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THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

APPENDIX 9

An Evaluation of the Technical Feasibility of Removing Ammonium Nitrate from Aqueous Effluents with Electrolysis

Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

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AN EVALUATION OF THE TECHNICAL FEASIBILITY OF REMOVING AMMONIUM NITRATE FROM AQUEOUS EFFLUENTS WITH ELECTROLYSIS

W.J.Voortman
Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

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SUMMARY

The AECI Chemicals and Explosives plant at Modderfontein produces large quantities of nitrogenous effluents as a consequence of the production of nitric acid, ammonia, ammonium nitrate and explosives. The concentrations of ammonium and nitrate ions in the effluent discharged to the Jukskei river exceed the limits allowed by the Water Act of the Republic of South Africa, 1956 as amended. The Modderfontein plant has an exemption permit issued by the Department of Water Affairs in terms of which all effluent handling is undertaken. The exemption permit expires at the end of 1990.

AECI is committed to reducing its nitrogenous effluent production and has supported research into nitrogenous effluent treatment as a result (see Sections 1.3 and 2.3). Many of the processes investigated to date have proved to be impractical or uneconomic (see Section 2). Negotiations between AECI and the Pollution Research Group at the University of Natal resulted in an agreement, in terms of which the technical feasibility of an electrolytic process for the removal of ammonium nitrate from aqueous effluents would be investigated (see Section 1.4).

The process removes ammonium nitrate from aqueous solution by using an electric current to reduce the ammonium ions to ammonia gas while simultaneously transporting the nitrate ions through an anion exchange membrane to a compartment in which calcium nitrate is formed. In this manner, the effluent stream is depleted of ammonium nitrate and a concentrate of calcium nitrate is produced. Calcium nitrate is used in the dusting of deciduous fruits and the concentrate may be suitable for this purpose. The process is described in detail in Section 3.

The development of the process took place at the University of Natal and the subsequent investigation was undertaken at Modderfontein. The parameters that were investigated included :- limiting current density, current efficiency, temperature, flowrate, power consumption, membrane life, electrode life and electrolyte concentrations. Section 4 discusses the interactions between these parameters and their effects on the process operation.

A small batch operation pilot plant was built at the University of Natal and consists of two electrolyte tanks which feed a pilot scale electrolysis cell. The electrolytes were circulated by centrifugal pumps and the cell was powered by a regulated power supply. Batch operation was chosen mainly for its ease of operation. A flowchart and equipment listing for the pilot plant is given in Section 5.

Two types of experiment were performed and are described in Section 6. Type 1 experiments were designed to gather data on the effects of temperature and concentration on the limiting current density, the current efficiency and the power consumption of the process, as well as to assess membrane and electrode life. Type 2 experiments were designed to allow the assessment of the optimum flowrate of electrolