mg Na.l⁻¹, Flow rate = 0.7 l.h⁻¹, Feed pH = 3

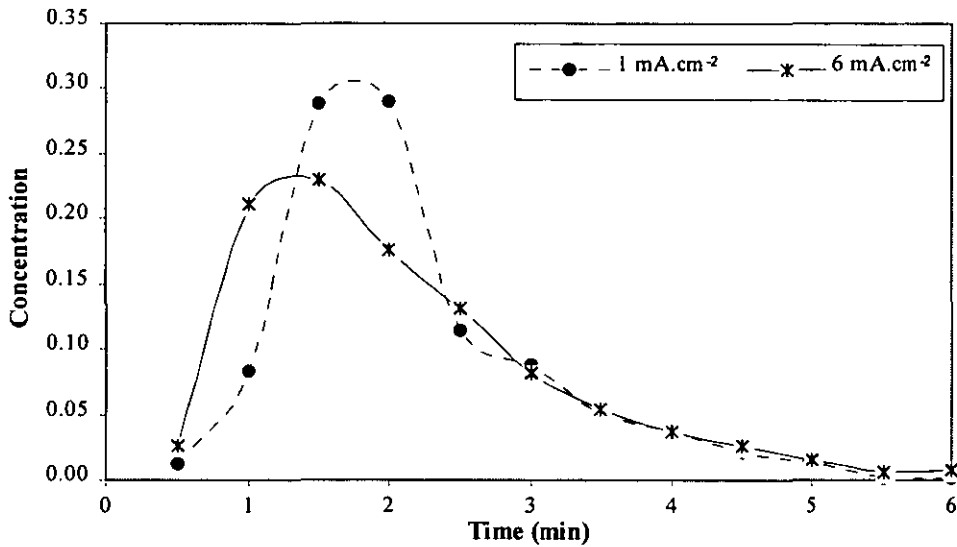


Figure 6.21: Outlet dye concentration at higher flow rate of 3 l.h⁻¹
Feed Concentration = 300 mg Na.l⁻¹, Flow rate = 3 l.h⁻¹, Feed pH = 3

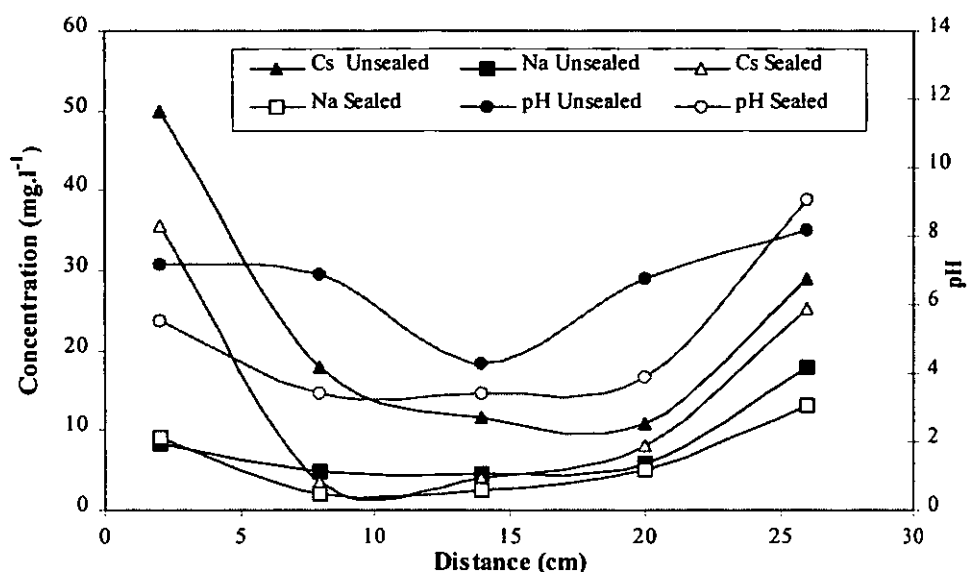


Figure 6.22: Concentration and pH profiles in the centre of unsealed and sealed S930 cell

Feed Concentration = 30 mg Cs.l⁻¹, Current Density = 3 mA.cm⁻²
Flow rate = 1 l.h⁻¹, Feed pH = 3.8

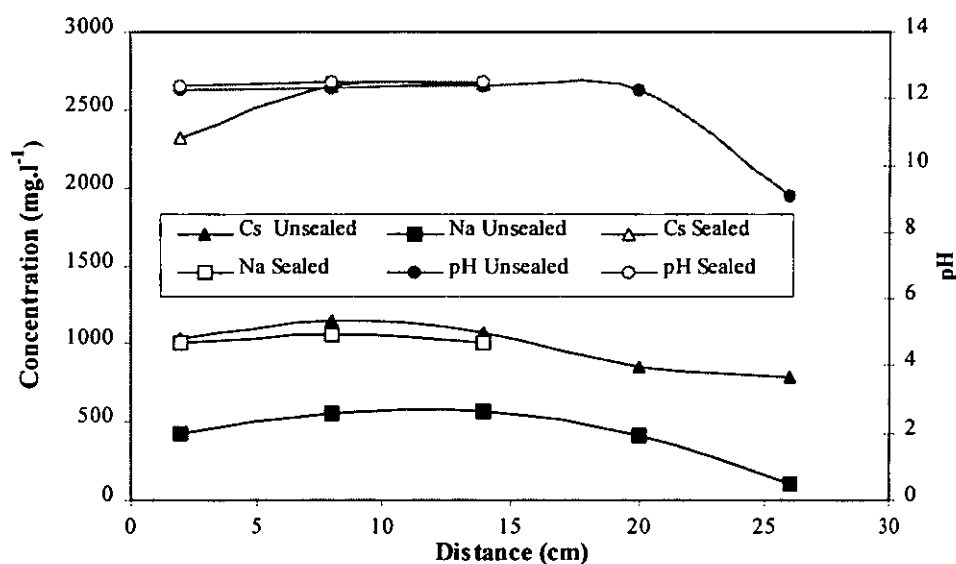


Figure 6.23: pH and concentration profiles at back of half cell 2 using unsealed and sealed cells

Feed Concentration = 30 mg Cs.l⁻¹, Current Density = 3 mA.cm⁻²
Flow rate = 1 l.h⁻¹, Feed pH = 3.8

Based on earlier results with the zirconium phosphate membranes and dye experiments there was an indication that there was material leaking from the back of the cell to the bulk solution in the centre of the cell. This was also observed in the cell containing the Purolite membranes where there was precipitation occurring at bottom of the cell. Experiments were conducted to measure the concentration and pH at back and centre of the cell using Purolite membranes.

Cells containing Purolite membranes were then modified as discussed in section 5.3. The tops of the membranes were not sealed to allow gases produced during electrolysis to escape. Experiments were carried out to compare the profiles before and after sealing of the cells containing S930 and S950 membranes. The Purolite membranes were used in sodium and hydrogen form and tests were conducted to examine the differences between the two forms. Initially, tests were carried out with sodium and caesium, in later experiments caesium was present in the system as well as sodium.

6.6.1 S930 Membranes

Figure 6.22 shows the concentration and pH profiles in the centre of the cell containing Purolite S930 membranes. The results were the values obtained for an unsealed cell and sealed cell after absorption experiments were conducted for 255 minutes. There was marked reduction in concentration of sodium and caesium when the cell was sealed. This indicated that leakage of material from the back of the cell was significantly reduced. The pH was markedly less in the centre of the cell after the back had been sealed. Only the pH at top of the cell remained unchanged. This was due to the top of the cell being unsealed to allow gases generated at the EIX electrode to escape which allowed material from the back of the cell to contaminate the bulk solution. This can be seen in Figure 6.22 with sodium and caesium concentration increasing at top of the cell even after the cell was sealed. The caesium concentration at bottom of the cell

was higher than the feed in the unsealed cell experiments. The results can be seen in Figure 6.22.

At the back of the cell, the situation was reversed where the concentrations of caesium and sodium were much higher in the sealed cell as shown in Figure 6.23. There was very little change in the pH but in terms of hydroxyl ion concentration at pH 12 considerable amount of ions were needed to have any appreciable effect on pH. The amount of caesium was nearly a hundred times greater at the back of the sealed cell than the feed. Another noticeable difference was in the amount of gas present at the back of the cell which increased with sealing of the cell. This made drawing of samples from the back of the sample very difficult and higher up the cell no samples could be taken. Both set of results indicated a reduction in amount of material leaking from the back of the cell to the bulk solution. All other experiments were conducted with sealed cells.

The sodium and hydrogen forms of the S930 membranes were used to study the removal of zinc from dilute solutions with a feed concentration of 30 mg Zn.l^{-1} . The results can be seen in figures 6.24 and 6.25 for a sealed cell. Figure 6.24 shows the concentration and pH profile in the centre of the cell. Zinc was steadily removed in both cases and there was a corresponding increase in the concentration of sodium, caesium and hydrogen ion concentrations. The caesium was present as absorption cycles were carried out using a feed solution containing caesium. Higher pH readings were found at top of the cell compared to the bottom section.

Sodium form of the S930 removed zinc better than the hydrogen form. Using the hydrogen form of the membranes, only trace quantities of sodium and caesium were detected in the cell. No trace of zinc was found at back of the cell when using the sodium form of the membranes. This is not surprising, as

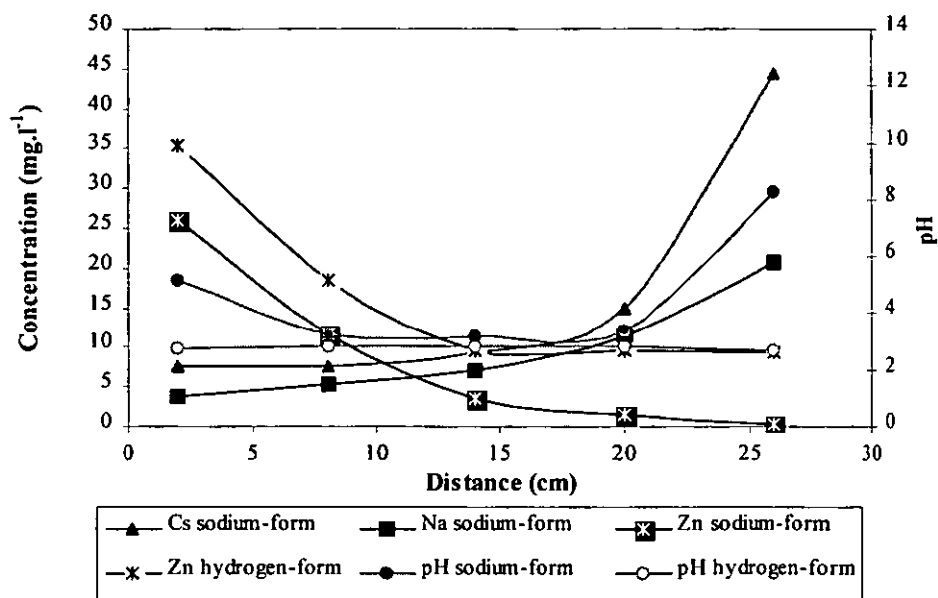


Figure 6.24: Concentration and pH values in the centre of sealed cell using hydrogen and sodium form of the membranes
Feed Concentration = 30 mg Zn.l⁻¹, Current Density = 3 mA.cm⁻²
Flow rate = 1 l.h⁻¹, Feed pH = 3.8

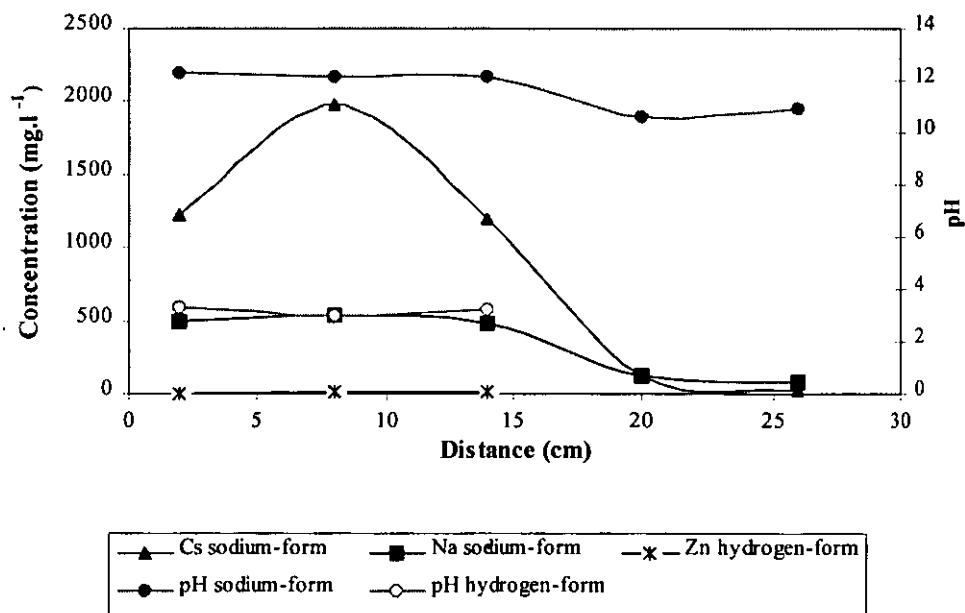


Figure 6.25: pH and Concentration profiles at the back of sealed cell using sodium and hydrogen form of membranes
Feed Concentration = 30 mg Zn.l⁻¹, Current Density = 3 mA.cm⁻²
Flow rate = 1 l.h⁻¹, Feed pH = 3.8

the conditions at the back of the cell were highly alkaline. Any zinc not removed by the ion exchange would have precipitated out of solution. The amount of zinc removed by ion exchange compared to precipitation could not be estimated since both are accompanied by the same change in pH.

Zinc was detected at the back of the cell operating with the membranes in the hydrogen form. The pH at the back of cell was lower compared to the alkaline conditions present in the back of the cell when the membranes were in sodium form. The zinc concentration at the bottom of the cell was greater than the feed concentration when using the hydrogen form of the S930 resin as shown in Figure 6.24. This indicated that there was leakage in the sealed cell. The most likely source of the contamination was zinc present at the back of the cell when using the membrane in hydrogen form.

6.6.2 S950 Membranes

Similar experiments were carried out with Purolite S950 membranes as those conducted using S930 membranes. These were conducted to compare zinc removal using sodium form and hydrogen form of the S950 membranes. Similar concentration and pH profiles were found within the cell. The concentration of zinc in the centre of the cell was lower in the sodium form of the S950 than the hydrogen form. Using the hydrogen form of the S950, the zinc concentration from the first two sample points was higher than the feed as the cell was unsealed and material leaked from the back of the cell. This profile was matched by the pH profile indicating that the zinc was in the hydroxyl form. It was possible that zinc had precipitated in the cell. Due to higher density the solid particles would float down towards the bottom of the cell. There was a balance between the upward force due to the flow and the settling force due to gravity. This was further highlighted by the experiments conducted at higher flow rates showing an increase in zinc concentration higher up the cell.

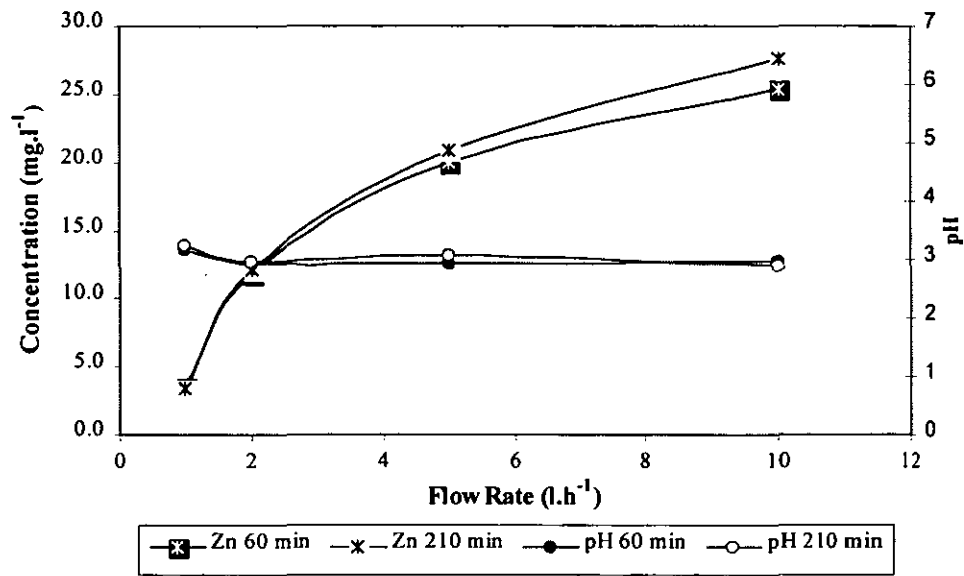


Figure 6.26: Change in zinc concentration and pH with time of samples collected at the top of the cell
Feed Concentration = 30 mg Zn.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 3

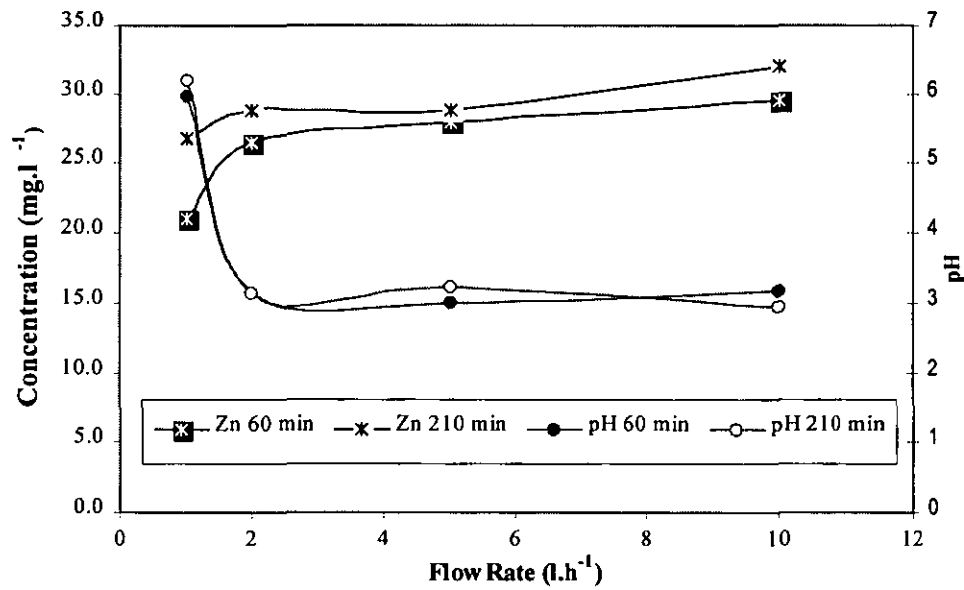


Figure 6.27: Zinc concentration and pH at different time during absorption cycle for samples collected at the bottom of the cell
Feed Concentration = 30 mg Zn.l⁻¹, Current Density = 3 mA.cm⁻², Feed pH = 3.4

Figures 6.26 and 6.27 show results of experiments conducted with the hydrogen form of sealed S950 for a range of flow rates. During the experiments, the pH and concentration at top and bottom of the cell changed with time. At the top of the cell, the variation in pH and concentration were insignificant over the time that experiments were conducted for.

At bottom of the cell the change in concentration of zinc was greater over the time that the experiments were carried out for. This can be seen in Figure 6.27, the concentration of zinc at the bottom of the cell increased between 60 minutes and 210 minutes indicating a leakage of material from the back of membranes to the bulk solution. The sealing of the bare part of the metal mesh that allowed the electrical contact to be made between the EIX electrode and the power supply had failed after repeated use. This created a gap which allowed the leakage of material from the back of the membrane. There was very little difference in the pH result between 60 minutes and 210 minutes.

6.7 Conclusions

There were several major findings which were highlighted in this section. These lead to modification in cell design and improved the performance of the EIX cell in terms of removal of material as well as reduction of precipitation in the bulk solution.

The main conclusions drawn from this series of experiments were as follows:

- There was a constant and gradual removal of cations from the inlet to outlet accompanied by a corresponding reduction in pH as result of ion exchange when using the hydrogen form of the resin.
- There was an increase in concentration and pH at the back of the cell which indicated that not all the cations transported into the membrane were removed from solution.

- The build-up of material was dependent on the length of time the experiments were carried out for as well as feed pH, current density and condition of the membrane.
- There was clear evidence to suggest that the bulk solution was contaminated by material leaking from the back of the cell which was drastically reduced by sealing the back of the membranes.
- The sealing of the back of the cell resulted in high solution concentration at back of the cell.
- A meniscus shape of current distribution was obtained for the EIX cell. The results showed that minimum current flowing through the centre section.
- The results indicated that the shape of the current profile was possibly due to high concentration of sodium ions.
- The thickness and loading of the membrane were also found to partially affect the current profile particularly at low current densities and high pH.
- Flow pattern experiments indicated there were two important factors which influenced the mixing within the cell. These were current density and flow rate. At high current density, the predominant dispersive action was due to bubbles generated at the counter electrode. At high flow rates, the superficial velocity was also a factor in the determining the flow patterns.
- Removal of zinc appeared to be by two mechanisms; ion exchange and precipitation.

The important findings outlined in this chapter were the extraordinary high concentrations of material found at the back of the cell, substantial leakage of material from the back of the cell to the bulk solution and the shape of the current distribution. The latter two were related to the high concentration of material at the back of the cell which was mainly due to the cations being pumped across the membrane. This could be partially solved by removal of the material from the back of the cell or increasing the ion exchange resin content of the membrane.

CHAPTER 7

EXPERIMENTAL III: Elution

7. INTRODUCTION

The discussion thus far has concerned loading of membranes under different process conditions described in Chapters 5 and 6. In absorption mode, a potential difference applied between the EIX electrode and a counter electrode drives cations into and across the membrane. During elution, the potential is reversed and the EIX electrode acts as an anode generating hydrogen ions within the membrane. This results in the protonation of the ion exchange resin embedded in the polymeric support.

Acidic conditions prevalent in the membrane ensure the exchange of metal ions for hydrogen ions. Under the influence of the potential applied across the EIX membrane, the cations are driven across the membrane and out into the bulk solution. Elution by pole reversal is one of the main advantages of EIX over other techniques. It offers a simple but effective way of recovering ions removed during the absorption cycle. All elution experiments were carried out in batch mode. The volume of waste solution can be reduced and concentration of the eluant maximised by running the process in batch.

7.1 Elution Experiments

Elution experiments were carried out under acidic conditions to avoid the precipitation of transition group metals. During elution cycles, the pH became more alkaline as result of exchange of hydrogen ions for metal ions and subsequent excess of hydroxyl ions present in solution. Nitric acid solution was used to adjust the feed pH during elution.

An initial feed solution was made up and placed in a feed tank. The solution was then passed through the cell in the same way as the feed during absorption cycle described in section 5.1. Voltage was applied across each half cell to

maintain a steady flow of current. Experiments were continued to obtain high concentrations of metals in the tank solution. A schematic diagram of the experimental rig can be seen in Figure 7.1.

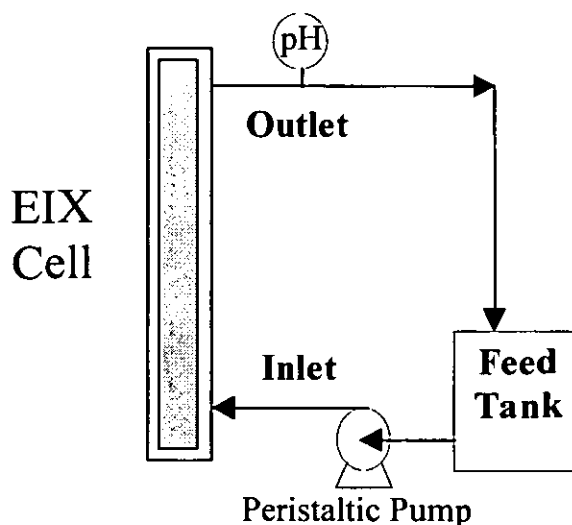


Figure 7.1: Schematic diagram of elution experiments

A series of elution experiments were carried out under different experimental conditions. An absorption cycle was carried out before each experiment. The loading of ion exchange membranes changed for each run because absorption cycles were conducted under different experimental conditions. Experiments were carried out at random to ensure the loading of the membranes did not affect the results. In most cases, the feed tank solution was dosed with acid to maintain feed pH at a desired value throughout the experiment.

The cell configuration was changed to examine the effect of using two or one counter electrodes in the centre of the cell. A series of experiments were conducted to study the influence of pH and current density on the performance of the EIX process during elution. Ten litres of distilled water were used in each experiment and the flow rate was 11 l.h^{-1} , unless otherwise stated. This was to ensure that the pH swing across the cell was kept to a minimum and

zirconium phosphate membranes were kept in acidic conditions to minimise hydrolysis.

7.2 Elution: Results & Discussion

Experiments were conducted with a tank feed pH of 1.7. This pH was to ensure that conditions were kept acidic throughout all experiments. This was only partially successful due to wide range of operating conditions. At the highest current density of 10 mA.cm^{-2} , extremely alkaline conditions were obtained in the feed tank and at the outlet. Figures 7.1-7.6 show the main results for these experiments.

7.2.1 Concentration

The tank and outlet sodium concentrations steadily increased during experiments as shown in Figures 7.2 and 7.3. Figure 7.2 shows the tank concentrations for experiments carried out with either one or two counter electrodes. The results indicate that in elution mode recovery of sodium ions was a function of current density. The higher the current density the greater the amount of cations eluted.

Figure 7.2 shows that similar results were obtained for experiments conducted with an EIX cell with one or two counter electrodes. The membrane gap did not effect the performance of the cell during elution as there were no significant differences between results obtained when using different cell configurations. The sodium concentrations leaving the cell can be seen in Figure 7.3. These indicate that the rate of regeneration was relatively constant throughout the experiments discussed here.

7.2.2 pH

The tank pH for all experiments was around 2 as seen in Figure 7.4.

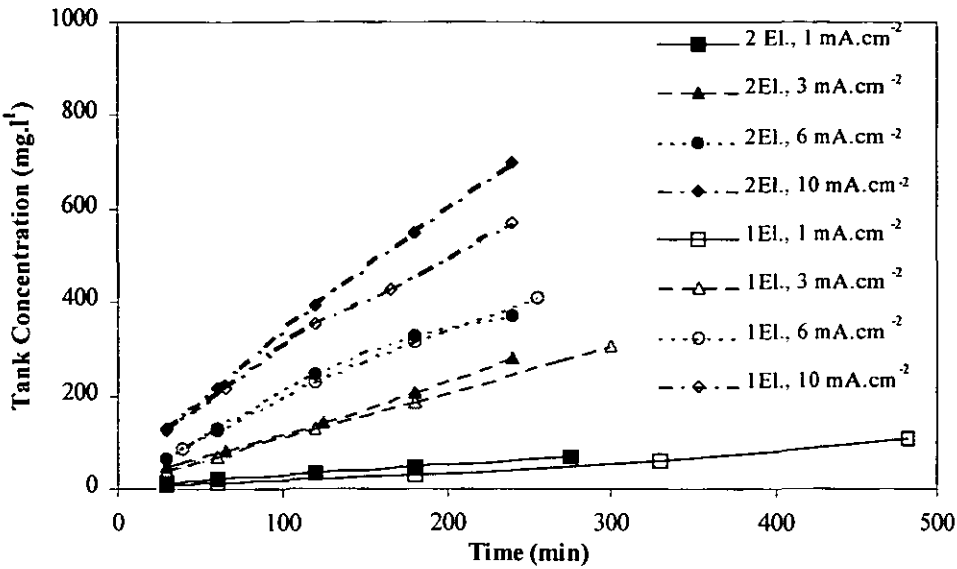


Figure 7.2: Tank concentrations during elution with different number of counter electrodes; 2El, two counter electrodes, 1El, one counter electrode
Starting pH = 1.7, Flow Rate = 1 l.h⁻¹, Current density = 1 - 10 mA.cm⁻²

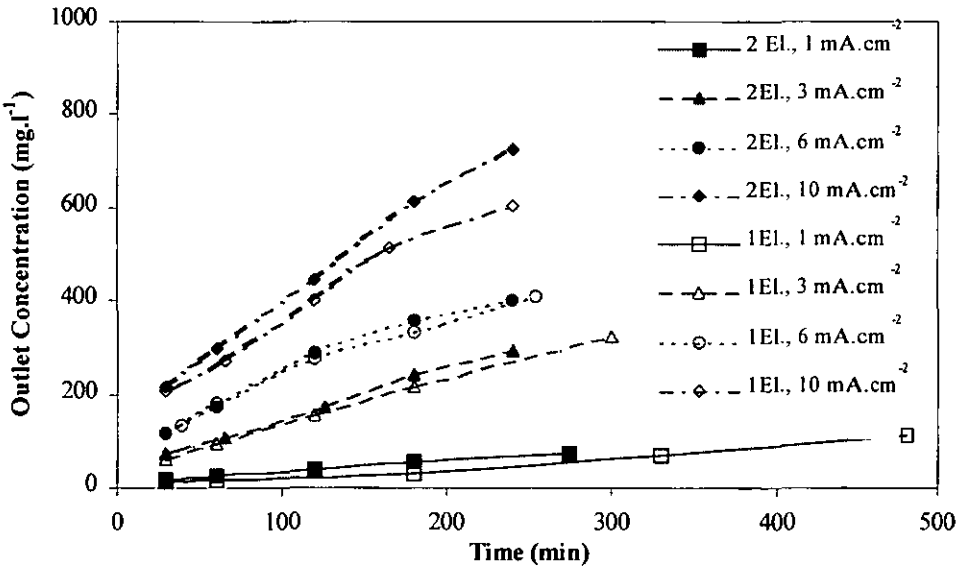


Figure 7.3: Outlet concentrations during elution with one or two counter electrodes; 2El, two counter electrodes, 1El, one counter electrode
Starting pH = 1.7, Flow Rate = 1 l.h⁻¹, Current density = 1 - 10 mA.cm⁻²

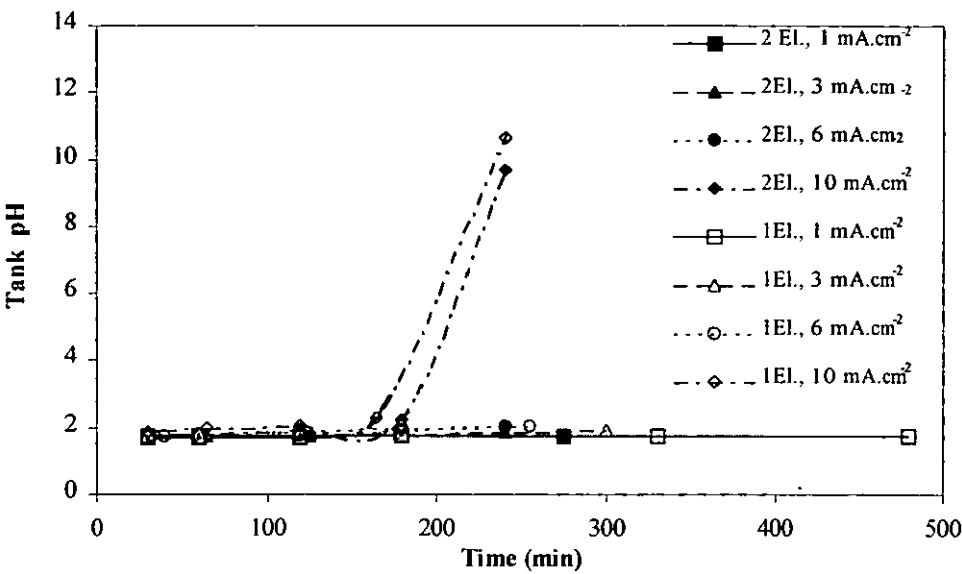


Figure 7.4: Tank pH during elution with different number of counter electrodes; 2El, two counter electrodes, 1El, one counter electrode
Starting pH = 1.7, Flow Rate = 11 l.h⁻¹, Current density = 1 - 10 mA.cm⁻²

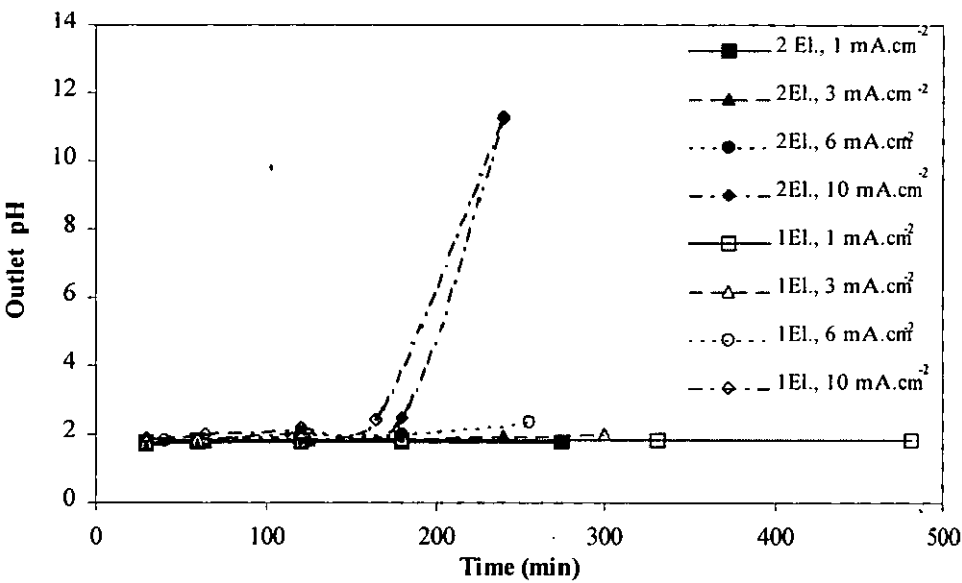


Figure 7.5: Outlet pH during elution with different cell configurations; 2El, two counter electrodes, 1El, one counter electrode
Starting pH = 1.7, Flow Rate = 11 l.h⁻¹, Current density = 1 - 10 mA.cm⁻²

Similar pH results were obtained for experiments carried out with two counter electrodes as compared with tests conducted with one counter electrode. Figures 7.4 and 7.5 show that the pH conditions were mostly acidic. Except for the experiments carried out at 10 mA.cm^{-2} when the outlet pH was 11.3 and the tank pH was 11.2 at the end of the experiments. This was due to the large amount of sodium eluted off the membrane. Acid was not added during the experiment, the pH was maintained by excess hydrogen ions present in the feed solution at the beginning of the experiments.

7.2.3 Elution rate

The elution rate was calculated based on the amount of cations recovered for a given time which was the change in tank concentration divided by the time taken for that change. The results that can be seen in Figures 7.6 and 7.7 indicate the elution rate was dependent on the current density and duration of experiments. For all current densities, the elution rate was comparatively high at the beginning of the experiment and steadily decreased to a steady value.

Elution rates for the experiments conducted using only one central counter electrode can be seen in Figure 7.7. Overall, similar results were obtained for both configurations. The membrane gap introduced between the counter electrode and the EIX membrane did not effect the elution rate under the process conditions used. The results indicated that there was a sufficient amount of ions in the membranes to maintain the elution rate even at the highest current density of 10 mA.cm^{-2} .

7.2.4 Total Metal Recovery

Figure 7.8 shows the total amount of sodium recovered after 240 minutes under different experimental conditions. Overall, there was not any significant difference between the amount of metal recovered by either of the cell configurations used. There was also a linear relationship between the amount of metal recovered and the current density.

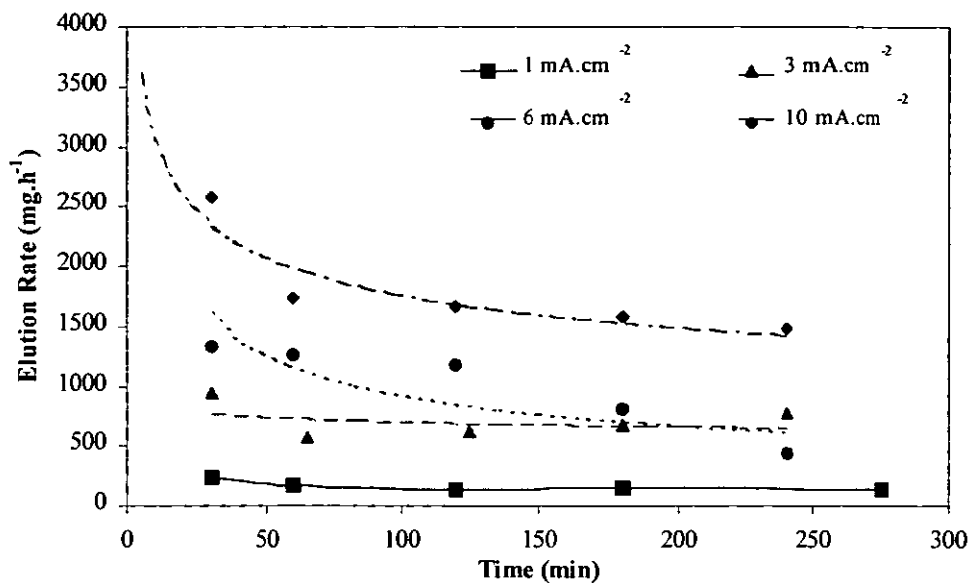


Figure 7.6: Elution Rate at different current densities of cell with two central electrodes
Starting pH = 1.7, Flow Rate = 11 l.h⁻¹, Current density = 1 - 10 mA.cm⁻²

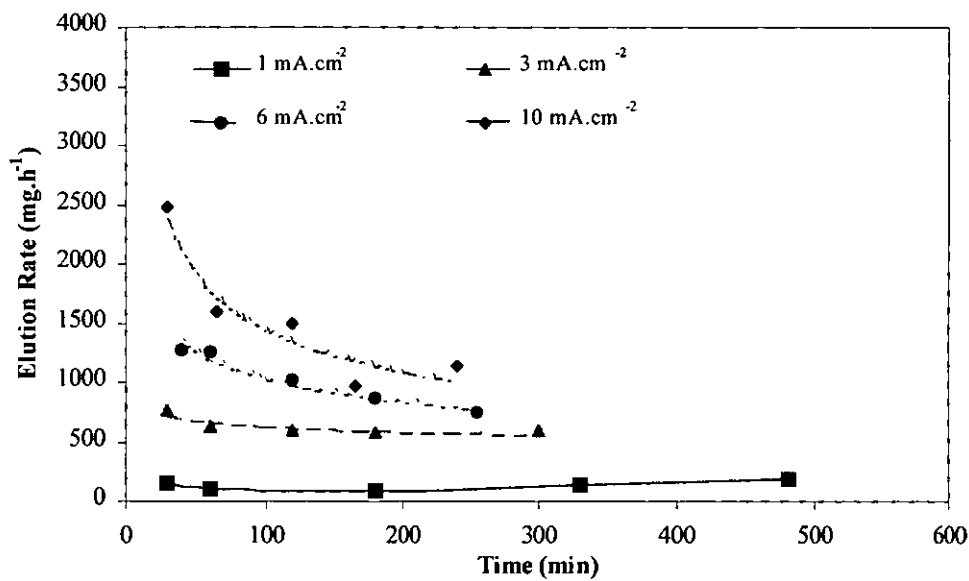


Figure 7.7: Elution Rate at different current densities of cell with one central electrode
Starting pH = 1.7, Flow Rate = 11 l.h⁻¹, Current density = 1 - 10 mA.cm⁻²

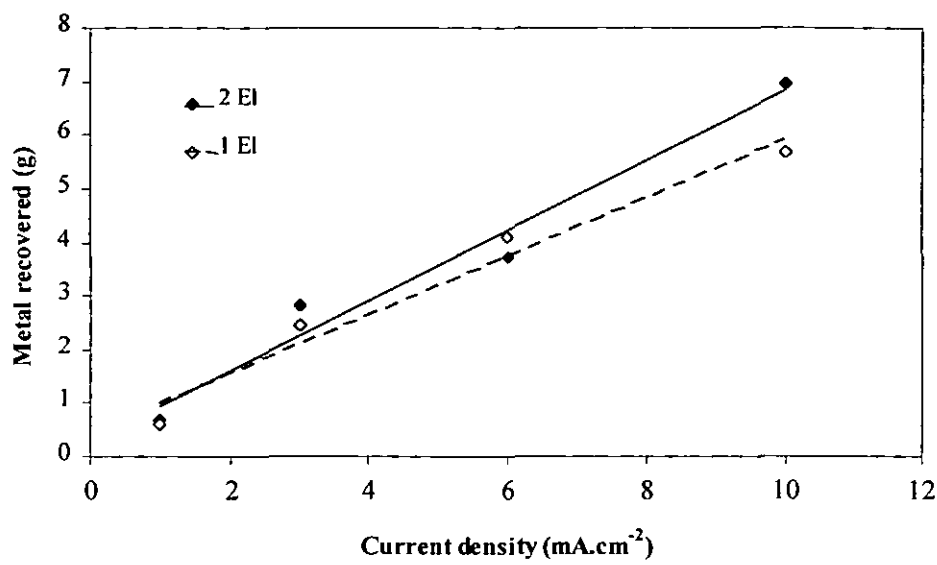


Figure 7.8: Total metal recovered with two central electrodes, 2 El, or one counter electrode, 1 El

Starting pH = 1.7, Flow Rate = 11 l.h⁻¹, Current density = 1 - 10 mA.cm⁻², Time = 240 min.

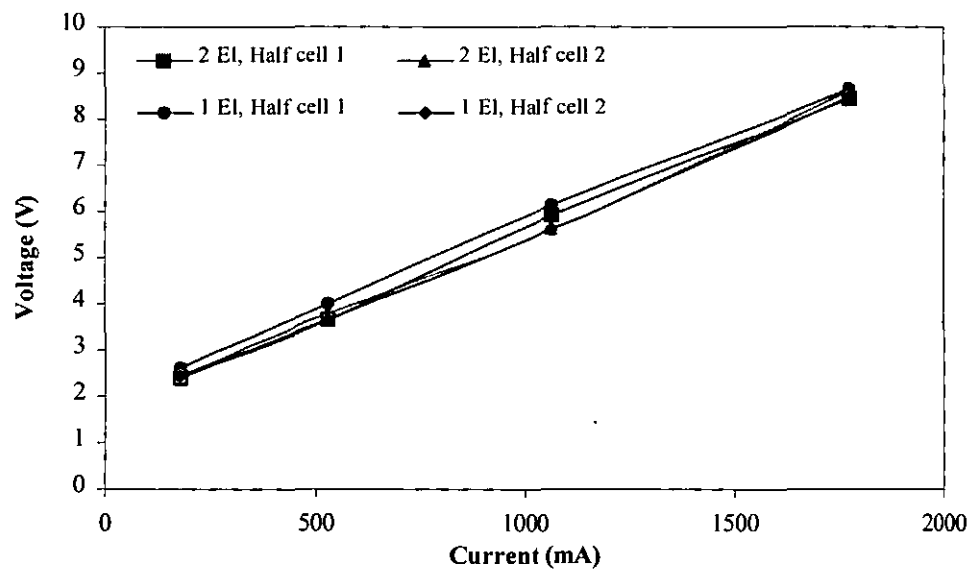


Figure 7.9: Applied voltages for both half-cells for the case with two central electrodes and one counter electrode

Starting pH = 1.7, Flow Rate = 11 l.h⁻¹, Current density = 1 - 10 mA.cm⁻²

7.2.5 Applied Potential

Applied voltages gave an indication of the power requirements during elution cycles. The applied voltages were generally lower than voltages during absorption cycles. During elution experiments, applied potentials required were similar and not affected by condition or cell configurations.

The relationship between applied voltage and current was ohmic as illustrated in Figures 7.9. There was no change from the start to end of experiments

7.2.6 Flow Rate

The effect of flow rate on elution was examined at two different flow rates and at a current density of 1 mA.cm^{-2} . Experiments were conducted at low current density to minimise the mixing effect of bubbles generated at the electrodes. The results can be seen in Figure 7.10. The tank and outlet concentration steadily increased with time. There was very little difference between tank and outlet concentrations at flow rates of 1.5 and 4 l.h^{-1} .

7.2.7 Current Profile

The current profile for the same experiments indicated that the profile was much more evenly distributed than in absorption mode, as seen in Figure 7.11. This was a further indication that the current profile obtained during absorption was as a result of internal concentration profiles within the membrane. The current through the thinnest section was the highest which may have been due to lower resistance. The centre section had the lowest current passing through it. This may be because in elution mode, hydrogen ions present in the membrane were readily exchanged for sodium ions. There was a lower current across this section as in the other sections hydrogen was predominantly carrying the current. Hence, The lowest current was measured where there was the most exchange of ions.

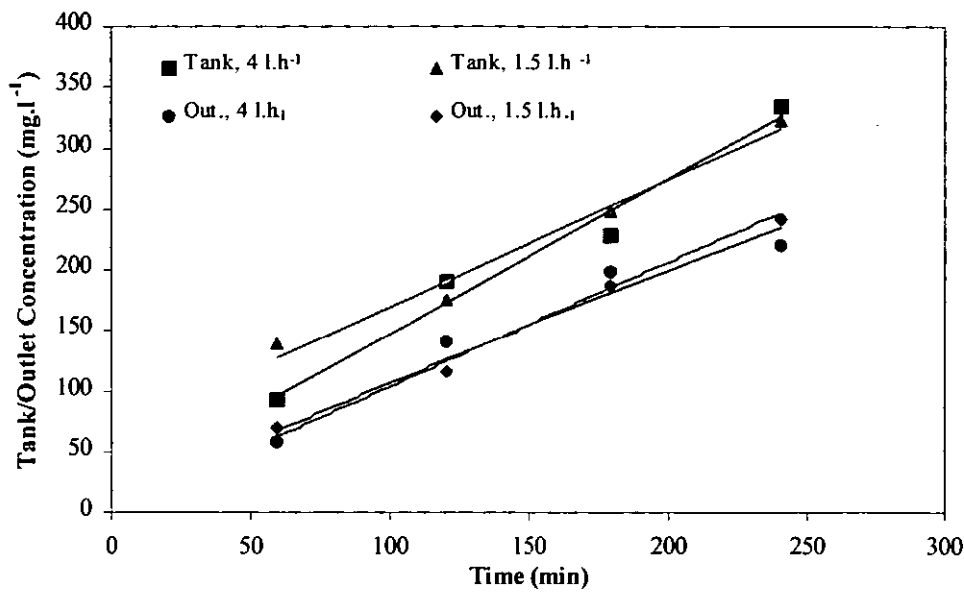


Figure 7.10: Tank and outlet Concentrations during elution carried out at two different flow rates
Starting pH = 2, Current density = 1 mA.cm⁻²

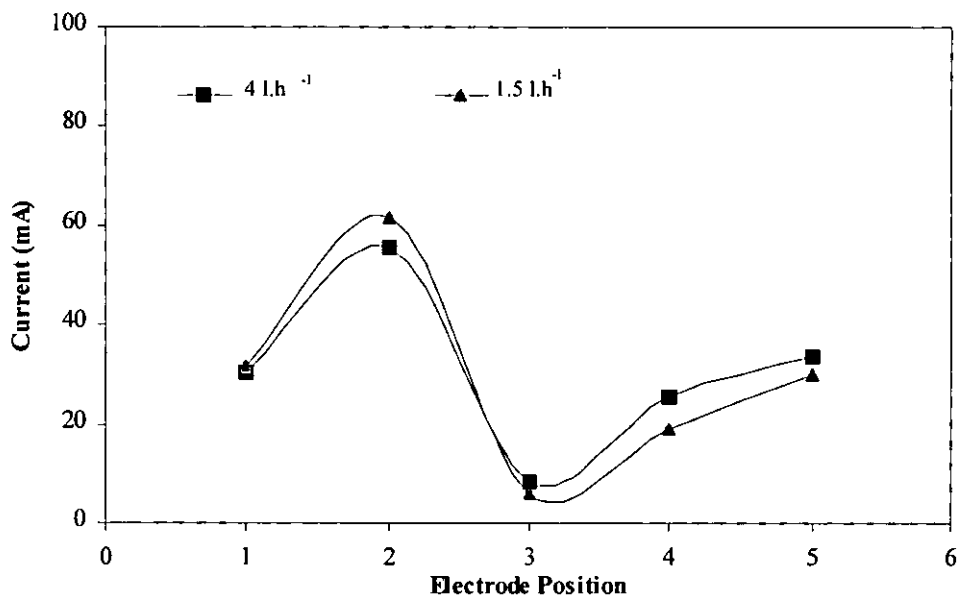


Figure 7.11: Current distribution during elution and current density of 1 mA.cm⁻²
Starting pH = 2, Current density = 1 mA.cm⁻²

7.2.8 Selectivity

After the zirconium phosphate membranes were used for removal of zinc, described in section 5.4.3, experiments were conducted to examine the selectivity of the membranes during elution. Elution was carried out in three batch cycles, at the beginning of each, 5 l of distilled water with the pH of 2 was used as the feed. Experiments were conducted at a flow rate of 0.5 l.h^{-1} and a current density of 3 mA.cm^{-2} .

The results for these series of experiments can be seen in Figure 7.12. At the beginning of the experiment, zinc and sodium outlet concentrations were respectively 8 mg.l^{-1} and 1660 mg.l^{-1} . By the end of the first batch, these concentrations changed to 3 mg.l^{-1} of zinc and 2270 mg.l^{-1} of sodium. Overall the indication was that the sodium was being eluted first. Once the sodium concentrations reached 500 mg.l^{-1} , zinc started to be eluted. This indicated a clear preference of the resin for the zinc. By the end of the third batch only 32 % w/w was recovered out of 323 mg of zinc loaded on the membrane during the absorption.

7.3 Purolite Membranes

The performance of Purolite membranes was also examined during elution cycles. The results of experiments using Purolite S930 membranes can be seen in Figures 7.13 -7.15.

A cell containing S930 membranes was used to remove zinc, copper and nickel before being used for an elution experiment the results of which can be seen in Figure 7.13. The results were similar to those obtained using zirconium phosphate membranes, sodium was eluted before any other cations. After 100 minutes, zinc outlet concentration increased once sodium had stopped being eluted. Nickel was only eluted after most of the zinc had been recovered. The copper concentration remained unchanged from the beginning of the

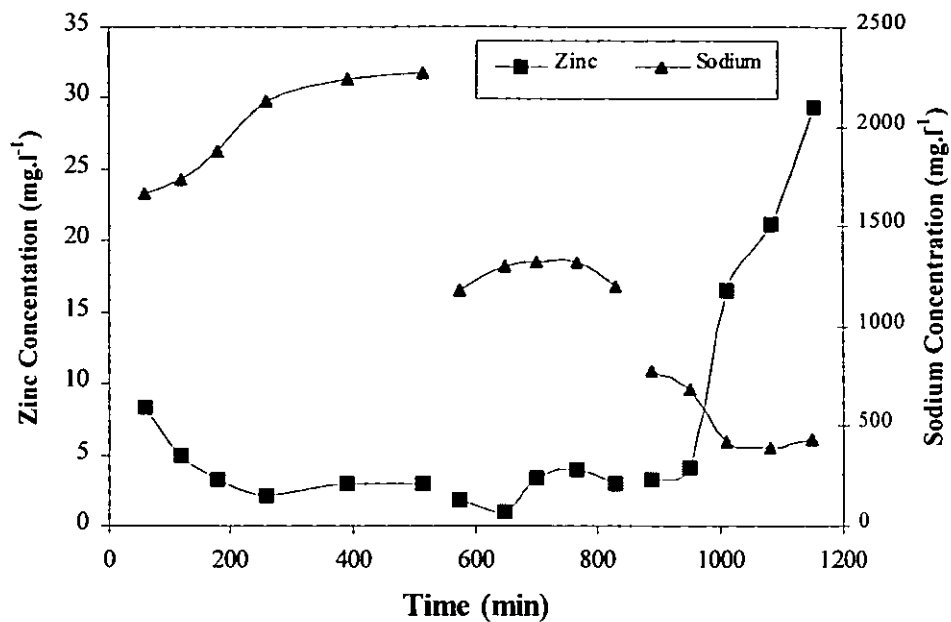


Figure 7.12: Outlet concentration of zinc and sodium during elution after selectivity experiments
Current density = 3 mA.cm⁻², Flow rate = 0.5 l.h⁻¹, Tank pH = 2

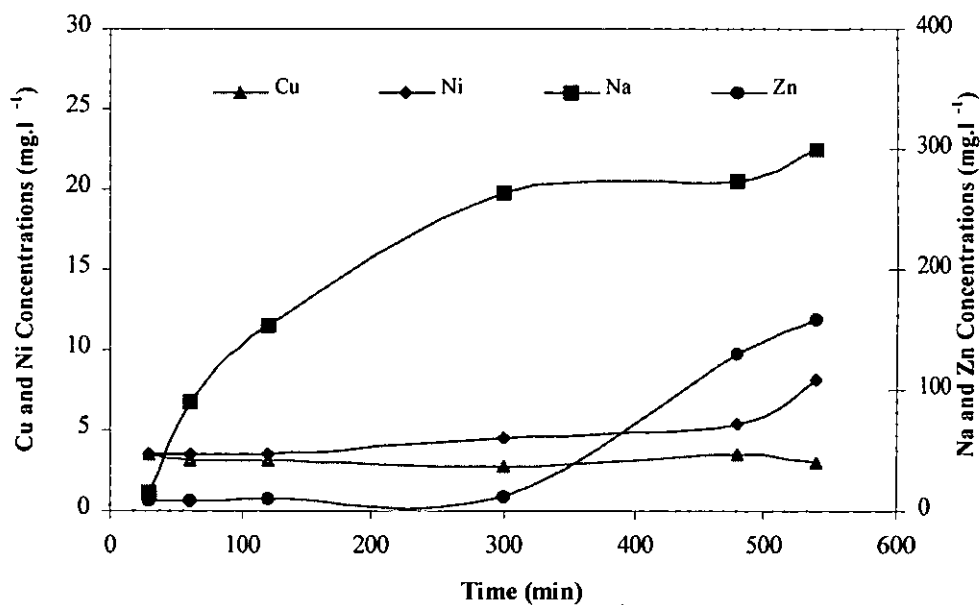


Figure 7.13: Elution of Purolite S930 membranes following an absorption cycle using a feed containing Na, Cu, Zn, and Ni

experiment to the end. This was due to partial electroplating of copper on the counter electrode acting as the cathode. Other elution experiments were carried out on the Purolite S930 membranes.

7.3.1 Zinc

Zinc absorption experiments were followed by elution cycles. Initially, the cell was eluted with 10 l of distilled water with a pH of 2.9. The current density was 3 mA.cm^{-2} and the flow rate through the cell was 3.8 l.h^{-1} . After 8 hours, the concentrations in the feed tank were 72 mg.l^{-1} sodium, 45 mg.l^{-1} caesium and 0.2 mg.l^{-1} zinc with a final pH of 11.2. The pH of the solution coming out of the cell was 11.3. The pH of the tank solution was adjusted to 2.3 by addition of 80 ml of 2 M nitric acid. The elution was continued for a further 6 hours. At end of this period, the concentrations of sodium, caesium and zinc were respectively 74, 48 and 18 mg.l^{-1} . Final pH tank solution was 11.9 and outlet pH was 10.7. There were solids present in the tank, the solution pH was adjusted to a pH of 2.5, dissolving the zinc and revealing a concentration of 64 mg.l^{-1} with no change in sodium or caesium concentrations.

The cell was completely eluted by a fresh 10 l solution with a pH of 1.5. After 3 hours, the tank and outlet solution pH were equal at 1.7. The final tank concentrations were 10.3 mg.l^{-1} zinc, 0.1 mg.l^{-1} sodium and 0.2 mg.l^{-1} caesium. All the zinc absorbed by the S930 membranes was recovered by the two elution cycles. Only 31% of the caesium was not recovered out of a total of 1270 mg removed during absorption. Fluctuations in the feed pH resulted in the precipitation of transition group metals. The results indicated that sodium and caesium were eluted before any zinc was recovered.

7.3.2 pH and Concentration Profiles

The pH and concentrations at the centre of the cell were also measured during elution which can be seen in Figure 7.14. The experiments were carried out after absorption tests on the sodium form of the Purolite S930. In the centre of

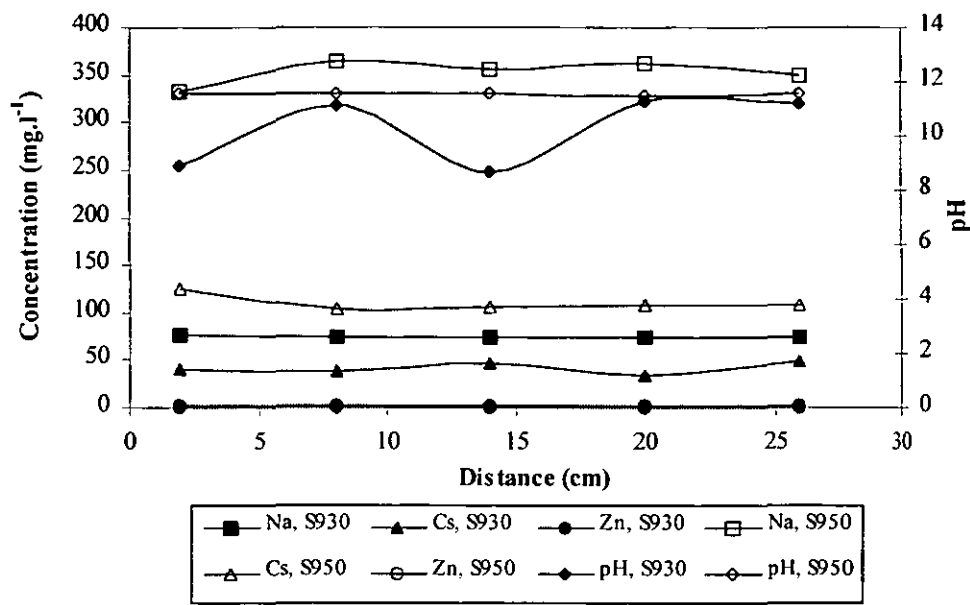


Figure 7.14: Concentration and pH values in the centre of cells with S930 and S950 membranes

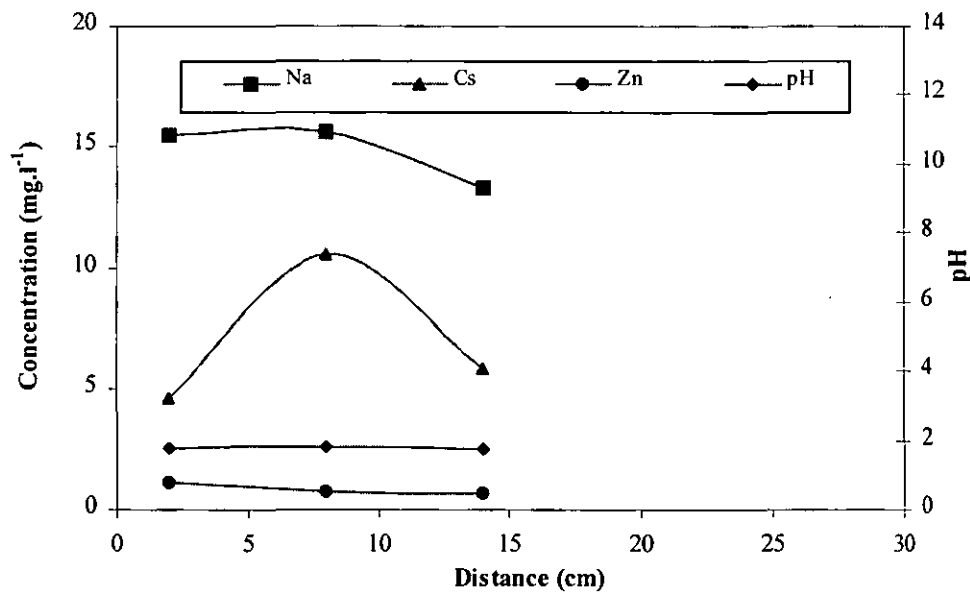


Figure 7.15: pH and Concentration profiles at the back of one half cell containing S930 membranes

the cell, there was a high concentration of sodium and caesium but zinc concentration was below the detection limit partly due to high pH. Zinc precipitated or remained within the membrane.

Concentration and pH at the back of the cell were also measured for the Purolite S930 and the results are shown in Figure 7.15. Samples were difficult to obtain from top of the cell due gas generated by electrolysis reactions. The result showed that the conditions at the back of the cell were acidic during elution. The concentration of material at the back of the cell was much lower than at the centre of the cell.

Similar results were obtained using the Purolite S950 membranes. A total mass balance carried out over all experiments indicated that during absorption, 608 mg of zinc was removed and 434 mg (71.4 % w/w) was recovered. The membrane was kept wet by a stagnant solution inside the cell between experiments. Material may have leaked off the membrane during this period. This may account for some of the material not recovered.

7.4 Conclusions

Overall, there were indications that the elution process was affected by current density and bulk solution pH. The use of one counter electrode did not make much difference to the performance of the elution process. Difficulties were encountered in maintaining the pH in acidic conditions particularly at high current densities. A better control system would be required to keep pH under pH 5 to reduce the likelihood of metals such as zinc precipitating.

The findings can be summarised by the following statements:

- There was a steady increase in outlet and tank concentrations of cations with time proportional to the current density

- Using different cell configurations did not significantly alter the performance of the EIX cell.
- Lower applied voltages were needed for elution compared to absorption cycles.
- There was a general ohmic relationship between current and applied voltage during elution experiments.
- Changes in flow rate did not affect the amount of sodium recovered during elution at a current density of $1 \text{ mA}\cdot\text{cm}^{-2}$.
- The current profile was more evenly distributed in elution mode compared to absorption mode.
- Sodium was the cation eluted first before any other target ions for all resins used.
- 100% of zinc was recovered from Purolite S930 membranes with respectively 32 % and 72% w/w recovered from zirconium phosphate and Purolite S950 membranes under the experimental conditions.

CHAPTER 8

MATHEMATICAL MODEL

8. THE MODEL

A theoretical model of the Electrochemical Ion Exchange process was developed based on the Nernst-Planck equation, discussed in section 4.3. The Nernst-Planck equation for ion transport, Equation 8.1, describes the ionic flux induced by the application of an electric field. The first term is the diffusion term followed by the electrical migration and convection terms respectively.

$$N_{ix} = -D_i \frac{dC_i}{dx} - \frac{D_i C_i z_i F}{RT} \frac{d\Phi_s}{dx} + C_i u_x \quad (8.1)$$

where :

N_{ix} Molar flux of the i th species in the x plane through a unit area of membrane per unit time, [mol.m⁻².s⁻¹]
 D_i Diffusion coefficient, [m².s⁻¹]
 C_i Concentration of i species, [mol.m⁻³]
 z_i valency of i ,
 F Faraday's constant, [C.mol⁻¹]
 R Gas constant, [J.mol⁻¹.K⁻¹]
 T Temperature, [K]
 $d\Phi_s/dx$, Potential gradient, [V.m⁻¹]
 u_x Velocity, [m.s⁻¹]
 x Linear direction

Figure 8.1 shows a small cross-section of an EIX membrane of length δy . Equation 8.1 can be applied across this small section of membrane. There are three main planes to be considered x is the plane going through the membrane and into the bulk solution. Plane y is tangential to the flux and parallel to the flow q . The last plane is the one across the face of the membrane in contact with the solution, w . Cumming et.al. (1997) reported on the prediction of the performance of the EIX process using this approach to compare experimental results with model data.

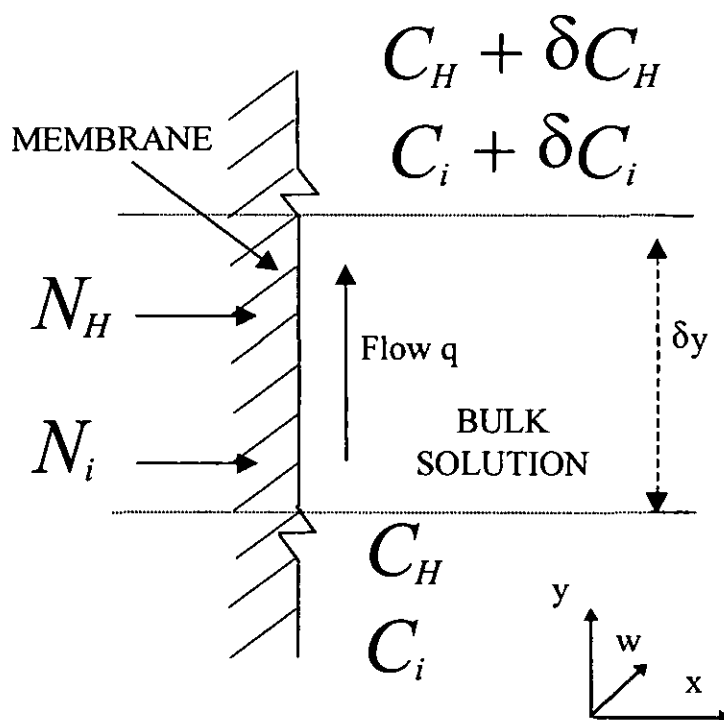


Figure 8.1: Incremental section of an EIX membrane

It has been assumed that there is perfect mixing within the flow cell and that there is no concentration boundary layer existing between the bulk solution and the surface of the membrane. This means that the diffusion and convection terms in the transport equation could be neglected in Equation 8.1 leaving only the electrical migration terms:

$$N_{ix} = -\frac{D_i}{RT} C_i z_i F \frac{d\Phi_s}{dx} \quad (8.2)$$

The system can be completely represented by considering the mass balance of each ionic species as well as the current passing through the cell. The current density can be obtained by using Faraday's Law:

$$I_i = F \sum z_i N_i \quad (8.3)$$

The material balance of each species i is given by:

$$C_i q - (C_i + \delta C_i) q - 2N_{ix} w \delta y + 2 \frac{I_i}{F} w \delta y = 0 \quad (8.4)$$

In - (Out) + Rate of production = 0

where q is the flow rate.

The total current is given by:

$$I_t = F \sum z_i N_{ix} w \delta y \quad (8.5)$$

In all cases electroneutrality is assumed to hold within the cell liquid:

$$\sum C_i z_i = 0 \quad (8.6)$$

8.1 Application

Equations 8.2 to 8.7 can be applied to the EIX system. These can be simplified and solved analytically by making the following assumptions:

- i. Interaction between ions was negligible since dilute concentrations of ions were present in solution.
- ii. There was good mixing within cell and no concentration barrier existed at the surface of the membranes and ionic transport was only limited by the current so the boundary layer resistance could be ignored.
- iii. All metal ions entering the membrane were adsorbed onto ion exchange material and all electrolytes were completely dissociated.
- iv. Transport of counter ions from the membrane was assumed to be negligible so only the cations need to be considered.
- v. The potential drop across the membrane was taken to be constant.

A simple system, containing just sodium and hydrogen ions, can be represented by using the equations discussed thus far. The material balance for sodium performed over the small element presented in Figure 8.1 gives:

$$C_{Na} q - (C_{Na} + \delta C_{Na}) q + 2N_{Na} w \delta y = 0 \quad (8.7)$$

where:

$$N_{Na} = \frac{-D_{Na}}{RT} z_{Na} F \frac{d\Phi}{dx} \left(C_{Na} + \frac{\delta C_{Na}}{2} \right) \quad (8.8)$$

For sodium the valency is 1 so $z_{Na}=1$. The negative term is due to the flux moving down the potential gradient. Assuming a constant potential drop across the system:

$$\frac{d\Phi}{dx} = b \quad (8.8b)$$

and applying the equation over a very small increment, $\lim. \delta y \rightarrow 0$ then we can obtain:

$$\frac{dC_{Na}}{dy} = \frac{D_{Na}}{qRT} 2Fbw C_{Na} \quad (8.9)$$

Integrating over the limits of sodium inlet concentration and outlet concentration we obtain:

$$C_{Na_{out}} = C_{Na_{in}} e^{(-\alpha_{Na}y)} \quad (8.10)$$

where:

$$\alpha_{Na} = \frac{D_{Na}}{qRT} 2Fbw \quad (8.11)$$

The material balance for hydrogen is given by:

$$q C_H - (C_H + \delta C_H)q - 2N_H w \delta y + \frac{2I}{F} w \delta y = 0 \quad (8.12)$$

Using equation 8.2, the hydrogen flux term is:

$$N_H = \frac{-D_H}{RT} z_H Fb \left(C_H + \frac{\delta C_H}{2} \right) \quad (8.13)$$

For hydrogen the valency is 1 so $z_H=1$. The current density represented by Equation 8.3 is then given by:

$$I = 2F(N_H + N_{Na}) \quad (8.14)$$

substituting Equation 8.10, 8.13 and 8.14 into Equation 8.12 the following equation is obtained:

$$\delta C_H = \frac{D_H}{qRT} 2Fbw C_{Na} e^{-\alpha_{Na}y} \delta y \quad (8.15)$$

The following expression is for the hydrogen outlet concentration:

$$C_{H_{out}} = C_{H_{in}} + C_{H_{in}} (1 - e^{-\alpha_{Na}y}) \quad (8.16)$$

The inlet hydrogen concentration can be calculated from the inlet pH condition:

$$C_{H_{in}} = 10^{-pH_{in}} \quad (8.17)$$

The overall electric current I_t can be derived by integrating incremental electric current:

$$\delta I = 2Fbw\delta y(N_H + N_{Na}) \quad (8.18)$$

over the length of the whole cell the total current can be expressed as:

$$I_t = \frac{-wF^2}{RT} b \left[D_H(C_{H_{in}} + C_{Na_{in}})y + \frac{(D_{Na} - D_H)}{\alpha_{Na}} C_{Na_{in}} (e^{-\alpha_{Na}y} - 1) \right] \quad (8.19)$$

Equations 8.10, 8.16 and 8.19 were solved by successive iterations. The value of the total experimental current was matched to a corresponding model calculated current by adjusting the value of the potential gradient $d\Phi/dx = b$. There is only one possible value for b which satisfies all three equations. The model does not simulate the experimental results by parameter fitting. Initially, the outlet concentrations for sodium and hydrogen were calculated and then the corresponding total current. The hydrogen ion outlet concentration gave pH of

the solution leaving the cell. The temperature was assumed to be 25 °C for all calculations. The Faraday constant was taken as 96485 C.mol⁻¹ and the gas constant 8.31 J.mol⁻¹.K⁻¹. The diffusion coefficient values were obtained from the literature (Newman, J.S.; 1991).

8.2 Comparison of experimental and model Data

Experimental results were obtained by using a similar set up as experiments carried out to assess the performance of the EIX cell, discussed in chapter 5. The data was mostly generated using zirconium phosphate membranes. Purolite membranes were also used in a few experiments. Experimental results were compared with model data for different current densities, flow rates, feed pH, feed concentrations and combined metal feed solutions. The range of experimental process conditions used can be seen in Table 8.1.

Table 8.1: Range of experimental process conditions used

Parameters	Minimum	Maximum
Flow rate [l h ⁻¹]	0.2	12
Feed pH	1	5
Cation feed concentrations [mg l ⁻¹]	0	500
Current density [mA cm ⁻²]	1	15

Parameters were chosen to demonstrate the scope of the model based on the Nernst-Planck equation and assumptions. The aim was to understand the process better by comparing the results and to reduce the number of experiments needed.

8.2.1 Current Density and Flow Rate

Figures 8.2 and 8.3 show results of experiments carried out for flow rates between 0.2 and 12 l.h⁻¹. The current densities ranged from 1 to 15 mA.cm⁻². The feed concentration of sodium was 300 mg.l⁻¹ and the feed pH was 2.8. There was very good agreement between results the low current densities of 1

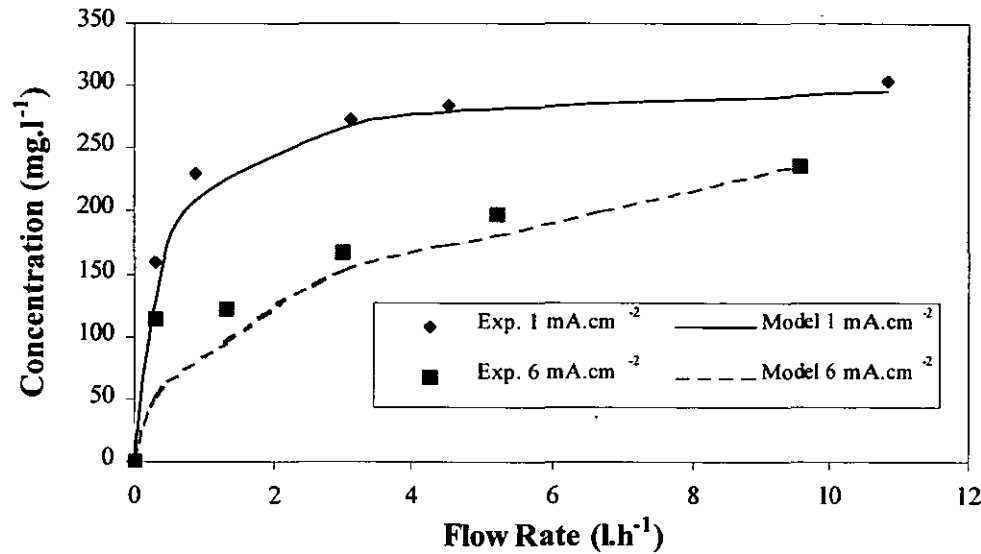


Figure 8.2: Comparison of experimental results with mathematical model data at low current densities
Feed Concentration = 305 mg Na.l⁻¹, Feed pH = 2.85

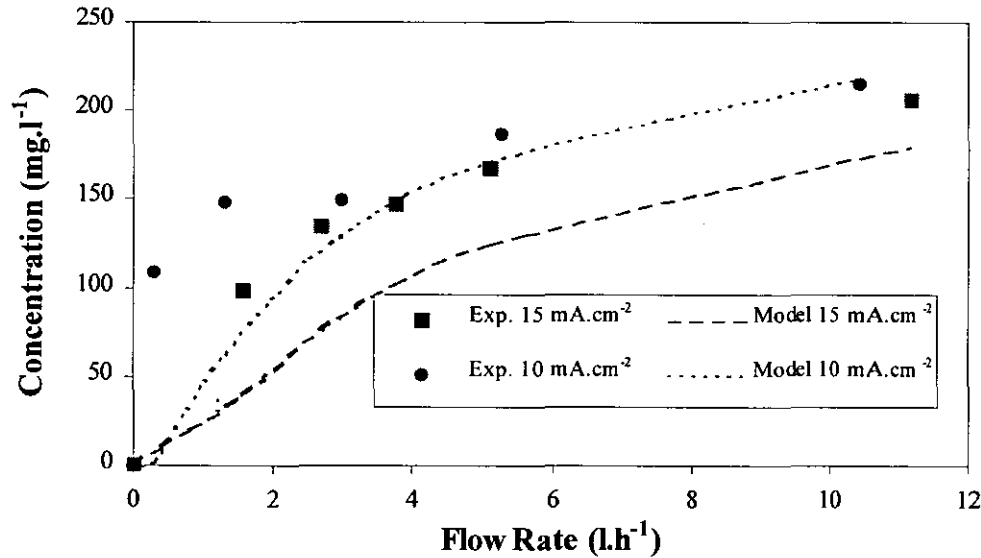


Figure 8.3: Comparison of experimental results with mathematical model data at high current densities
Feed Concentration = 300 mg Na.l⁻¹, Feed pH = 2.82

and 6 mA.cm^{-2} which can be seen in Figure 8.2. Over the range of flow rates used, there was no marked difference between the two sets of results.

At higher current densities of 10 and 15 mA.cm^{-2} , the results indicated that data generated by the model did not fit experimental results as well as for low current densities. These can be seen in Figure 8.3 that shows the difference between two sets of results was very significant at low flow rates. This was thought to be due to excessive temperature increases at these higher current densities of 10 and 15 mA.cm^{-2} . There was a significant temperature increase of 15°C in the case of experiments carried out at a current density of 15 mA.cm^{-2} and flow rate of 1 l.h^{-1} . The calculations were carried out at a temperature of 25°C and this may be part of the reason for the discrepancy between the model and experimental results at higher current densities.

However, the most plausible explanation would be that at higher current densities the sodium concentration at the back of the cell is much greater than at lower current densities. Hence, the leakage of material from the back of the cell to the bulk is that much greater. Overall, the removal was less than if there was no leakage as discussed in Chapter 6.

Other results indicated that there was a good agreement between the experimental results and model data at lower current densities and flow rates. The trends of experimental results are matched by the predicted data over the most of the range of process conditions used.

8.2.2 Feed pH

The model data were fitted the experimental results quite well at different feed pH which can be seen in Figure 8.4. The feed concentrations varied between 330 and 487 mg.l^{-1} and flow rate ranged between 0.2 and 1.6 l.h^{-1} . Experiments

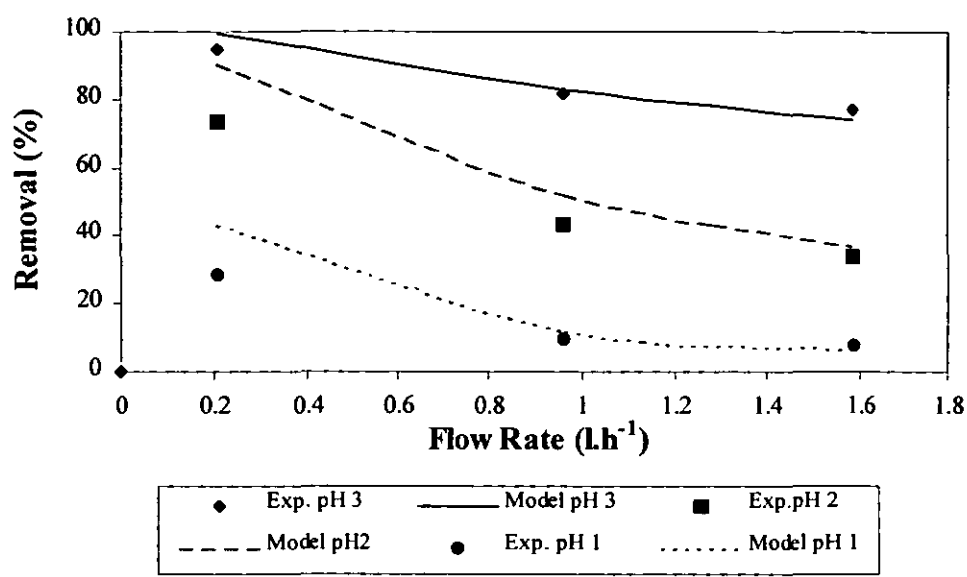


Figure 8.4: Model and experimental results at different feed pH
Feed Concentration = 330 mg Na.l⁻¹ at pH = 3, Feed Concentration = 447 mg Na.l⁻¹ at pH = 2
Feed Concentration = 487 mg Na.l⁻¹ at pH = 1, Current Density = 6 mA.cm⁻²

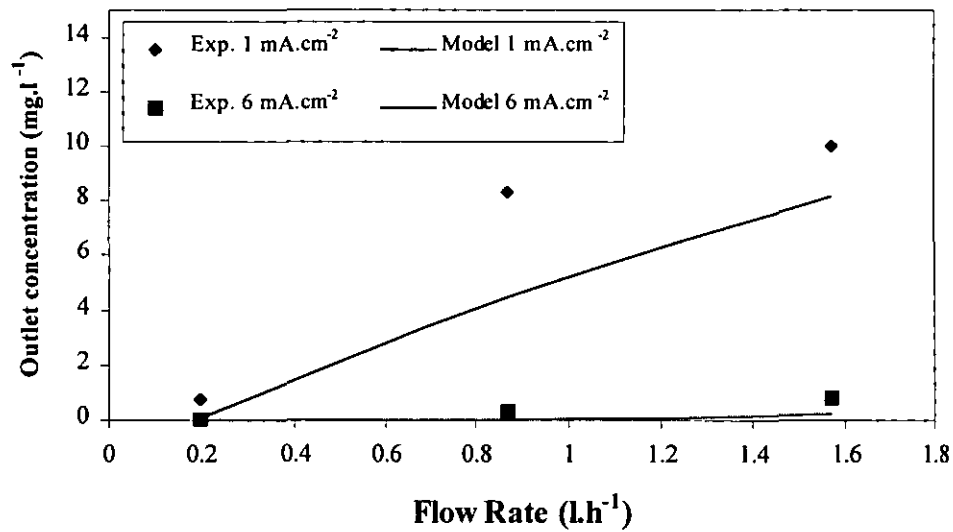


Figure 8.5: Comparison of data for a feed concentration of 20 mg.l⁻¹ and current densities of 1 and 6 mA.cm⁻²
Feed Concentration = 20 mg Na.l⁻¹, Feed pH = 3

were carried out at feed pH of 1 to 3 and The results of mathematical model correspond well to experimental results.

The effect of inlet hydrogen ion concentration on the removal of sodium is also found in the model data with a very good fit particularly at higher flow rates. The model did not seem to fit the experimental data as well at low flow rates which may be due to very high hydrogen ion concentrations in the cell, as at lower flow rates the pH swing across the cell is significantly higher. Typically, the outlet pH at a flow rate of 0.2 l.h^{-1} was about 1.8 when feed pH was 3. At higher flow rates the outlet pH was well above 2.

The effect of hydrogen ions can be seen clearly, as the pH decreases so does the removal. The large difference between results at pH 1 and pH 2 to 3 is due to the logarithmic nature of pH scale.

8.2.3 Concentration

Figures 8.5 and 8.6 show the result for experiments carried out at feed concentrations of 20 and 330 mg.l^{-1} . Current densities of 1 and 6 mA.cm^{-2} were used for these tests. The results were closer at high current density of 6 mA.cm^{-2} and concentration 330 mg.l^{-1} . The reason for the better fit is most probably due to better mixing. The results did not compare very well for a current density of 1 mA.cm^{-2} and feed concentration of 20 mg.l^{-1} that may have been due to poor mixing under these conditions. Overall, there was reasonable agreement between the two sets of data.

The results clearly show good agreement between data obtained experimentally and the mathematical model results under these process conditions. The model covered the whole range of concentration from 20 mg.l^{-1} to nearly 500 mg.l^{-1} well. This includes the results from experiments carried out over a wide range of flow rates and current densities.

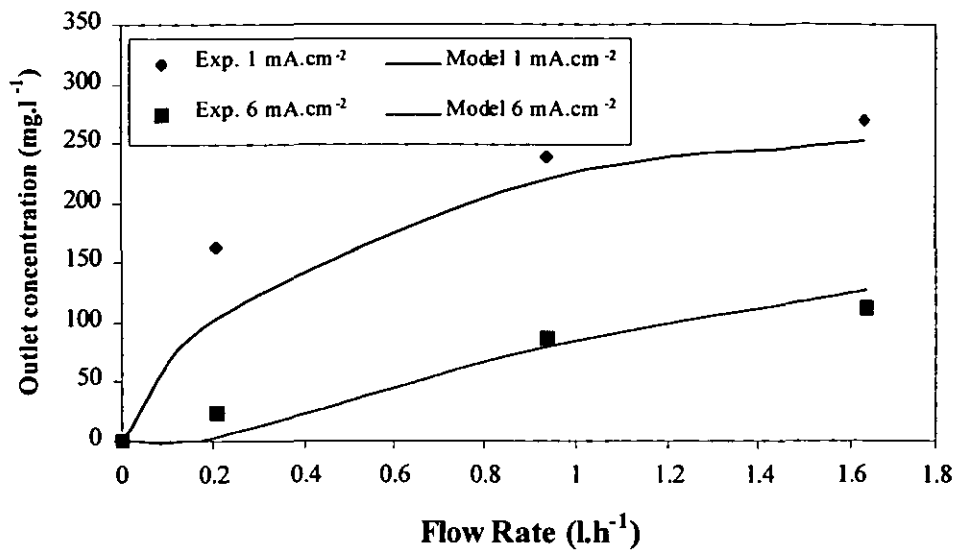


Figure 8.6: Comparison of data for a feed concentration of 330 mg.l⁻¹ and current densities of 1 and 6 mA.cm⁻²
Feed Concentration = 330 mg Na.l⁻¹, Feed pH = 3

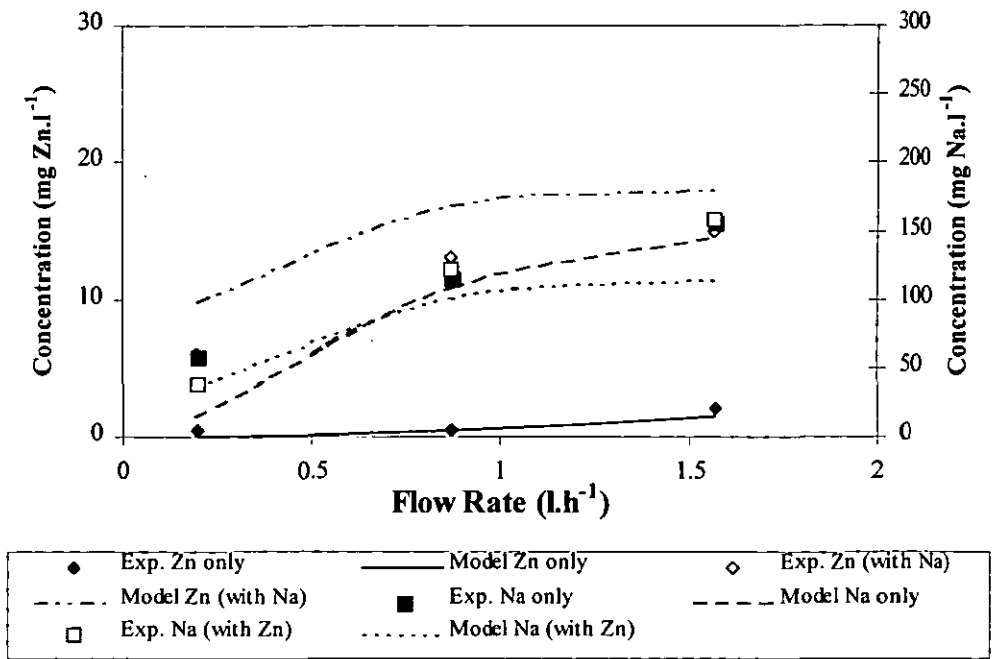


Figure 8.7: Zinc and sodium concentrations in selectivity experiments
Feed Concentration sodium only = 300 mg Na.l⁻¹, zinc only = 30 mg ZnNa.l⁻¹
Combined Feed Concentrations = 300 mg Na.l⁻¹ and 30 mg Zn.l⁻¹
Feed pH = 5, Current Density = 3 mA.cm⁻²

8.2.4 Combined feed of sodium and zinc

Experimental results from some selectivity tests were compared with model data. Equations for zinc were derived in a same manner as for sodium. There was an extra equation for the zinc outlet concentration and extra terms in the total current equation. In the case of zinc the charge z must also be considered. The following are the general equations which can be derived by considering a solution containing i number of ions.

The general expression for outlet concentration of i species leaving the cells is;

$$C_{i_{out}} = C_{i_{in}} e^{(-\alpha_i y)} \quad (8.20)$$

where:

$$\alpha_i = \frac{D_i}{qRT} 2Fbw \quad (8.21)$$

The hydrogen outlet concentration can be expressed as :

$$C_{H_{out}} = C_{H_{in}} + \sum_1^n C_{i_{in}} (1 - e^{(-\alpha_i y)}) \quad (8.22)$$

and the total current is given by:

$$I_t = Fq \left[-\sum_1^n C_{i_{in}} (e^{-\alpha_i y} + 1) + \alpha_H y (C_{H_{in}} + \sum_1^n C_{i_{in}}) + \alpha_H \sum_1^n \frac{C_{i_{in}}}{\alpha_i} (e^{-\alpha_i y} - 1) \right] \quad (8.23)$$

Figure 8.7 shows sodium and zinc concentrations in experiments carried out using just one or both of the metals in the feed solution. The feed concentrations were 300 mg.l⁻¹ of sodium and 30 mg.l⁻¹ of zinc and at a feed pH of 5 to minimise any interference from hydrogen ions. The current density was 3 mA.cm⁻². Results at low concentration, zinc only at 30 mg.l⁻¹, were very

close to the theoretical results. Sodium outlet concentrations were similar for experiments with or without zinc, the sodium feed concentrations was 300 mg.l^{-1} .

However, there were marked differences between the results obtained by the model and experiments for zinc removal when the feed contained a mixture of sodium and zinc. The experimental results indicate that zinc concentration was lower than that predicted by the model. The difference was most probably due to the enhanced removal of zinc by precipitation as well as ion exchange. The reduction in removal by increasing the flow rate can be seen both for experimental results as well as the model.

8.2.5 Purolite membranes

Results were obtained by using Purolite membranes containing chelating resins S930 and S950. These were compared to model data which can be seen in Figure 8.8. The experiments were carried out over a wide range of flow rates from 1 to 9.8 l.h^{-1} and at a feed concentration of 30 mg.l^{-1} of zinc. The feed pH was 3 and the current density was 3 mA.cm^{-2} . Chelating resin results indicate that the fit was not as good as for experiments using zirconium phosphate membranes. The difference may be attributed to the nature of the resin and the condition of resins. In both cases the resins were in the sodium form and it is likely that a significant amount of hydrogen ions was being exchanged for sodium instead of the target ion zinc. The pH operating range of sodium from of the resin is between 5 and 9 and the results from experiments carried out at a feed pH of 3 would suggest that substantial amount of sodium was being eluted. Chelating resin kinetics are also known to be slower than ordinary ion exchange and that may have an adverse effect on the performance of the membranes when compared with the ideal case. The ions may be going through the membrane to the back of the cell and leaking into the bulk solution recontaminating the liquid flowing through the module.

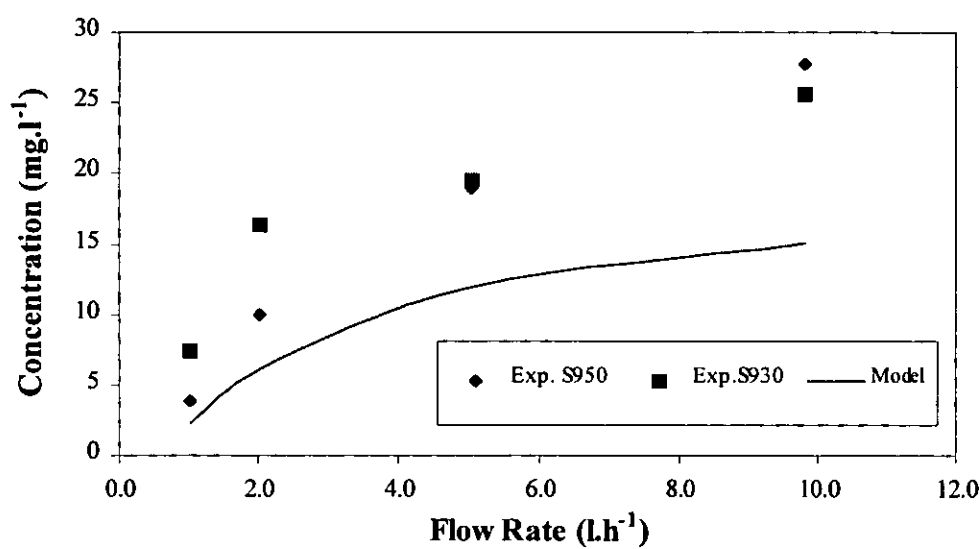


Figure 8.8: Comparison of model and experimental results for Purolite resin.
Feed Concentration = 20 mg Zn.l⁻¹, pH = 3, Current Density = 3 mA.cm⁻²

8.3 Conclusions

A model was developed to form a theoretical basis for Electrochemical Ion Exchange. The Nernst-Planck equation was chosen because of its versatility and simplicity of application. The model was tested against a wide range of process conditions and proved to be in good agreement with experimental results. The comparison of results allowed for the following conclusions to be drawn.

- The model data closely corresponded to experimental results particularly at lower current densities.
- At a high current density of 15 mA.cm^{-2} , there were significant differences between the experimental and model results, probably due to the extreme conditions created by the high current density.
- The difference between the model and the experimental results when using the chelating resins may have been due to slower kinetics of these resins.
- The predicted data agreed well with test results obtained over a wide range of flow rates, current densities, feed concentration and feed pH.
- The model results showed similar trends in the outlet concentration of target ions with changes in process conditions.
- The model appears to underpredict the removal in some cases when precipitation was occurring as well as sorption.

CHAPTER 9

EXPERIMENTAL IV: Pilot Plant

9. PILOT PLANT STUDIES

Trials were conducted to determine the viability of the EIX process on pilot plant scale. Experiments were also used to examine the effectiveness of changes made to the EIX cell design. These alterations were the sealing of different parts of the cell to reduce precipitation and contamination caused by leakage from the back of the cell as described in Section 5.3. Alternative process schemes were considered based on parallel and series mode, with or without use of anionic cells to reduce pH. The aim was to obtain a process that combined good removal of target ions with relatively high current efficiencies.

The best scheme was thought to be one which had an anionic cell placed between two cationic cells all in series. It was envisaged that the pH swing across the first EIX cell would be reversed by the anionic cell to allow the third cell to remove the remaining target cations in solution at a higher electrical efficiency. Alternatively, during elution cycles the anionic cell could be used to make the solution entering the third cell more acidic and reduce mineral acid consumption. The Purolite resins used in the manufacture of the membranes were cationic S930 and anionic PrAOH (experimental resin). Membranes were fabricated at AEA, Harwell laboratories and incorporated into EIX cells before delivery. The order of cells was cationic, anionic and cationic in series.

The pilot plant scheme used three cells of the same specification as those described in Chapter 5. Experiments were conducted for several days to treat large volumes of stimulant effluent. Tests were carried out under different process conditions to achieve optimal process conditions. A schematic diagram of the process can be seen in Figure 9.1. The equipment consisted of EIX cells, power supplies, pH meters, controller unit, peristaltic pump and computer.

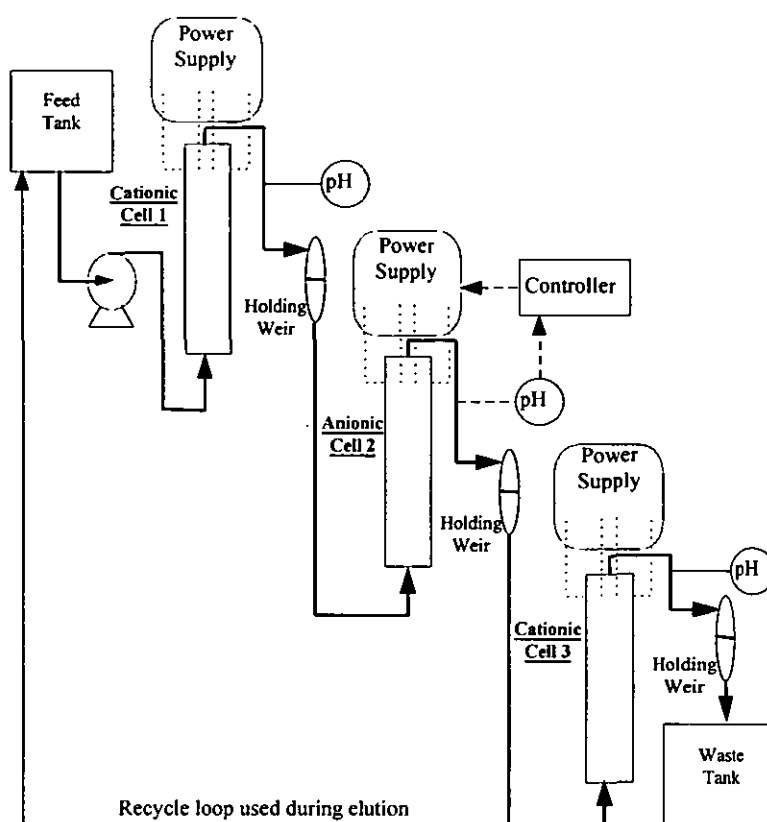


Figure 9.1: Schematic diagram of the pilot plant

The feed solution was pumped into the first cell and then allowed to flow through cells two and three under gravity. The levels of the solution entering and leaving these cells were adjusted to ensure that constant flow rate was maintained. This was done to minimise the risk of any cell running dry at any time. The applied voltages, outlet pH and control action were all recorded using a computer.

9.1 Materials

The power supplies used were two Thurlby PL320QMD and two Kenwood PA36-3A which allowed the power input into the anionic cell to be controlled. The Kenwood power supplies could provide a maximum voltage of 36V and current of 3A. A Watson-Marlow model 101U/R was used to pump the solution through the system. The appropriate pump tubing was selected to obtain the

desired flow rate. Silicone tubing was also supplied by Watson-Marlow. The pH was measured by a Philips PW9420 and two Mettler Toledo 320 pH meters. An IBM computer equipped with a CIL AlphaA-16 data logging card was used to gather data from pH meters and power supplies. The controller unit was Newtronic Micro96 controller with an input range of 0-140 mV corresponding to a pH 0 to 14 and an output of 0-10 V.

9.2 Control Loop

A control loop was installed around the anionic cell to automatically control the outlet pH. This was for two reasons, firstly to obtain a better removal in the last cell by adjusting the inlet pH and secondly to avoid any likelihood of transition group metals precipitating. The applied voltage to the anionic cell was altered to give the desired outlet pH from the second cell. Figure 9.2 shows the basic outline of the control loop with the pH meter, controller unit and the power supply.

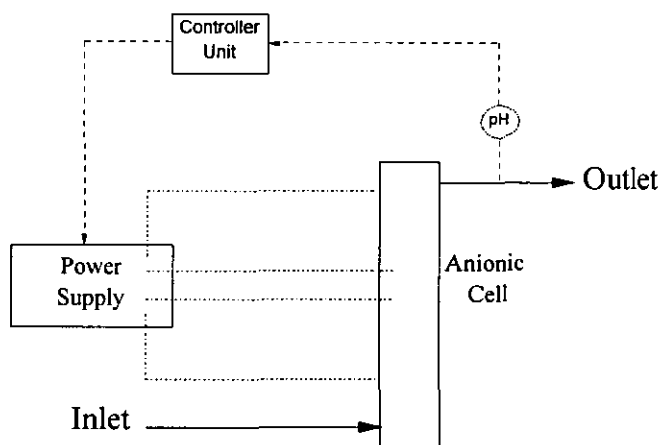


Figure 9.2: Control loop around the anionic Cell

The power supplies could apply a voltage of 0 to 36V across each half cell proportional to an input voltage of 0 to 10V. The input voltage was provided in turn by the controller unit. This unit compared the measured pH with a set point and took appropriate action based on the controller gain set by the operator. It also allowed setting of upper and lower limits of output as well as

an approach value. In this case, the approach value was the applied voltage as the system approached steady state, the output limits were the maximum and minimum values of the potential applied across each half cell during normal operation. A pH meter acted as the measuring device and completed the control loop.

9.3 Experimental Conditions

Current densities used for the cationic cells were between 1.5 and 8 mA.cm⁻² and between 0.5 and 6 mA.cm⁻² for the anionic cells. These current densities were used during absorption and elution cycles. During some experiments current densities in the cationic cells were not maintained as a result of high voltage requirements. The current in the second cell was controlled to give the desired outlet pH, in most cases the set point was 3.2. The flow rate ranged between 0.85 and 2 l.h⁻¹ and feed pH was 3 for all experiments. Tai and Cumming (1997) reported preliminary results on the pilot plant performance of the EIX process.

9.4 Pilot Plant: Results & Discussion

The pilot plant series of experiments were conducted to combine study of the overall changes made to EIX cell with the realistic aim of removing a combination of metal ions in presence of moderate concentrations of interfering cations such as sodium. The modification made to the EIX cell were discussed in Sections 5.3.

9.4.1 Sodium Feed

Initially, an experiment was carried out with a feed containing only 125 mg.l⁻¹ of sodium at a feed pH of 3. This allowed the performance of the pilot plant to be tested without the risk of precipitation. The results for this experiment can be seen in Figures 9.3-9.4. The sodium outlet concentration progressively rose to a constant level as shown in Figure 9.3. As expected, sodium concentrations leaving cell one and two were the same as the anionic cell removed no sodium.

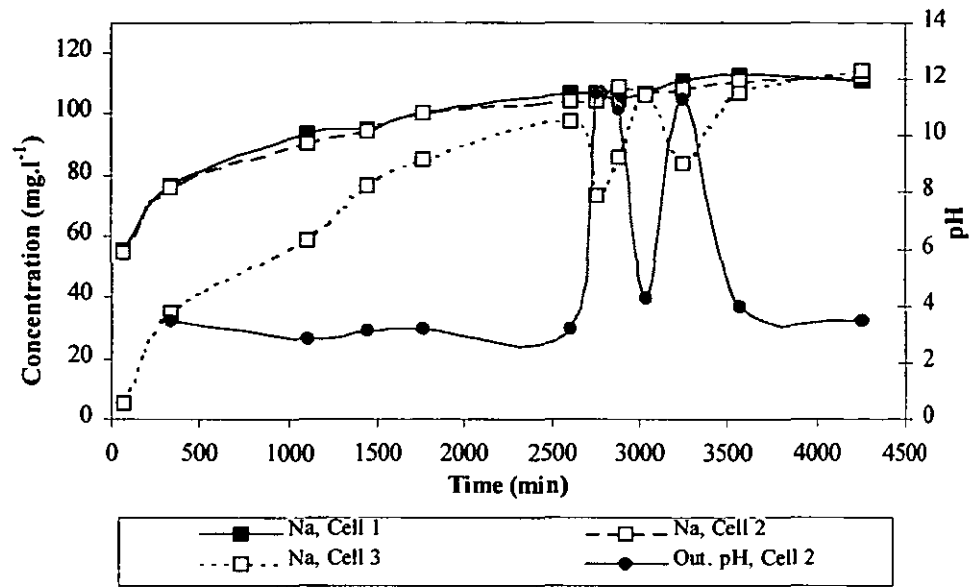


Figure 9.3: Sodium concentration of outlet solutions leaving all three cells and Outlet pH of the second cell

Feed Concentration = 125 mg Na.l⁻¹, Feed pH = 3, Flow Rate = 0.85 l.h⁻¹,
Current density = 3 - 8 mA.cm⁻²

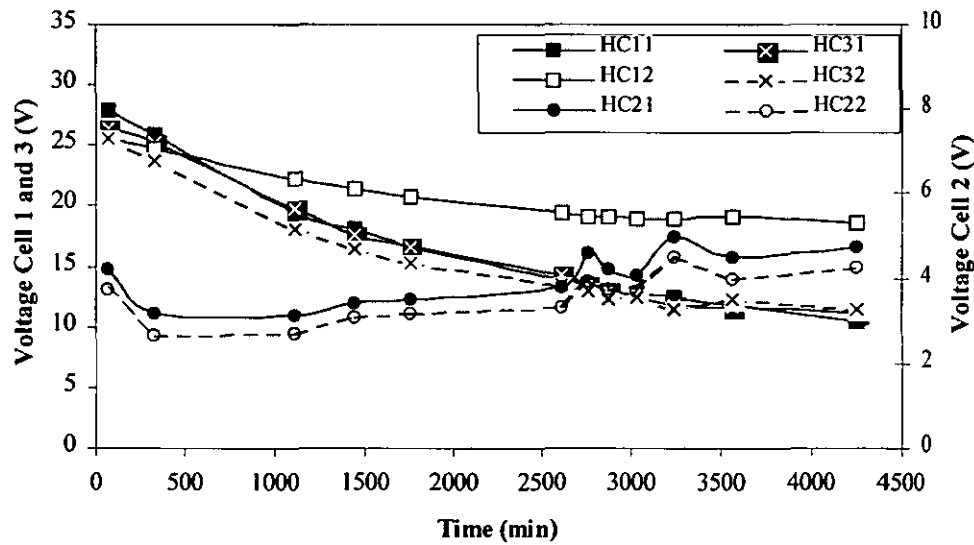


Figure 9.4: Applied Voltage for all three cells during experiment with feed solution bearing only sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

Feed Concentration = 125 mg Na.l⁻¹, Feed pH = 3, Flow Rate = 0.85 l.h⁻¹,
Current density = 3 - 8 mA.cm⁻²

The outlet concentration leaving the third cell gradually approached the feed Concentration of 125 mg.l^{-1} .

The performance of the second cell was tested in relation to improvements in sodium removal by the third cell. This was done by increasing the pH of the solution leaving the second cell which corresponded with a drop in outlet sodium concentration from the third cell. This can clearly be seen in Figure 9.3 between 2500 and 3500 minutes, an increase in pH solution leaving the second cell resulted in drop in sodium concentration leaving the third cell. This was because there was less interference from hydrogen ions and more sodium ions carried the current.

The applied voltages to cells one and three steadily decreased. This indicated a reduction in the resistance of the solution and membrane. The ionic concentration within the membrane increased and the membrane was converted to the sodium form resulting in lower applied voltages as the experiment was continued. The voltage profile for all cells can be seen in Figure 9.4. 'HC' denotes half cell and the first number is the cell number and the second is the number of the half cell.

Different voltages for each half cell suggests that they were not all at the same condition. This may have been partly due to the way cells were sealed resulting in different concentration profiles across each membrane. The half cell that was sealed better would have had less sodium leakage from the back of the cell to the bulk solution resulting in a higher concentration of sodium at back of the cell. This would have resulted in a higher applied voltage requirement to drive the current across the membrane against a higher concentration gradient of sodium ions. The anionic PrAOH membrane required a lower applied voltage than the chelating S930. After 2600 minutes, the current to the second cell was

increased. This was to observe the relationship between the pH out of the second cell and the removal of sodium in the third cell.

The anionic cell did not perform as well as expected. The pH of the solution leaving the cell did not remain constant with time of operation. However, the performance of the cell improved after elution. This may have been due to the PrAOH membranes needing to be conditioned and be converted to the hydroxyl form. A Batch elution cycle was carried out for 30 hours using 20 l of distilled water. The current densities for the cationic cells were 3 mA.cm^{-2} and for the PrAOH cell was 5 mA.cm^{-2} . At the end of the experiment, the sodium concentration leaving the third cell was 183 mg.l^{-1} and the final tank solution contained 108 mg.l^{-2} of sodium. This indicated 80% of sodium was recovered during the elution cycle. The final outlet pH was 12 as no acid was added during the experiment.

A series of absorption cycles were conducted with a mixture of sodium, copper, zinc, and nickel. There were two broad aims, firstly to determine the effect of concentration of interfering ions on the performance of the process and the feasibility of using the anionic cell to adjust the pH into the third cell. The performance of the pilot plant was examined under set process conditions to minimise the affect of changes in these parameters. The experiments were conducted for a feed concentration of 10 mg.l^{-1} of copper, nickel and zinc. Sodium concentration ranged between 66 and 300 mg.l^{-1} . Other experimental conditions were stated in Section 9.3.

9.4.2 Mixed Feed with 66 mg.l^{-1} of sodium

Figures 9.5-9.11 show the results for a experiment with a sodium feed concentration of 66 mg.l^{-1} . Feed concentrations of copper, zinc and nickel were respectively 10.3, 9.6, 10.1 mg.l^{-1} . The flow rate for the experiment was 2 l.h^{-1} feed pH was 3. The current densities in the first and the last cells were

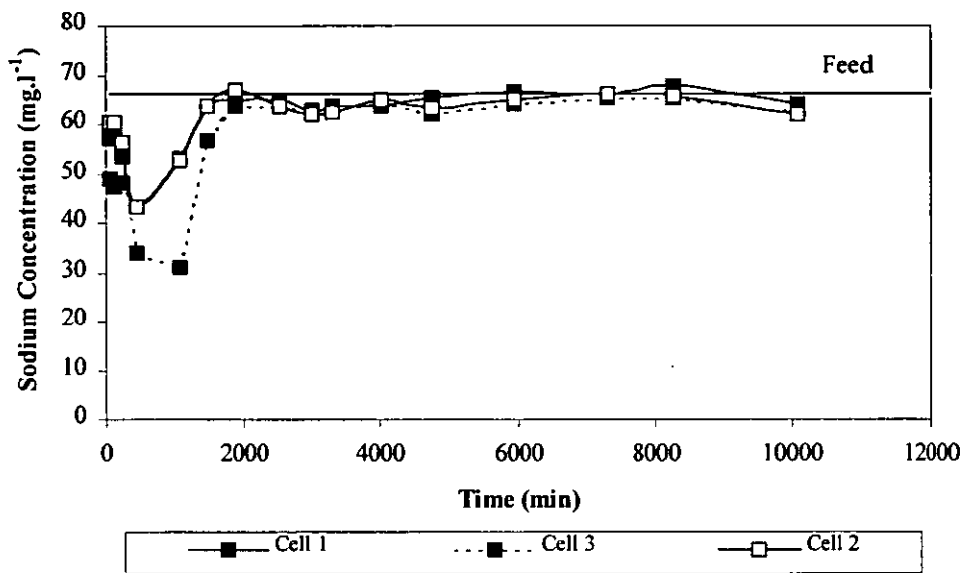


Figure 9.5: Sodium Concentration leaving all cells using a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

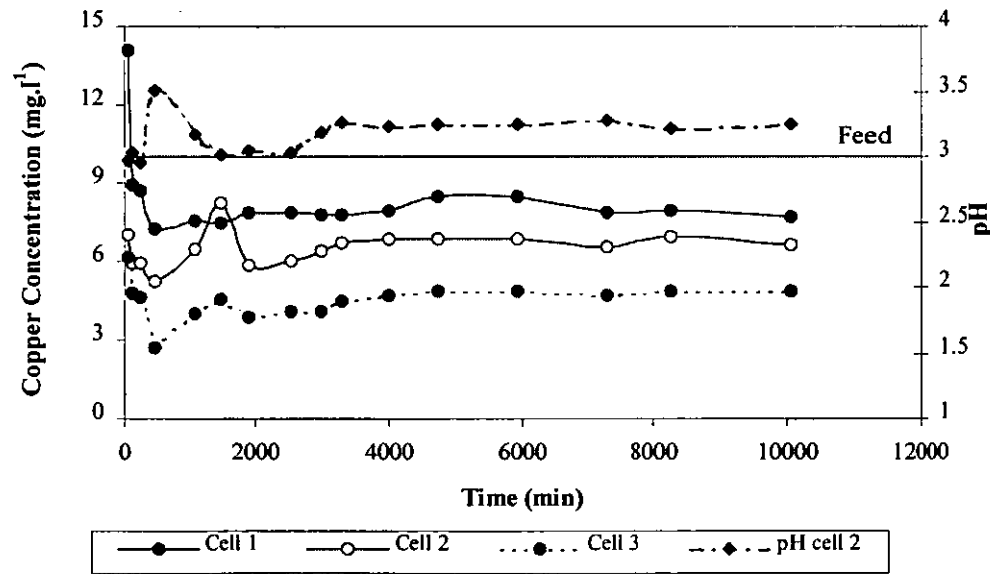


Figure 9.6: Copper Concentrations and solution pH leaving cell 2

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

initially 3 mA.cm^{-2} decreased due to voltage limitations. The second cell operated between a current density of 0.4 and 3 mA.cm^{-2} . It was expected that higher resin cation loading would be obtained by running the experiment for longer periods of time. This was to observe if there was any change in the cell performance with change in loading. The experiment was carried out for 168 hours.

Figure 9.5 shows outlet sodium concentration decreasing at first and then increasing to reach the feed value. In the early part of the experiment, the membranes were being converted to the sodium form. After 30 hours, there was no net removal of sodium by the system. Sodium concentrations leaving the first and second cell were identical throughout the experimental run. In the early stages of the experiment, there was a significant difference between the amount of sodium leaving the second cell and the third cell, indicated by the difference in sodium concentration seen in Figure 9.5. Outlet Sodium levels from the last cell gradually increased to equal the feed concentration. This was because the first cell membranes were converted to the sodium form before the third cell.

Outlet concentration of copper, nickel and zinc can be seen in Figures 9.6 to 9.8 for all cells. The pattern for the concentration of all metal leaving each cell was very similar. There was a distinct difference between the change in concentration of sodium and transition group metals. In the case of sodium, the concentration initially dropped before returning to the feed concentration of 66 mg.l^{-1} . Concentrations of copper, nickel and zinc were lower than the feed and after the initial stages were constant throughout duration of the test. There was also a significant difference between metal cation concentrations entering the anionic cell and outlet. This was due to precipitation and electroplating in the second cell contributing to removal of target ions.

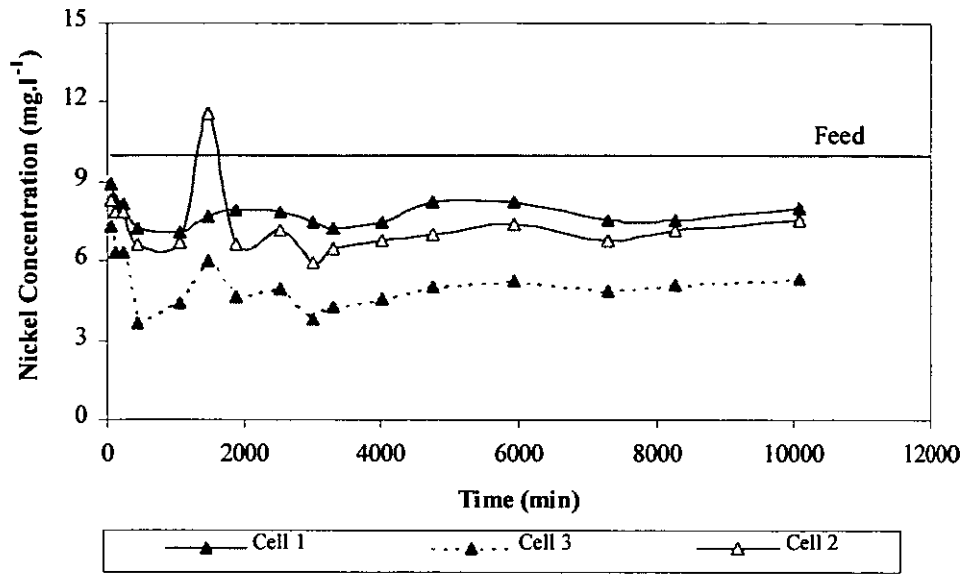


Figure 9.7: Nickel outlet concentrations for all cells during experiments using a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

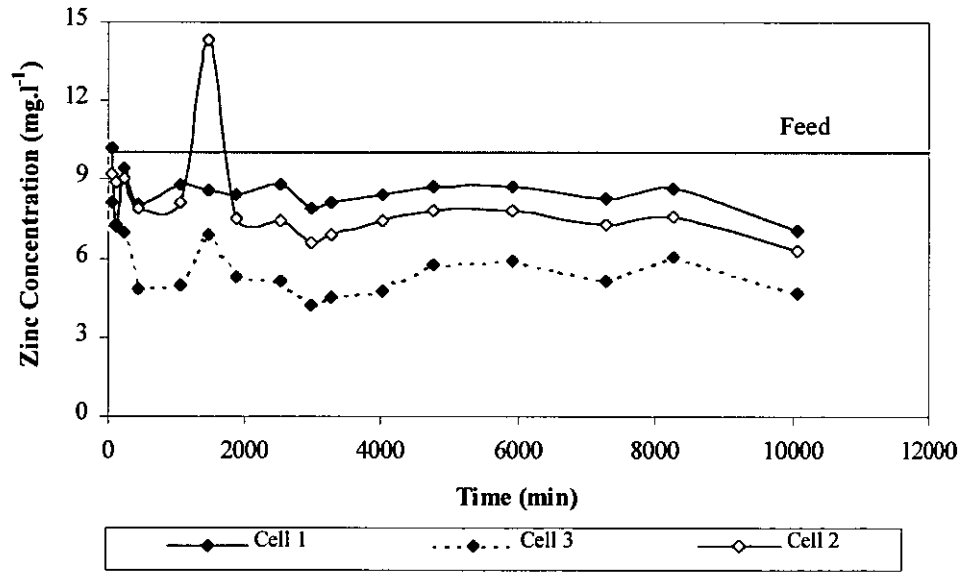


Figure 9.8: Outlet concentrations of zinc in experiments with a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

At 1470 minutes, the outlet concentration of copper, nickel and zinc peaked before decreasing to steady state values. The reason was that sodium ions had stopped being exchanged for hydrogen, resulting in a negligible pH swing across the first cell. This was a step disturbance into the control loop and the response resulted in higher pH within the second cell and transition group metals precipitated out of solution. Once the system had reached steady state and pH profiles were restored, they dissolved back into solution as indicated by increase in their outlet concentrations leaving cell 2 at 1470 minutes.

A total of 341.3 l of simulated solution was treated with the average waste solution containing 72 mg.l⁻¹ of sodium, 4.8 mg.l⁻¹ of copper, 5.04 mg.l⁻¹ of zinc and 5.04 mg.l⁻¹ of nickel.

The outlet pH from all three cells can be seen in Figure 9.9. The pH changes during the step disturbance cannot be seen as the response time was of the order of minutes but samples were taken every hour. Otherwise, the pH was maintained between 2.2 and 3.7. The second cell was successfully used to reverse the pH change of the first cell. This was particularly evident in the first part of the experiment. Once the cationic membranes were converted to the sodium form, there was no significant change in the pH across the first cell. This can be seen by the constant outlet pH of all cells after 1000 minutes.

Figure 9.10 shows removal of all metal ions by the pilot plant. The results clearly indicate removal of all metals improved from the start of the experiment until membranes were converted to the sodium form. After this, there was no net removal of sodium but the removal of other cations was constant at about 50%. The experiment was conducted for over 6 days, there were small fluctuations in the removal of copper, nickel and zinc but after the initial stage they were selectively removed in presence of 66 mg.l⁻¹ of sodium. The

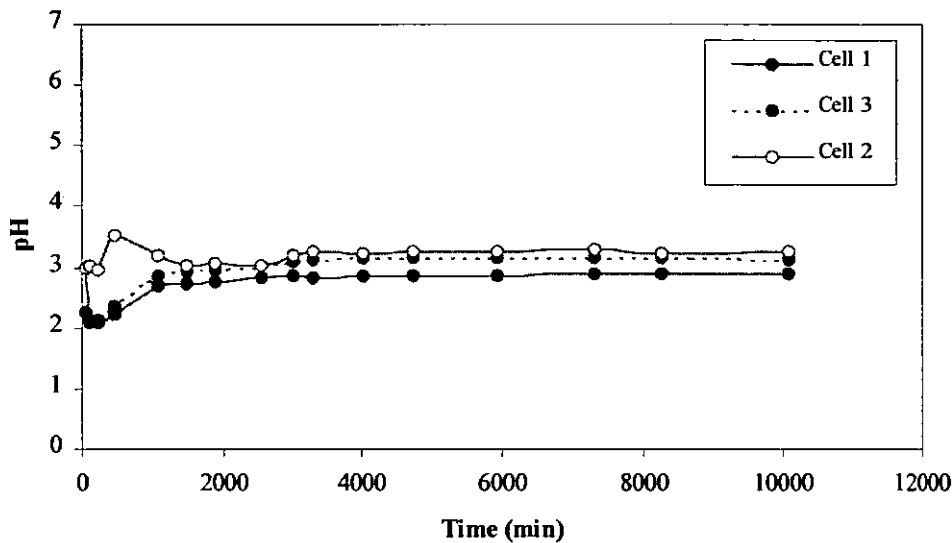


Figure 9.9: Outlet pH during experiment conducted with a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

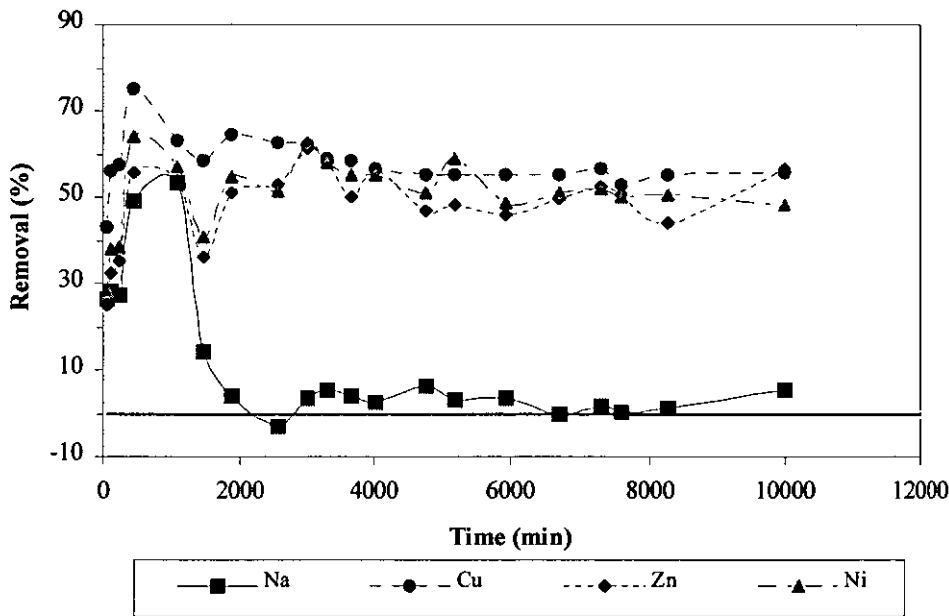


Figure 9.10: Overall removal of sodium, copper, nickel and zinc
Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

removals might have been higher but for the limits of power supply as the maximum operating voltages had been reached. The maximum potential that could be applied was 32 V.

The applied voltage requirements for the experiment can be seen in Figure 9.11. Except in the early stages of the experiments, the applied voltages were constant, it was 32 V for cells 1 and 3 and in the anionic cell it was 2.8 V across both half cells.

The currents flowing through each half cell can be seen in Figure 9.12. The second cell required less current because the pH swing across the first cell was smaller. The currents through cationic membranes were much lower at the end of the experiment than at the beginning. This could have been due to a lack of ions to carry the current, although, the condition of the solution was sufficient to support a current of 3 mA.cm^{-2} . Also, the conductivity of the membrane in the sodium form is lower than that of hydrogen form.

One explanation could be as the membranes were close to be converted to sodium form less hydrogen ions were exchanged which could in turn carry the current. Once the membranes were converted to the sodium form any hydrogen entering the membrane was neutralised due to the high pH conditions within the membrane. Sodium or hydroxyl ions would have carried the bulk of the current. As the sodium concentration was already very high in the membrane and at the back of the cell, the voltage had reached its maximum value to maintain this concentration profile. There was no net removal of sodium by the system as shown in Figure 9.10. Hence, the current was reduced to 1.3 mA.cm^{-2} which could be maintained by the maximum applied voltage of 32 V. The electrical efficiencies with and without sodium are shown in

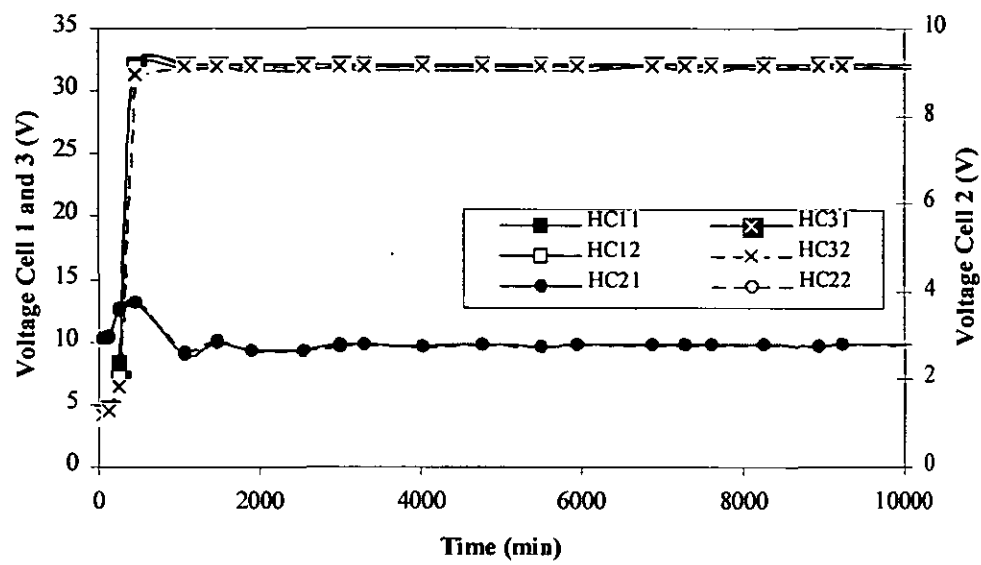


Figure 9.11: Applied voltage for all three cell during experiment conducted with 66 mg.l⁻¹ of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

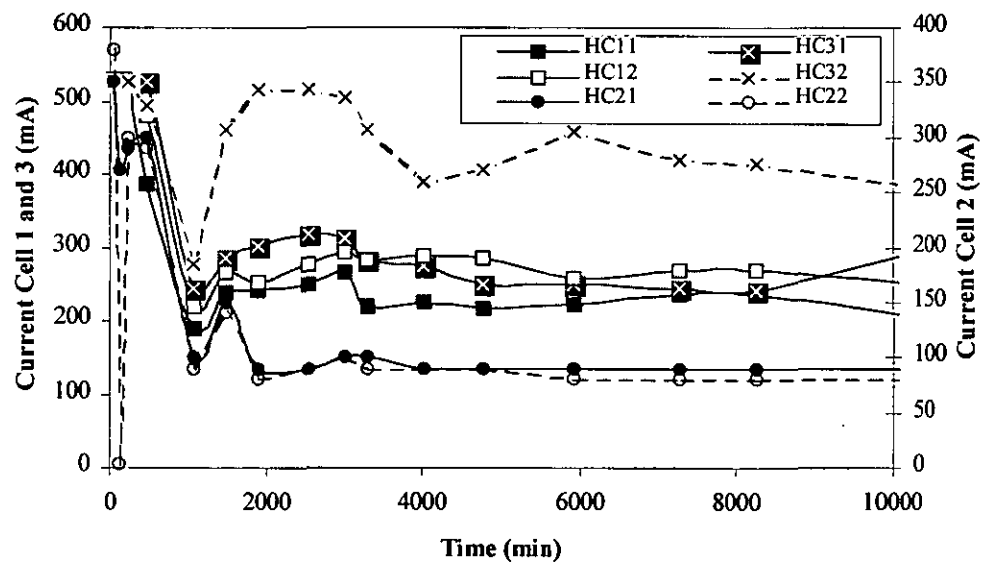


Figure 9.12: Currents for all three cell during experiment conducted with 66 mg.l⁻¹ of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

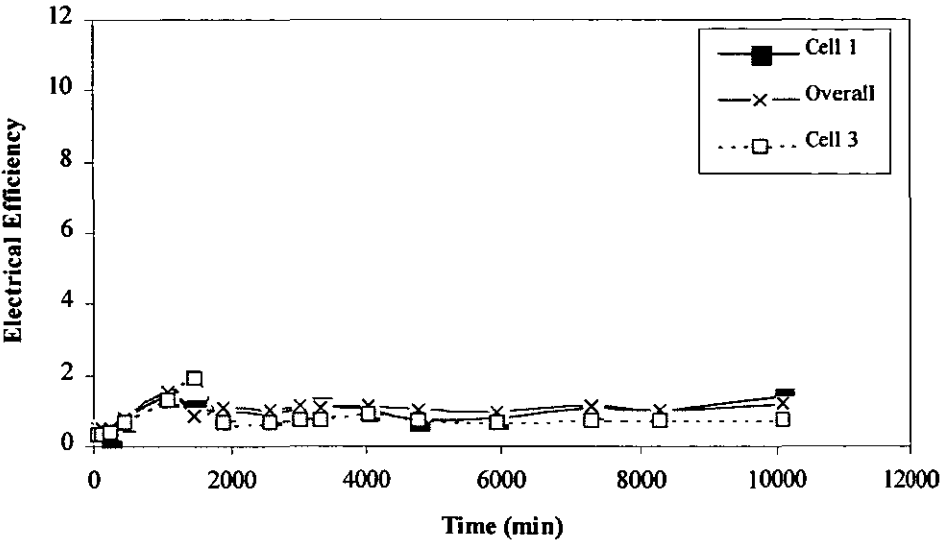


Figure 9.13: Electrical efficiency of cells and the process without sodium contribution

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

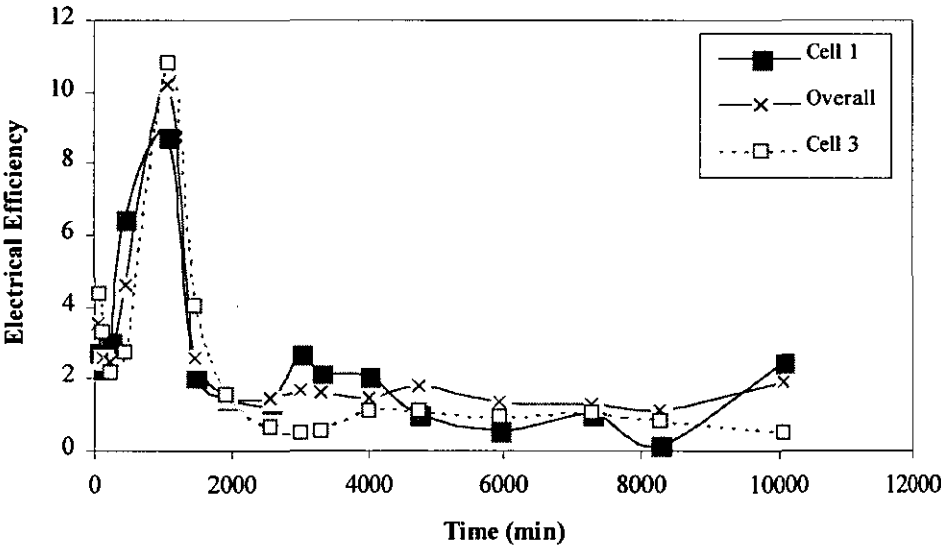


Figure 9.14: Electrical efficiency of cells and the process with sodium contribution

Feed Concentration = 66 mg Na.l⁻¹, 10.3 mg Cu.l⁻¹, 9.6 mg Zn.l⁻¹, 10.1 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.4 - 3 mA.cm⁻²

Figures 9.13 and 9.14. These show the high current efficiencies obtained at the beginning of the experiment particularly for cell 3 that gained the most benefit of favourable pH conditions created by the anionic cell. Once the system had reached steady state, the current efficiencies were decreased to below 2 %. Overall current efficiencies were between 1 and 2 %.

A series of other experiments were carried out with feed solutions containing higher concentrations of interfering ion, sodium, to show the effect of concentration on the performance of the pilot plant.

9.4.3 Mixed Feed with 130 mg.l⁻¹ of sodium

Figures 9.15-9.19 show the results for the experiment carried out with the feed concentrations of 130 mg.l⁻¹ of sodium, 10 mg.l⁻¹ of copper, 7.3 mg.l⁻¹ of nickel and 10 mg.l⁻¹ of zinc. The feed pH was 3 and the flow rate used was 1.2 l.h⁻¹. This experiment was the first experiment carried out in the series of pilot plant tests discussed here. It was thought more appropriate to present this series of experiments in order of sodium feed concentrations ranging from 66 to 300 mg.l⁻¹. The sodium outlet concentration did not reach the feed values as shown in Figure 9.15. This may have been due to the condition the membranes were in before this experiment was carried out. The membranes would have been in a combined hydrogen and sodium form as cells were previously used for short term experiments which lasted less than 6 hours. Otherwise, similar results were obtained compared to the experiment carried out with sodium feed concentration of 66 mg.l⁻¹.

Figures 9.15 and 9.16 show the sodium and copper concentrations throughout the pilot plant. Outlet concentrations of nickel and zinc were very similar to copper. The concentration of sodium leaving cell 1 was identical to the outlet concentration of the second cell. There was removal of copper, nickel and zinc by the anionic cell. Most of the copper removed by the anionic cell was by

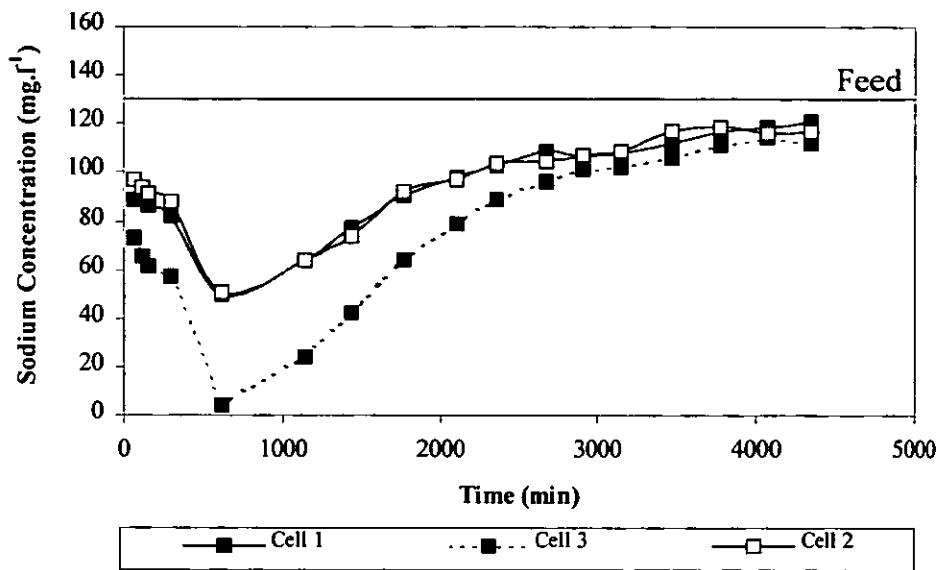


Figure 9.15: Sodium Concentration leaving all cells using a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 130 mg Na.l⁻¹, 10 mg Cu.l⁻¹, 10 mg Zn.l⁻¹, 7.3 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 1.2 l.h⁻¹, Current density = 0.3 - 3 mA.cm⁻²

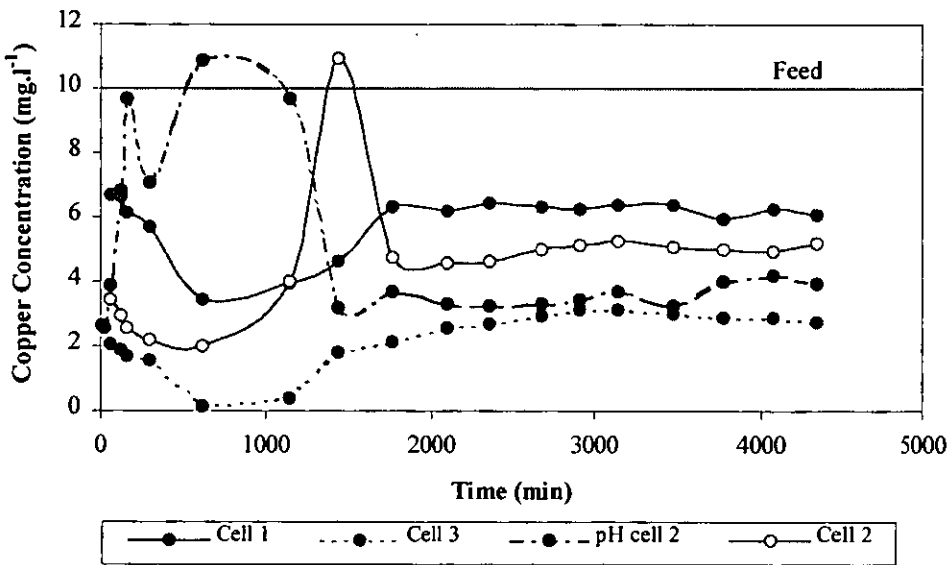


Figure 9.16: Copper Concentrations and solution pH leaving cell 2

Feed Concentration = 130 mg Na.l⁻¹, 10 mg Cu.l⁻¹, 10 mg Zn.l⁻¹, 7.3 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 1.2 l.h⁻¹, Current density = 0.3 - 3 mA.cm⁻²

electroplating on the counter electrode. This electrode was exposed to the bulk solution in the centre of the cell and signs of copper coating were clearly visible.

Black dendritic solids were formed during the selectivity experiments at the top of the cell. These mainly formed around the metal mesh of the EIX electrode at the top of the cell. The bare metal was covered with binder material as previously discussed in Section 5.3. More binder material was applied to areas where there was sign of solid formation. This reduced the formation of the solids in later experiments but did not eliminate it completely.

After 600 minutes, the concentration of all cations was almost zero. The reason for the complete removal was due to the large reduction in cation concentration in the first cell and high outlet pH out of the second cell as seen in Figure 9.17. The voltage reached maximum only in the first cell in the early part of the experiment. However, there were sufficient ions in the system to support a current density of 3 mA.cm^{-2} , so maximum applied voltage was not required through out this test. The currents flowing through each half cell can be seen in Figure 9.18. The sodium concentration leaving cell 1 and 3, shown in Figure 9.15, approached but was not equal to sodium feed concentration. Hence, there was a net removal of sodium indicating that cationic membranes were not converted completely to the sodium form. The same patterns were seen in the previous experiment but in that case cationic membranes were converted completely to the sodium form.

The current in the second cell was controlled in the early part of the experiment. The pH out of the anionic cell was allowed to go above 7 to observe the process under alkaline conditions. As expected, the removal of metal increased due to better conditions for ion exchange enhanced by precipitation of transition group metals. Once the solution was made acidic by

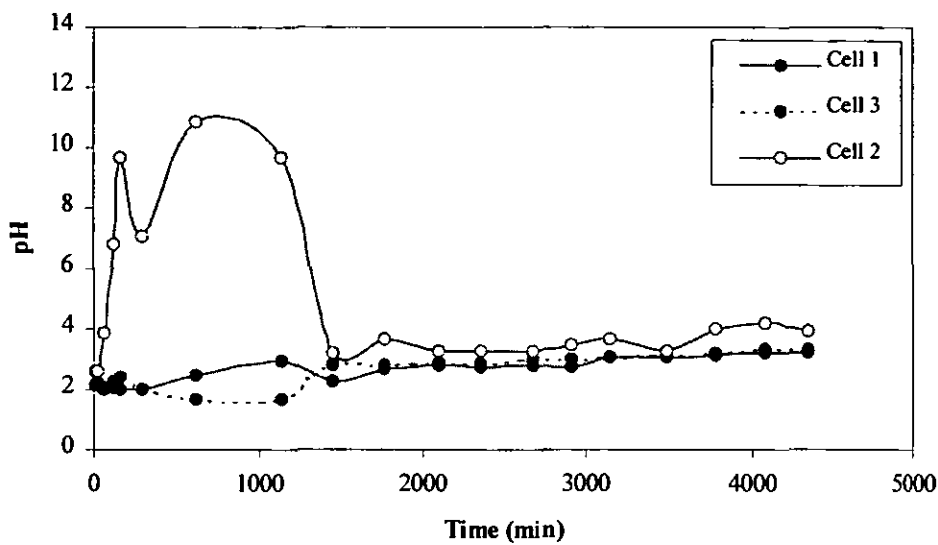


Figure 9.17: Outlet pH during experiment conducted with a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 130 mg Na.l^{-1} , 10 mg Cu.l^{-1} , 10 mg Zn.l^{-1} , 7.3 mg Ni.l^{-1} ,
 Feed pH = 3, Flow Rate = 1.2 l.h^{-1} , Current density = $0.3 - 3 \text{ mA.cm}^{-2}$

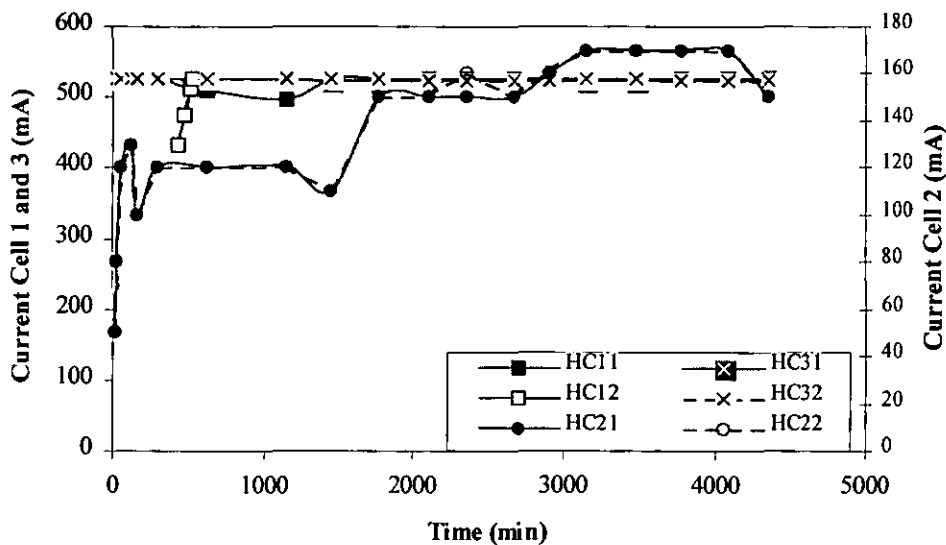


Figure 9.18: Currents flowing through all half cells during experiment conducted with 130 mg.l^{-1} of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

Feed Concentration = 130 mg Na.l^{-1} , 10 mg Cu.l^{-1} , 10 mg Zn.l^{-1} , 7.3 mg Ni.l^{-1} ,
 Feed pH = 3, Flow Rate = 1.2 l.h^{-1} , Current density = $0.3 - 3 \text{ mA.cm}^{-2}$

reducing the current applied across the second cell an increase of about 6 mg.l^{-1} was measured for copper. This was mostly out of the second cell indicating that the removal was mostly due to the precipitation.

The applied voltages for the experiment carried out with a sodium feed concentration of 130 mg.l^{-1} can be seen in Figure 9.19. This shows the applied voltage to the cationic cells increasing at same time as total removal of all metal ions. Once maximum removal had been reached, the voltage gradually decreased. This effect was only evident in membranes that were partly in the hydrogen form and partly in the sodium form. Other experiments were conducted with membranes completely in the hydrogen form this was ensured by carrying out several elution steps and then passing acidic solution through the cell for several days. These were carried out as part of a final year project and are not reported here. Results from these showed that there was an increase in applied potential to a maximum of 20 V for feed concentration of 300 mg.l^{-1} .

Indications were that as the membrane were loaded with sodium and other metals, there was a lack of ions getting across to carry the current. This was because the hydrogen ions entering or being ion exchanged were neutralised, as the conditions inside the membranes were alkaline. Also, the ion exchange resin adsorbed most of the metal ions entering the membranes. Once the resin was converted to sodium form, the applied voltage decreased as sodium exchanged for other metal ions could help carry the current across the membrane which also increased the sodium concentration in the membranes.

The overall removal by the pilot plant can be seen in Figure 9.20. The results show that there was almost complete removal of all metal ions in the early part of the experiment. Sodium removal gradually decreased from this maximum to below 20%. Removal of copper, nickel and zinc was reduced but

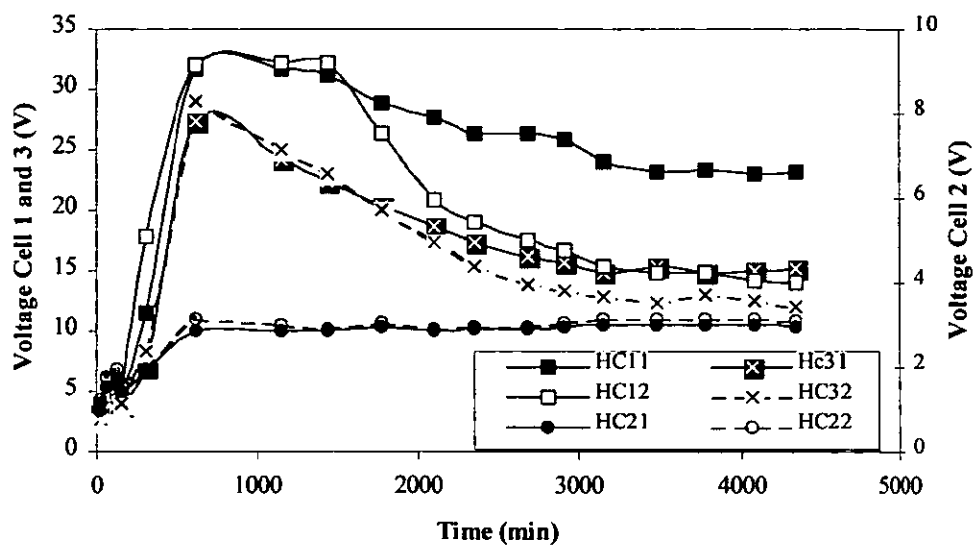


Figure 9.19: Applied voltage for all three cell during experiment conducted with 130 mg.l⁻¹ of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1
Feed Concentration = 130 mg Na.l⁻¹, 10 mg Cu.l⁻¹, 10 mg Zn.l⁻¹, 7.3 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 1.2 l.h⁻¹, Current density = 0.3 - 3 mA.cm⁻²

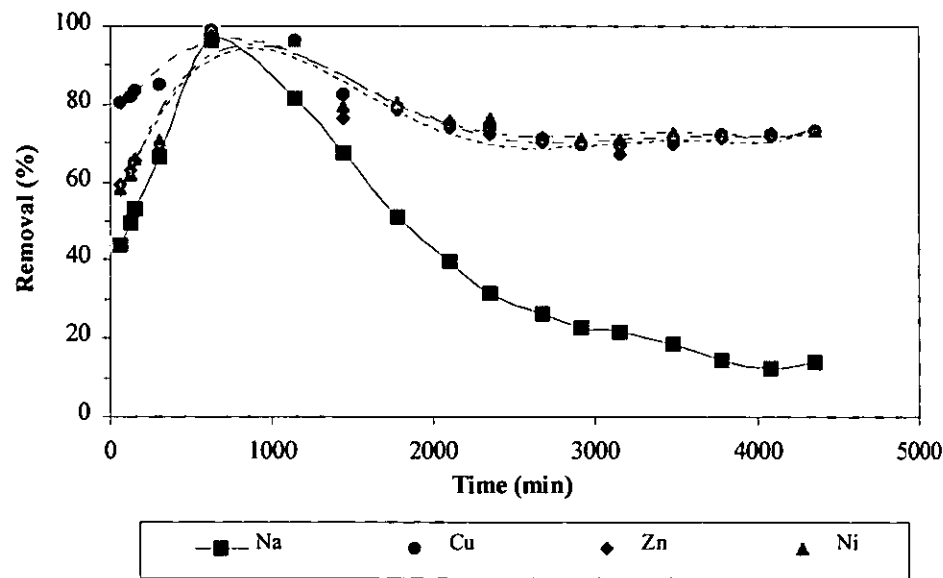


Figure 9.20: Overall removal of sodium, copper, nickel and zinc
Feed Concentration = 130 mg Na.l⁻¹, 10 mg Cu.l⁻¹, 10 mg Zn.l⁻¹, 7.3 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 1.2 l.h⁻¹, Current density = 0.3 - 3 mA.cm⁻²

remained considerably higher at about 70%. The removal stayed constant between 2000 and 4000 minutes.

Nearly seventy litres of simulated solution was treated and a total of 3.3 g of sodium, 0.55g of copper, 0.5 g of zinc and 0.39g of nickel were removed from solution. The overall removal of sodium was about 36 % with an average removal of 77 % for copper, nickel and zinc. The loading of the cationic membranes was about 2.6% assuming that S930 chelating resin had a capacity of 2 meq.g⁻¹ and all the metals ions were removed by ion exchange.

9.4.4 Mixed Feed with 180 mg.l⁻¹ of sodium

The next experiment was conducted with higher concentration of sodium of 180 mg.l⁻¹ and at a flow rate of 2 l.h⁻¹. The results of this experiment can be seen in Figures 9.21-9.25. The outlet sodium concentration gradually approached 180 mg.l⁻¹, which can be seen in Figure 9.21. Nickel and zinc outlet concentrations were similar to copper seen in Figure 9.22 (about 3 mg.l⁻¹).

The overall removals can be seen in Figure 9.23. Results were similar to those obtained using a feed containing 66 mg.l⁻¹ of sodium. The maximum removal did not approach a hundred percent probably due to the higher flow rate and sodium feed concentration. Although, a maximum removal did occur at about the same time as other experiments.

The current to the second cell was automatically controlled. The voltage profile for all three cells can be seen in Figure 9.24. The first cell voltage reached a maximum and then the current density decreased from 3 mA.cm⁻² to 2.1 mA.cm⁻¹. The voltage to the third cell increased to follow the maximum removal and then decreased as the pH out of the second cell was controlled.

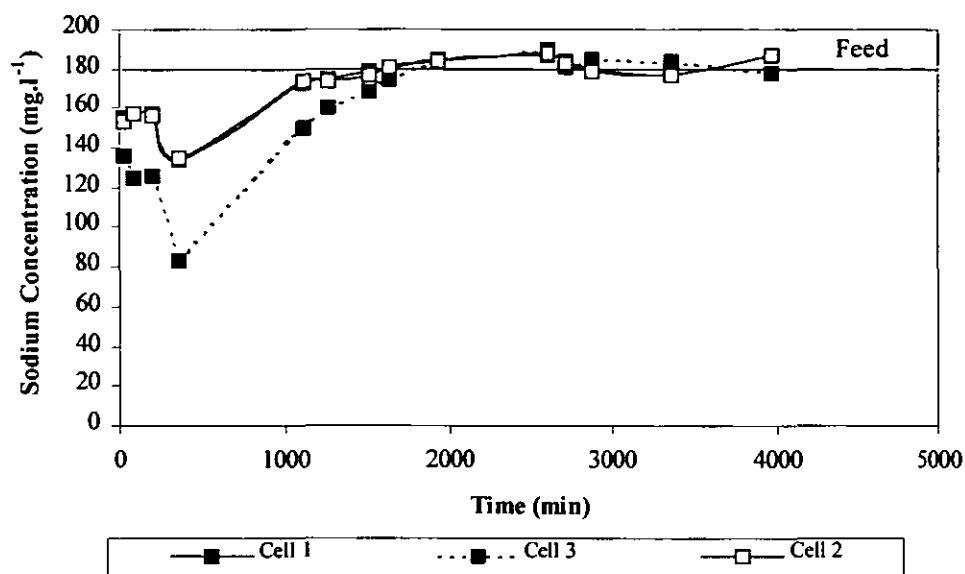


Figure 9.21: Sodium Concentration leaving all cells using a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 180 mg Na.l^{-1} , $10.7 \text{ mg Cu.l}^{-1}$, 9.7 mg Zn.l^{-1} , $10.2 \text{ mg Ni.l}^{-1}$,
 Feed pH = 3, Flow Rate = 2 l.h^{-1} , Current density = $0.85 - 5.5 \text{ mA.cm}^{-2}$

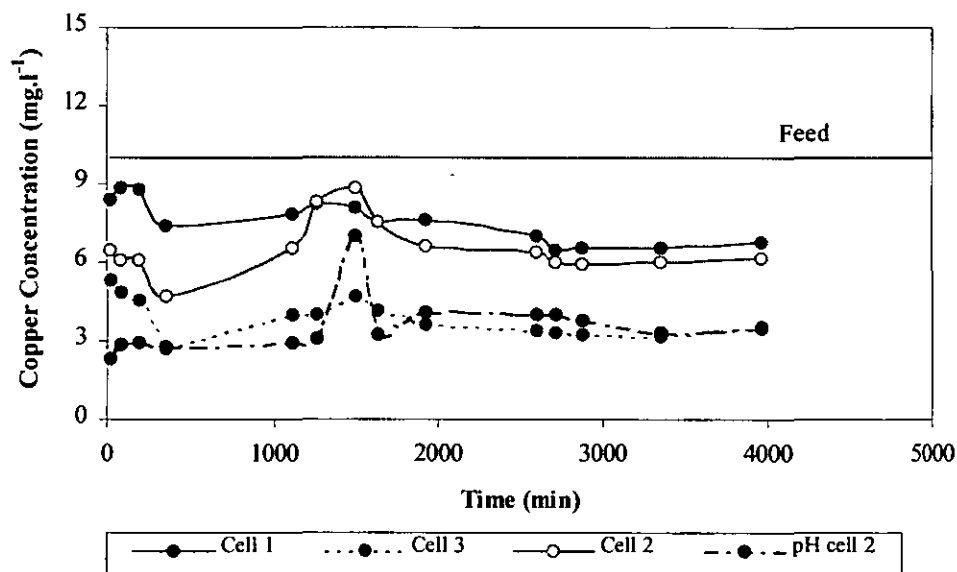


Figure 9.22: Copper Concentrations and solution pH leaving cell 2

Feed Concentration = 180 mg Na.l^{-1} , $10.7 \text{ mg Cu.l}^{-1}$, 9.7 mg Zn.l^{-1} , $10.2 \text{ mg Ni.l}^{-1}$,
 Feed pH = 3, Flow Rate = 2 l.h^{-1} , Current density = $0.85 - 5.5 \text{ mA.cm}^{-2}$

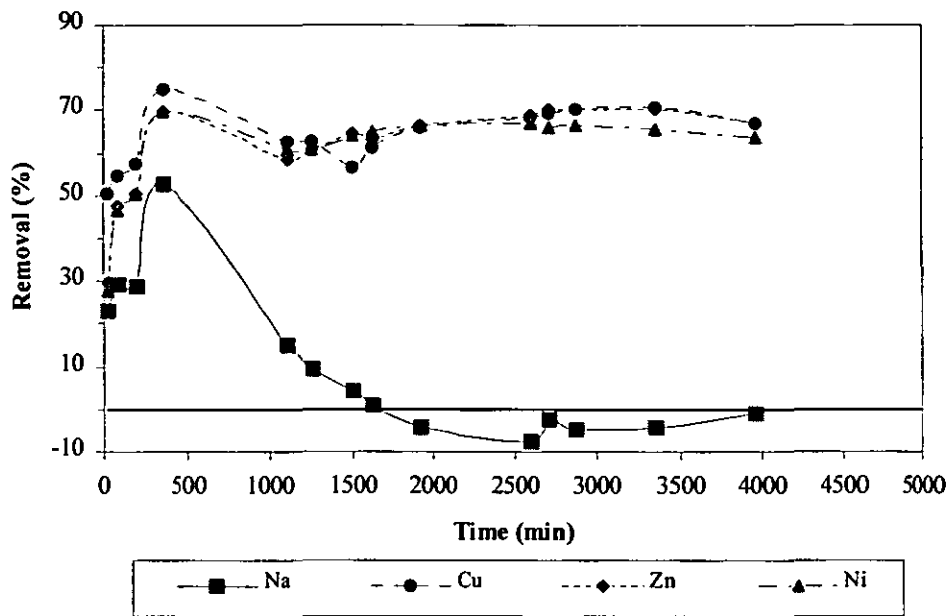


Figure 9.23: Overall removal of sodium, copper, nickel and zinc
Feed Concentration = 180 mg Na.l⁻¹, 10.7 mg Cu.l⁻¹, 9.7 mg Zn.l⁻¹, 10.2 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.85 - 5.5 mA.cm⁻²

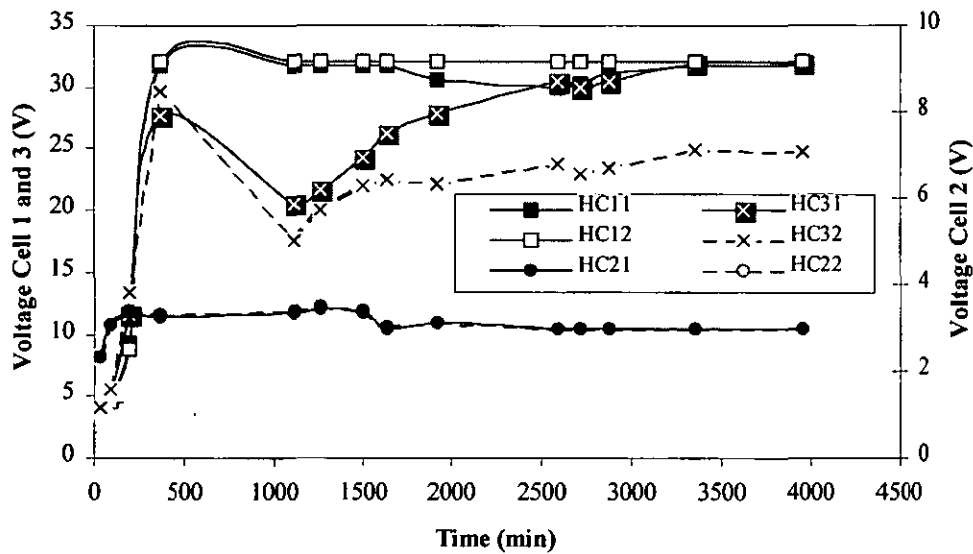


Figure 9.24: Applied voltage for all three cell during experiment conducted with 180 mg.l⁻¹ of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1
Feed Concentration = 180 mg Na.l⁻¹, 10.7 mg Cu.l⁻¹, 9.7 mg Zn.l⁻¹, 10.2 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.85 - 5.5 mA.cm⁻²

As the experiment was continued, the pH out of the first cell approached that of the feed. The controller output was then reduced, as only a small pH adjustment was needed by the anionic cell to increase the pH from 3 to 3.2.

At 1260 minutes, the current density in the third cell was increased to 5.5 mA.cm^{-1} . This was to see if any further improvement in the removal could be made. The currents for all cells can be seen in Figure 9.25. As the results show, in Figures 9.22 and 9.23, there was very little improvement in the removal but the applied voltage gradually increased to 32 V for one half cell and to 23 V for the other. The power requirement was increased by two and a half times the original steady state value while the removal increased by only 8% from 62% to 70%.

Overall, the average amount of cations removed were 4.5 % of sodium, 65 % of copper, 63 % of zinc and 63 % nickel. One hundred and thirty litres of simulated solution were treated. The waste solution had an average concentration of 170 mg.l^{-1} of sodium, 4.1 mg.l^{-1} of copper, 4.2 mg.l^{-1} of zinc and 3.9 mg.l^{-1} of nickel with a pH of about 3.2 slightly higher than the feed solution. There was some solid formation at top of the cell 3. This was thought to be due to the higher pH in cell 3 and improper sealing.

9.4.5 Mixed Feed with 300 mg.l^{-1} of sodium

The next experimental run was conducted using a feed concentration of 300 mg.l^{-1} of sodium, 10.8 mg.l^{-1} of copper, 10.2 mg.l^{-1} of nickel and 11.2 mg.l^{-1} of zinc. The feed pH was 3 and the flow rate 2 l.h^{-1} . The total amount of solution treated was 232 l. The results for this experiment can be seen in Figures 9.26-30.

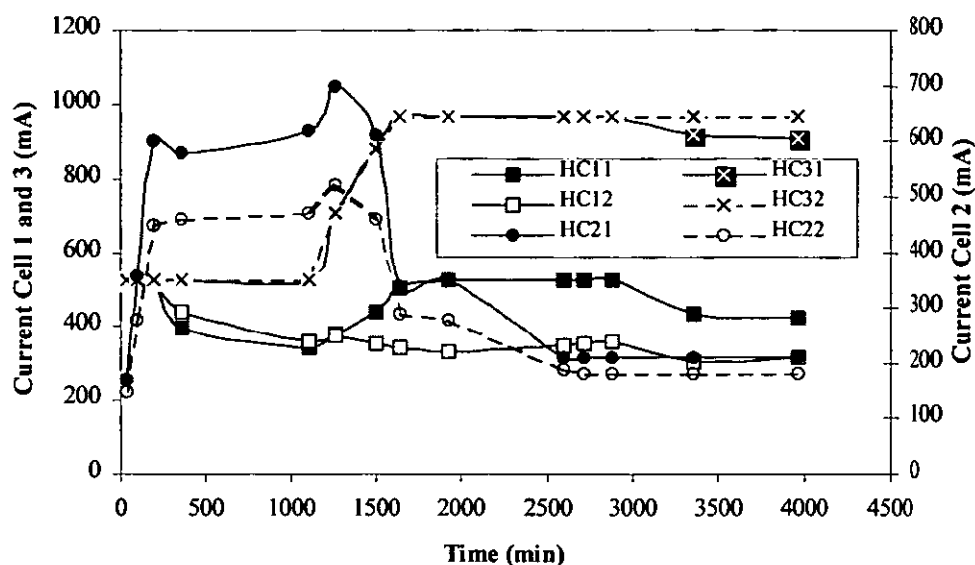


Figure 9.25: Currents flowing through all half-cell during experiment conducted with 180 mg.l^{-1} of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

Feed Concentration = 180 mg Na.l^{-1} , $10.7 \text{ mg Cu.l}^{-1}$, 9.7 mg Zn.l^{-1} , $10.2 \text{ mg Ni.l}^{-1}$,
Feed pH = 3, Flow Rate = 2 l.h^{-1} , Current density = $0.85 - 5.5 \text{ mA.cm}^{-2}$

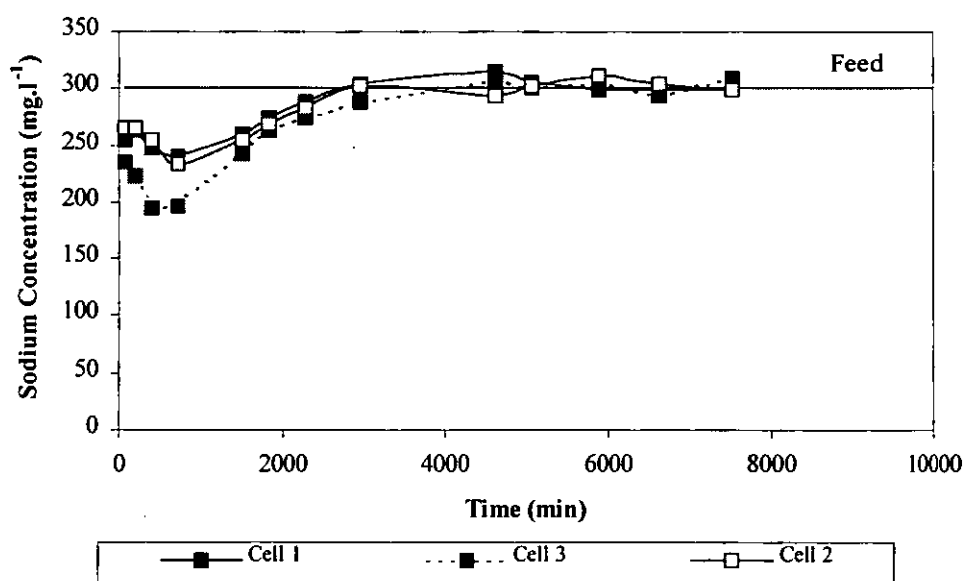


Figure 9.26: Sodium Concentration leaving all cells using a combined feed of sodium, copper, nickel and zinc

Feed Concentration = 300 mg Na.l^{-1} , $10.8 \text{ mg Cu.l}^{-1}$, $11.2 \text{ mg Zn.l}^{-1}$, $10.2 \text{ mg Ni.l}^{-1}$,
Feed pH = 3, Flow Rate = 2 l.h^{-1} , Current density = $0.2 - 4.3 \text{ mA.cm}^{-2}$

The outlet sodium concentrations for all cells can be seen in Figure 9.26. The results showed that the sodium concentration steadily decreased and after 3000 minutes increased to the same as the feed value. In all experiments, the minimum sodium concentrations were obtained between 300 minutes and 750 minutes. These corresponded to the maximum applied voltages which occurred at same time. These were the same results obtained for experiments carried out with feed solutions containing 66 and 180 mg.l⁻¹ of sodium. This indicated that sodium ions were transported into the membrane and were removed by ion exchange. The sodium concentration within the membrane and back of the cell was so high that the applied voltage increased to maintain the concentration gradient and the current. Increasingly less hydrogen ions were available to carry the current. Hence, there was not sufficient ions transported across the membrane to support a current density of 3 mA.cm⁻².

Figure 9.27 shows the copper outlet concentration for all cells and pH of the solution leaving cell 2. The outlet pH of cell 2 was maintained between 2 and 4. This demonstrated the successful application of the control loop around the anionic cell. At the beginning of the experiment, the copper concentration leaving all cells was higher than the feed concentration. Copper electroplated on the counter electrode of cationic cells during elution. During regeneration, the counter electrode acted as the cathode and a fine film of copper was formed on the electrode. As the current was reversed for an absorption cycle, the copper was dissolved back into the solution. This also occurred during an earlier experiment for sodium feed concentration of 66 mg.l⁻¹. In some experiments, 1M nitric acid prior was circulated around the system prior to an absorption experiment so that most of the electroplated copper could be recovered. Another solution would be to run a small volume of acidic solution through the cell in absorption mode and recover the copper before commencing the absorption cycle. This problem was only encountered for copper.

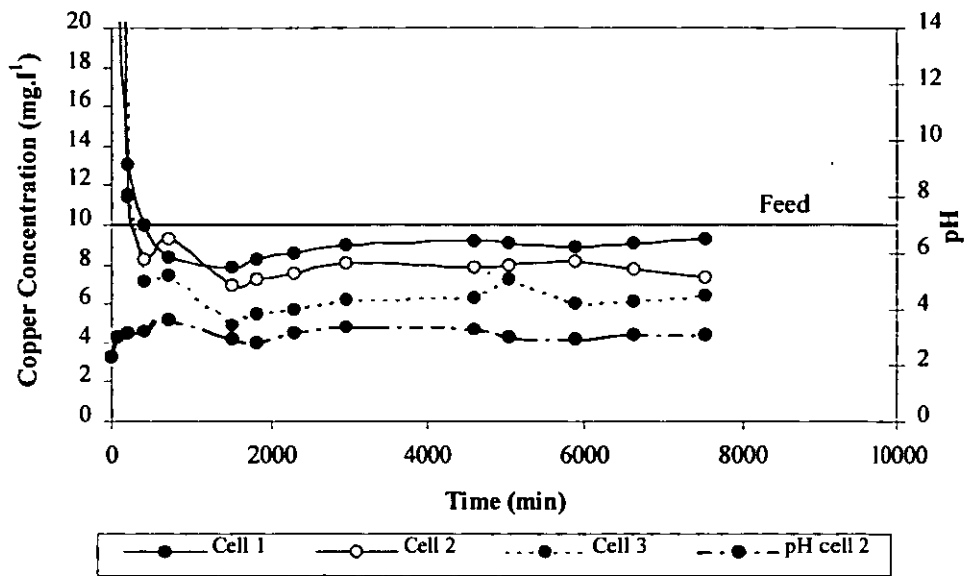


Figure 9.27: Copper Concentrations and solution pH leaving cell 2
Feed Concentration = 300 mg Na.l⁻¹, 10.8 mg Cu.l⁻¹, 11.2 mg Zn.l⁻¹, 10.2 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.2 - 4.3 mA.cm⁻²

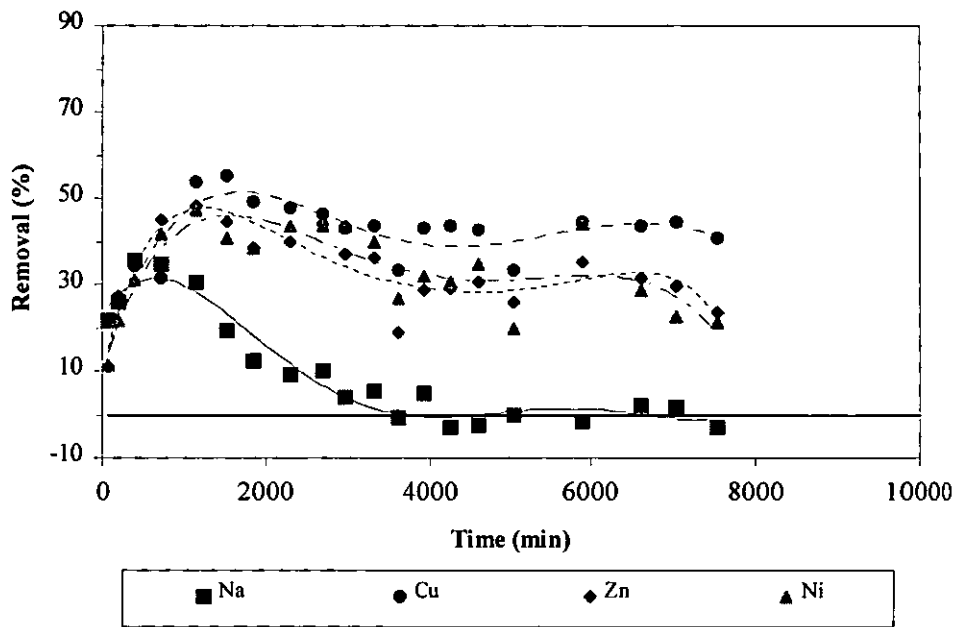


Figure 9.28: Overall removal of sodium, copper, nickel and zinc
Feed Concentration = 300 mg Na.l⁻¹, 10.8 mg Cu.l⁻¹, 11.2 mg Zn.l⁻¹, 10.2 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.2 - 4.3 mA.cm⁻²

The average removal was 10 % for sodium, 40 % for copper 34 % for zinc and nickel. The overall removal can be seen in Figure 9.28. The results show that there was a maximum removal of all metal ions before the sodium removal was reduced to zero. Other metals showed similar removal characteristics which were also evident in all other absorption experiments discussed in this chapter.

In the early part of the experiment, applied voltages for both cationic cells were very low as shown in Figure 9.29. This was probably due to the high concentration of cations present within the system. This was because relatively high concentration of ions in the system, sodium in the feed and copper recovered after electroplating during elution. The applied potential increased as in experiments carried out with a feed concentration of 66 and 180 mg.l⁻¹ of sodium. The voltages did not stay at the maximum value for very long because of the high concentration of sodium ions present. However, the maximum applied voltage corresponded to the maximum removal the same as the other experiments. The applied voltage required for half cell 2 in cell 1 (HC12) was drastically less than the other half cells in the cationic cells. This was thought to be due to the failing seal around the back of the cell after repeated use. This would have resulted in lower concentrations of sodium at the back of the cell resulting in lower required voltage.

The applied voltage of the second cell was relatively high at the beginning of the experiment. It steadily decreased from about 4V to 2 V. After 3000 minutes, there was no change in solution pH from inlet to the outlet of the first cell. This was due to the membranes being completely in sodium form and any ion exchange taking place was between sodium and other cations. Therefore, the second cell changed the pH from 3 to 3.2 which required a current density

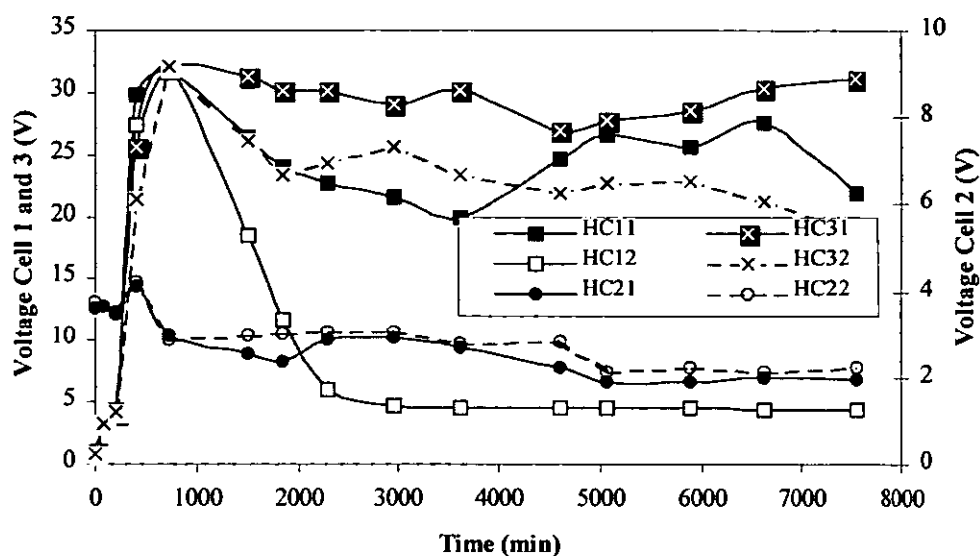


Figure 9.29: Applied voltage for all three cell during experiment conducted with 300 mg.l⁻¹ of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

Feed Concentration = 300 mg Na.l⁻¹, 10.8 mg Cu.l⁻¹, 11.2 mg Zn.l⁻¹, 10.2 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.2 - 4.3 mA.cm⁻²

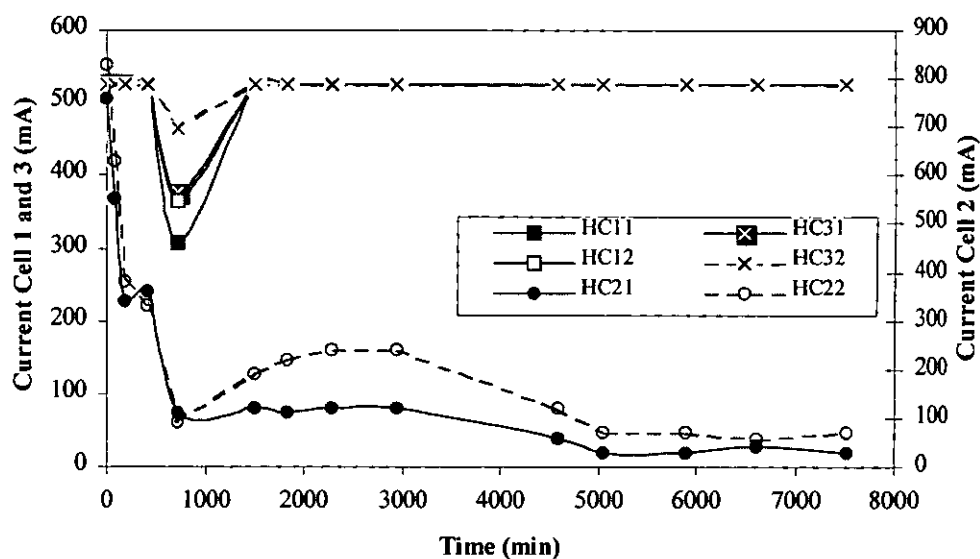


Figure 9.30: Applied voltage for all three cell during experiment conducted with 300 mg.l⁻¹ of sodium

Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

Feed Concentration = 300 mg Na.l⁻¹, 10.8 mg Cu.l⁻¹, 11.2 mg Zn.l⁻¹, 10.2 mg Ni.l⁻¹,
Feed pH = 3, Flow Rate = 2 l.h⁻¹, Current density = 0.2 - 4.3 mA.cm⁻²

of only 0.3 mA.cm^{-2} compared to 4.5 mA.cm^{-2} at the beginning of the experiment. This change in current can be seen in Figure 9.30.

During the experiment, the current density was 3 mA.cm^{-1} for both cationic cells. This decreased to 1.8 mA.cm^{-2} when the maximum removal was achieved at 730 minutes. After this time the current density was constant with corresponding applied voltages which were generally lower than most of the other experiments.

The results of the absorption cycle indicated that there were significant advantages to be gained by using an anionic cell when there was significant amount of sodium being removed in the first cell. However, there was electroplating of copper in the second cell and precipitation of other metals, which partly enhanced the overall removal. The precipitation could take place within any part of the cell, this would mean that solid pieces of metal could be washed out of cell 2. If these dissolve back into solution in time to be removed by the third cell then there is no risk of contamination of the effluent. If these solids washed out with the outlet solution then this would pose a major problem in a working plant. The solution can be filtered but this would add to the running cost and complicate the process. The solids could dissolve back into the solution if filters are not continuously cleaned.

After each absorption cycle, there was an elution cycle to recover the metals removed from the simulated solution. A total mass balance was carried out over the absorption and regeneration cycles to determine the amount of metal ions removed and recovered. These are discussed in the next section.

9.5 Elution

The concepts of elution and pole reversal were discussed in Chapter 7. One modification was the addition of the anionic cell during elution. As in the

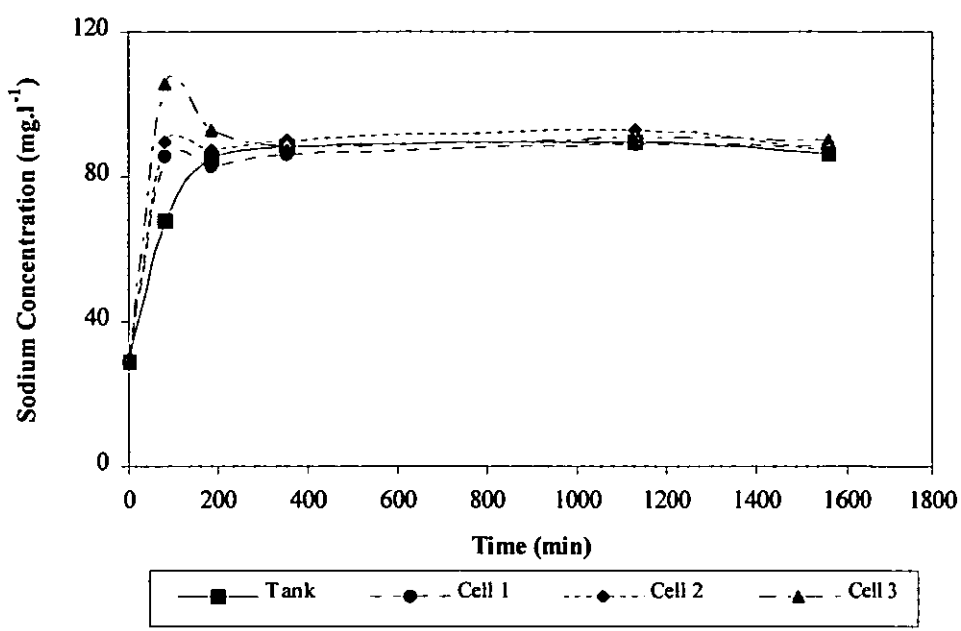


Figure 9.31: Sodium concentrations during elution cycle
Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²

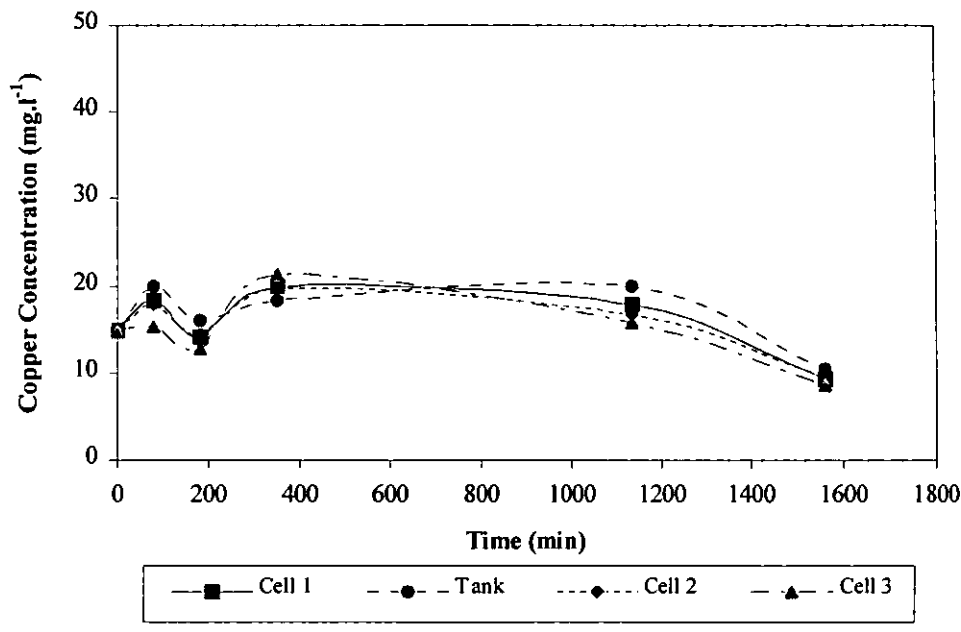


Figure 9.32: Copper concentrations during elution cycle
Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²

absorption, the cell reversed any pH change in the first cell. This partly helped to reduce the amount of mineral acids used during the elution cycles. The elution cycles were all conducted in batch mode and acid was added to the feed tank when required.

9.5.1 Elution: sodium feed concentration of 66 mg.l^{-1}

The elution following this absorption experiment was carried out in two batches of 10 litres. The first experiment was carried out for 26 h and the second for 50 h. The feed solution with a pH of 2 was circulated around the system for 15 h before the current was switched on for the first elution batch. At the end of this period, the 10 l of water contained 29 mg.l^{-1} of sodium, 15 mg.l^{-1} of copper, 25 mg.l^{-1} of zinc and 18 mg.l^{-1} of nickel. This was from residual precipitates, electroplated metal and some elution off the membrane. The high concentration of sodium meant that material had been eluted off the membrane. There was also visible sign of copper dissolving back into solution off the counter electrodes and there were no sign of any solids within the system.

In the first experiment, the pH was maintained at 2. The results for this experiment can be seen in Figures 9.31-9.38. The concentration history of sodium leaving all cells and in the feed tank can be seen in Figure 9.31. The results indicate that sodium was rapidly eluted to a maximum concentration of 86 mg.l^{-1} and remained constant during the rest of the experiment. The copper concentration was relatively constant throughout the experiment as shown in Figure 9.32. There were signs of copper electroplating on the cathodes of cell 1 and 3. The copper that was eluted off the cationic membranes formed a film on the counter electrode of the same cell. During the experiment, a maximum copper concentration of 20 mg.l^{-1} was obtained.

The concentrations of zinc and nickel leaving the third cell were very different to copper. The results in Figure 9.33-9.34 show a steady increase in outlet concentration. After 1000 minutes, the concentration of both metals were

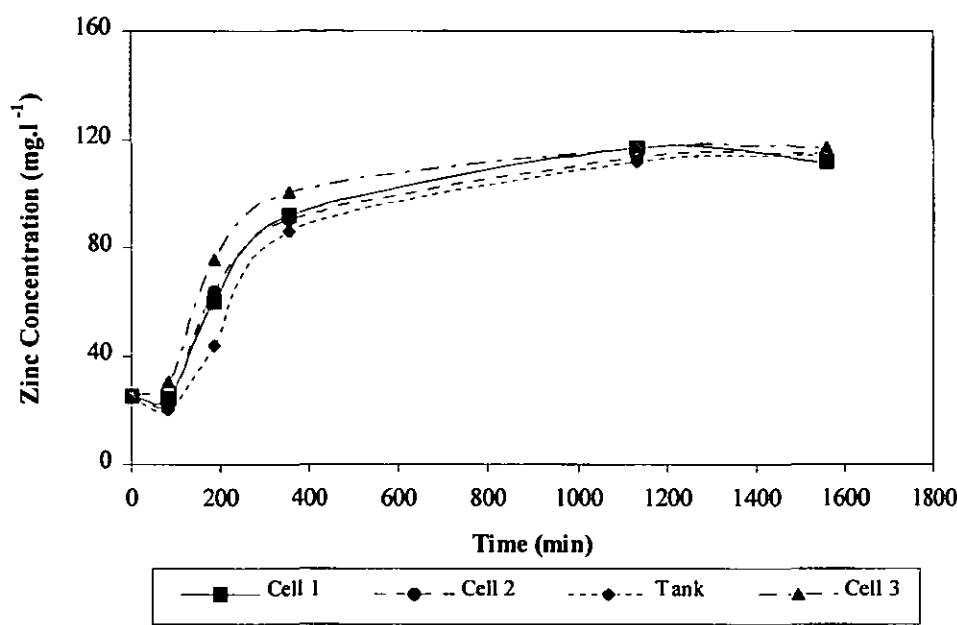


Figure 9.33: Zinc concentrations during elution cycle
Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²

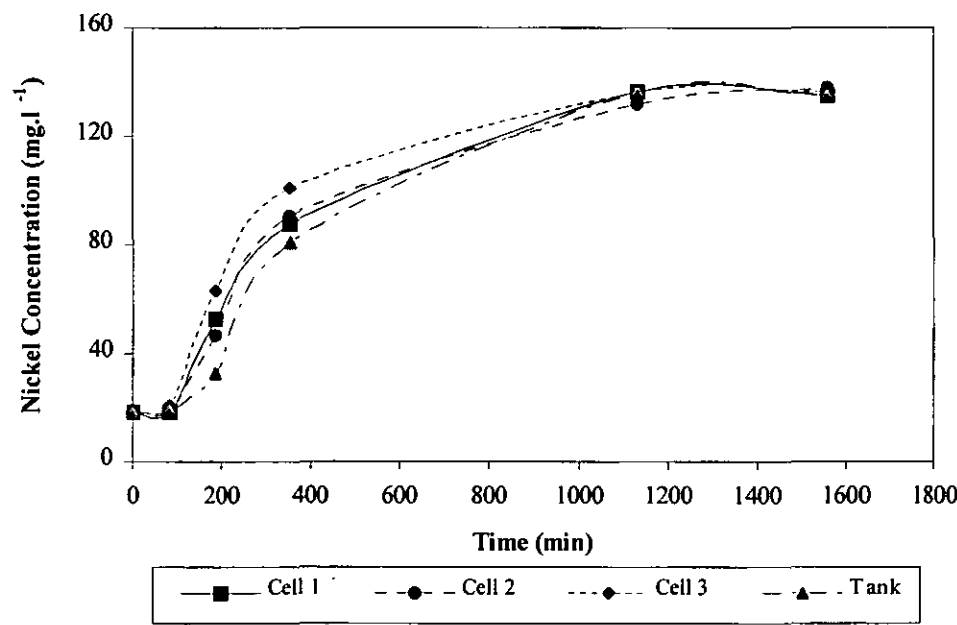


Figure 9.34: Nickel concentrations during elution cycle
Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²

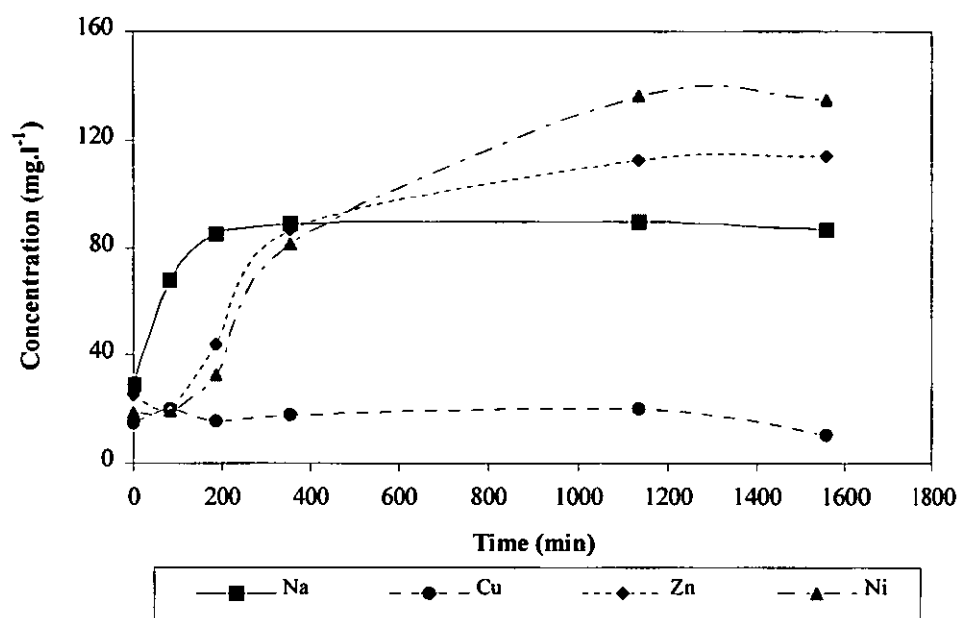


Figure 9.35: Concentrations of sodium, copper, nickel and zinc in the feed tank during elution cycle

Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²

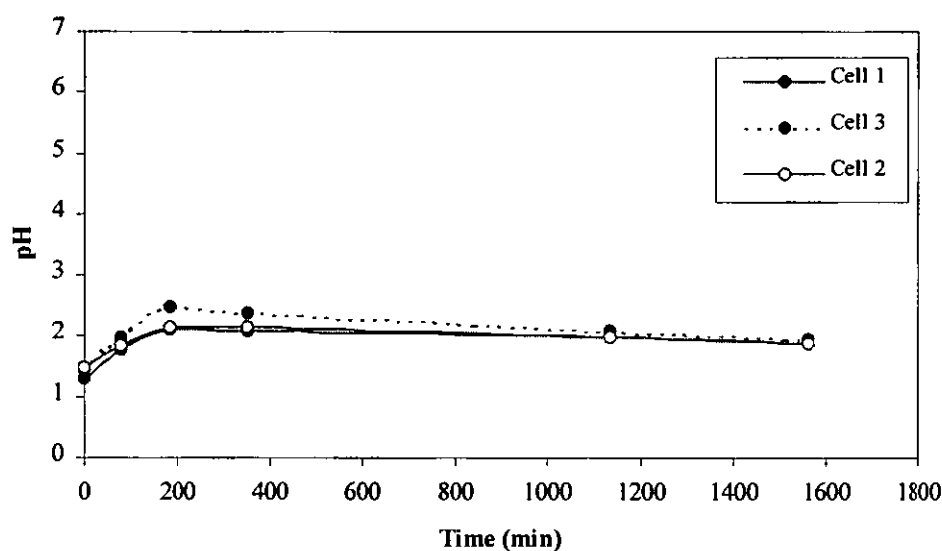


Figure 9.36: Outlet pH of solution leaving all cells during elution cycle

Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²

constant at 113 mg.l^{-1} of zinc and 135 mg.l^{-1} of nickel, which was 99 % of zinc and 98 % of nickel were removed during the absorption cycle. In comparison, only 6 % of copper and 37 % of sodium were recovered during the elution cycles. In total, 80 ml of 16M nitric acid solution was used to maintain the pH during the elution cycle.

The concentration of metal ions in the feed tank can be seen in Figure 9.35. The final concentration of the tank solution was 86 mg.l^{-1} of sodium, 111 mg.l^{-1} of zinc, 130 mg.l^{-1} of nickel and 10.5 mg.l^{-1} of copper. It can be seen that very little of the transition group metals were eluted before the highest sodium concentration was obtained. Similar results were discussed in Chapter 7.

The outlet pH values can be seen in Figure 9.36. These show that the pH was maintained around 2. Although, the presence of the anionic cell helped to maintain the pH, it was not enough and a substantial quantity of concentrated nitric acid was needed to ensure all the metals remained in solution.

Figures 9.37-38 show applied voltages and currents for all three cells during the same experiment. These illustrate that the applied potentials in the cationic cells were much lower during the elution cycle than in the absorption mode. This was because during absorption the voltage helped to maintain a significant concentration gradient from the bulk solution to the back of the cell. In elution, there is hardly any concentration gradient from the back to the centre of the cell, the applied voltage is purely to facilitate the transport of cations across the membrane. The current density for both cationic cells was 3 mA.cm^{-2} . In the anionic cell, the applied voltages and currents were kept relatively high to maximise the pH swing across the second cell to minimise the use of nitric acid.

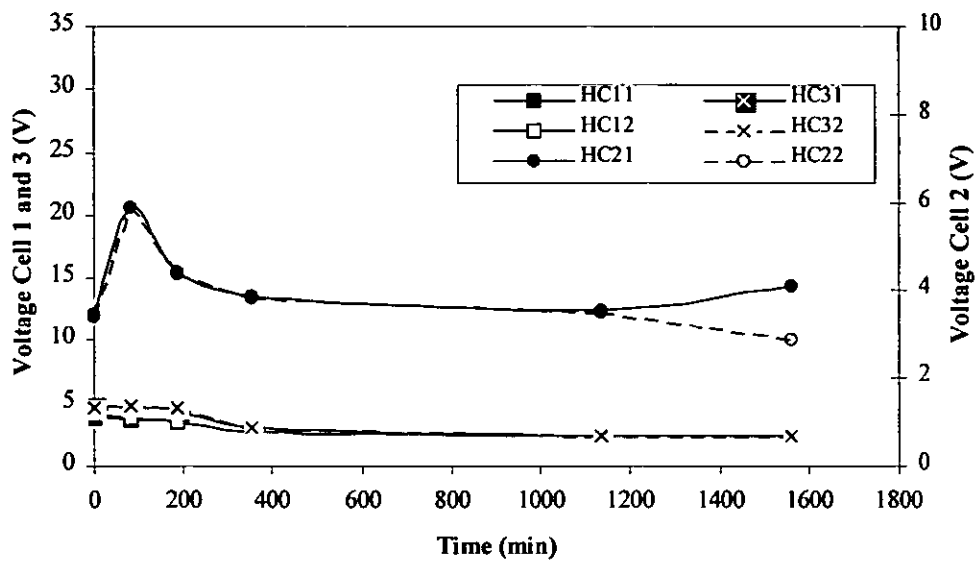


Figure 9.37: The applied voltages to all cells during the elution cycle
Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²
Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

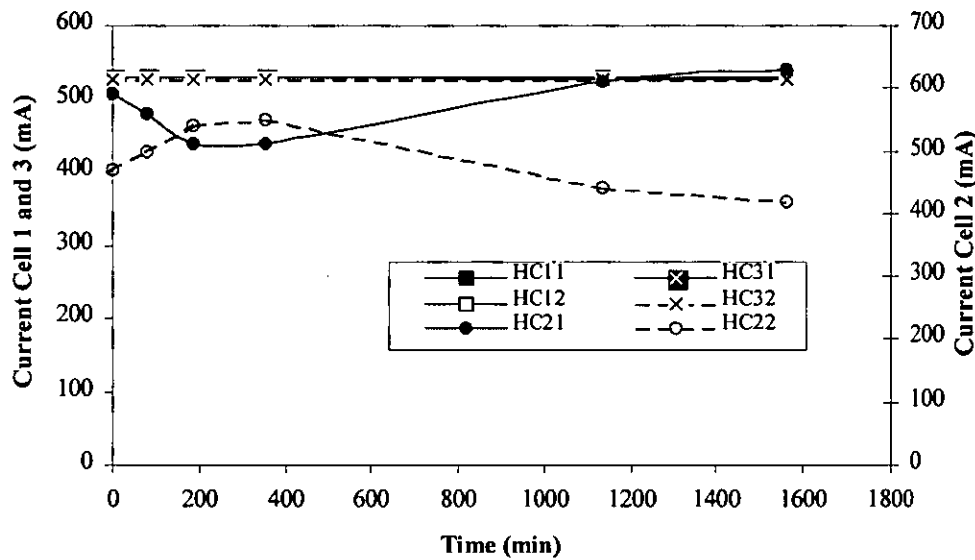


Figure 9.38: The applied voltages to all cells during the elution cycle
Starting pH = 2, Flow Rate = 11 l.h⁻¹, Current density = 3 - 5.7 mA.cm⁻²
Key: HC - Half Cell, 11 denotes cell 1 and half cell 1

A second elution experiment was conducted to recover the remaining copper. 10 l of acidic solution was used to carry out the experiment. The experiment was conducted for about fifty hours and the pH was maintained around 2.2. At the end of this period, only a further 10 % of the copper remaining on the resin was eluted. Most of the copper remained in the system in the electroplated on the bare metal mesh electrodes. It was decided before the next absorption cycle to run the pilot plant in absorption mode prior to any further experiment. The total weight of the copper further recovered was 186 mg which was only about 7.4 % of the copper removed by the system during absorption.

Similar results were obtained for other elution cycles. In the next two sections only the main details of some of these will be discussed.

9.5.2 Elution: sodium feed concentration of 130 mg.l^{-1}

Two elution batches were conducted following experiments carried out using a sodium feed concentration of 130 mg.l^{-1} . In each batch 10 l of distilled water was used. The starting solution was made acidic by addition of nitric acid. The feed pH at the beginning of the each experiment was 2. As previously stated, there was signs of electroplating onto the surface of exposed cathodes in either cationic cells, even in very acidic conditions reducing the recovery efficiency. The problem was solved by switching to absorption mode at the end of the elution run and passing the metal ions back into solution as part of the elution before starting the absorption cycle.

The total amount of metal recovered in the first batch was a fraction of the material removed by the resin during absorption. In the first batch 60 mg of copper, 137 mg of zinc, 74 mg of nickel and 2300 mg of sodium were recovered. The experiment was conducted for 31 hours. A total of 35 ml of 16M nitric acid solution was used to avoid the precipitation of metal ions during elution.

A second batch elution cycle was carried with fresh distilled water to avoid high concentrations of sodium present in the feed tank after the first batch. The total amount of metals recovered by both experiments were 75.4 mg of copper, 310 mg of zinc, 184 mg of nickel and 3500 mg of sodium. The percentage of each metal recovered was 14 % copper, 62 % zinc, 47 % nickel and 82 % of sodium. This meant that a large amount of metal remained on the resin and the resin was partially converted to the hydrogen form. These results indicate that zinc was more readily recovered than other ions and copper was the most difficult to elute. This is not surprising as the chemistry of copper suggests it can form complexes easier than zinc and nickel.

9.5.3 Elution: sodium feed concentration of 180 mg.l⁻¹

Another elution experiment was conducted after the experiment conducted using a feed containing 180 mg.l⁻¹ of sodium. After cells were loaded with sodium, copper, nickel and zinc, they were regenerated with 10 l of distilled water. The starting feed pH was 2. The feed was circulated around the system without any current being switched on for 15 hours. This resulted in an initial tank concentration of 16 mg.l⁻¹ of sodium, 1.3 mg.l⁻¹ of copper, 0.72 mg.l⁻¹ of zinc and 0.4 mg.l⁻¹ of nickel. This was partly because metals had precipitated during the absorption cycle and partly due to elution of these metals.

The elution was carried out close to 3200 minutes, at the end of the experiment, the total weight of metals recovered were 2270 mg of sodium, 190 mg of copper, 440 mg of zinc, 400 mg of nickel. However, the highest amounts sodium, zinc and nickel were 2340, 748 and 660 mg respectively at a time of 1900 minutes. This was 88 % of zinc and 78 % of nickel. The maximum recovery corresponded to the lowest pH of 2.38. There were signs after this highest concentration was reached that solids were forming around the system. There was adsorption of metal ions by membranes as sodium concentration also

decreased. The indication was that solution pH must be kept acidic, otherwise, the elution is hampered by electroplating and precipitation of target ions.

At the end of the experiment, the amount of sodium recovered was 86% of that removed during the absorption experiment. This further confirmed that the resin remained partially in the sodium form even after the elution step. This could be due to the equilibrium conditions within the membrane. Since, during elution the concentration of cations within the membrane is high. Even if conditions in the bulk are acidic ion exchange still will take place due to the high concentration of cations present within the membrane. This is also partly due to the chelating nature of the resin.

The amount of metals recovered during elution were 23 % of copper, about 50 % of zinc and nickel. At the end of elution, the concentration of zinc and nickel were twice that of the feed for the absorption experiment. The concentration of sodium and copper were less than the feed used for the absorption experiment. Total amount of acid used was 50 ml of 16M nitric acid solution.

9.6 Conclusions

The findings can be summarised by the following statements:

- Reasonable removal of transition group metals was achieved with respect to sodium concentrations in the feed
- Removal of target ions such as copper, zinc and nickel was reduced with increase in sodium feed concentration
- There was evidence of electroplating and precipitation on cathodes during absorption and elution cycles
- Substantial amounts of copper were electroplated onto the cathode of the anionic cell which could only be recovered by pole reversal

- Copper electroplated during elution cycles could be partially recovered by running an acidic solution through the system
- The control loop around the anionic cell was used successfully to control inlet solution pH into the third cell
- The anionic cell improved the performance of the cell in the early part of each experiment but was not needed once the cationic membranes were converted to the sodium form
- The cell voltage often reached the maximum of 32V when the cation membranes stopped absorbing any more sodium
- Transition metals were not easily recovered in the elution cycles
- Elution cycles were often slow and complicated so that more of the target ions could be recovered

CHAPTER 10

CONCLUSIONS & FUTURE WORK

10. CONCLUSIONS

Design of the EIX cell was examined by studying the effect of the main parameters on the performance of the cell. The work included the determination of concentration and pH profiles, current distribution, hydrodynamics of the cell, absorption and elution characteristics, the development of a mathematical model and pilot plant studies. The work was carried out as part of a European project which considered different aspects of Electrochemical Ion Exchange.

The work discussed was aimed at covering all aspects of the design of an Electrochemical Ion Exchange (EIX) cell which had been developed by AEA, Harwell laboratories. The materials of construction and the basic design of the cell were examined extensively before obtaining the cell design described in Chapter 4. Tests were carried out to evaluate and enhance the performance of the EIX flow cell design. Apart from experiments, a mathematical model was developed to understand and examine the cell in relation to a theoretical basis. Overall, studies of the cell design resulted in a cell with modifications which was tested on a pilot plant scale.

Only some data from the considerable amount generated were included in this treatise on the basis of their importance. Results were selected and highlighted to demonstrate the significance of a series of experiments or findings.

Initially experiments were conducted to examine the performance of the EIX flow cell under different conditions. Zirconium phosphate membranes used in these experiments showed loss of ion exchange capacity. This was due to

hydrolysis of zirconium phosphate resin at high pH condition prevailing within the membrane. This could only be partially restored using phosphoric acid.

The results indicated that an important factor in the performance of EIX process was the hydrogen ion concentration. Most of the electric current is carried by this highly mobile ion when present in excess. Hence, electric current efficiency reduced with decreasing pH. The concentration of other interfering ions such as sodium also affected the relative removal of target ions such as zinc.

Under alkaline conditions, removal of sodium was improved by using one central counter electrode but higher voltages were required to pass the current. The outlet concentration of cations and current efficiency increased with decreasing current density and increasing flow rate. This was mainly due to lower hydrogen ion concentration under these conditions. The cell characteristics were altered by changing the gap between the two halves of the cell which resulted in a small improved removal at low flow rates.

Some aspects of selectivity were examined and it was found that the form of membrane, i.e. hydrogen or sodium, affected the removal of target ions with Purolite S930 showing the best overall results for removal of zinc.

Basic concentration and pH profiles of the flow cell were determined by taking samples from all areas of the cell. The current distribution was obtained by directly measuring the current flowing through the membrane along the whole length of the membranes.

The concentration of cations in the bulk solution decreased steadily from the inlet to the outlet. This corresponded to an equivalent reduction in pH when

using the hydrogen form of the membranes. At the back of the cell, very high concentrations of cations were measured, which was a function of the length of time experiments were conducted, feed conditions and current density. This resulted in leakage of material contaminating the bulk solution. This leakage was significantly reduced by modifications made to the cell.

The current profile results indicated that minimum current was flowing through the centre section of the membranes. The currents increased moving away from the centre towards inlet and outlet. The meniscus shape of the current distribution was thought to be partly due to high pH in the centre sections of the membrane. High removals of cations were obtained by ion exchange leaving fewer ions to carry the current. This was particularly so as conditions inside the membrane was highly alkaline any hydrogen exchanged would have been neutralised. Also, the sodium ion concentration would have been extremely high in the centre section and to maintain the concentration a higher potential was required. The applied voltage to each section was constant, therefore, the current decreased.

Current density and flow rates were found to be two factors which influenced mixing within the cell. Higher flow rate and current density improved mixing by respectively increasing the superficial velocity and the amount of bubbles generated at the counter electrodes.

Modifications to cell design were carried out after studying the effect of change in process parameters on the performance of the EIX process. The main objectives were to remove metal ions more efficiently and reduce the precipitation of transition group metals in the cell.

Precipitation occurred in some absorption cycles when using transition group metals but was also encountered if the solution pH was high during elution. An advantage of EIX process is the ease by which elution can take place i.e. pole reversal. This works well when eluting such cations as sodium but is not as effective during desorption of transition group metals.

During elution studies, it was found that there was a linear relationship between the amount of material eluted with time. However, rate of elution was proportional to the current density and changing the flow rates had negligible effect on the recovery of sodium. Results indicated that the power requirements were significantly lower during elution cycles compared to absorption cycles. Experiments conducted with a combination of metals loaded onto the membranes indicated that sodium was eluted first before any transition metals.

A mathematical model was developed based on the Nernst-Planck equation. Although a simplified model, it predicted the performance of the EIX process over a wide range of conditions. There was scatter in some results which was partly due to analysis and partly due to the varying conditions of the membranes. The model represented the process well and it showed the same trends in the outlet concentration of ions as experimental results with change in process conditions such as flow rate and current density. At high current densities, the model and the experimental results did not match very well because under these conditions a significant amount of sodium was transferred across the membrane from the bulk solution to the back of the cell. This caused a build up of concentration at the back of the cell which caused significant leakage of the material back into the bulk solution.

In some other cases, outlet concentration obtained in experiments was close or less than the results generated by the model. This was because there was precipitation of transition group metals which enhanced the performance of the cell.

A pilot plant scheme was developed and set up to evaluate the performance of the EIX process at a larger scale. A selective removal of transition group metals was obtained in presence of relatively higher concentrations of sodium ions. The higher the concentration of sodium the lower the overall removal of transition group metal ions. Modifications reduced precipitation to a minimum but it continued to occur, particularly in the anionic cell. Precipitation and electroplating were difficulties that were not completely resolved due to lack of time. These could be managed by changing the working schedule of the plant to include short absorption and rinse cycles between runs. The anionic cell was used to control the pH into the third cell. It became partially redundant once the first cell had been converted to sodium form. A control loop was implemented around the anionic cell, it was successfully tuned and used in several runs.

A large amount of data was generated during the series of studies discussed. It was found that EIX process is best suited to effluent streams that have low ionic concentrations. The results suggested that it could be used to selectively remove metal ions such as copper, nickel and zinc in presence of relatively high concentration of sodium ions but the elution process is rather slow and complicated.

The ion exchange resins used in the process did not have very high capacities. A resin with a higher uptake capacity may alleviate some of the problems encountered during the process namely the high concentration at the back of the

cell. This can also be solved by removal of the solution from back of the cell to reduce the contamination of the bulk solution but this would mean the cell is more like a electrodialysis cell than an electrochemical ion exchange cell. However, there are several aspects of the process that can be studied further.

10.1 Further Work

The relationship between interfering ions and target ions can be investigated by using other interfering ions beside sodium. The influence of the selectivity of the ion exchange resin can also be studied in more detailed. However, if the process is to be used for recovery of metal ions such as copper then it would seem better to try to find an alternative to chelating resin such as S930 and S950 which has lower resistance and higher capacity. Resins with a higher capacities can be also tested to see if the problems encountered during the pilot plant run can be solved by reducing the build up of material at the back of the cell. It might be possible to include conducting polymers in the backbone of the membranes to decrease their electrical resistance.

The effect of high concentrations developed at back of the EIX membranes which probably caused the high voltage required during the tests needs to be further examined

The plant could be run for much longer, as the membranes loading were quite low even after six days of absorption. The absorption and elution cycles were not optimised. The working schedule of a working plant would require rinse and short cycles to recover the electroplated metals. Also, the elution cycle could be adjusted to recover a solution with the maximum concentration of metal. The performance of the anionic cell should be experimentally tested to examine its effectiveness fully.

The mathematical model might be further developed to include other aspects of the process such as ion exchange kinetics of the membrane and the leakage of material from the back of the cell.

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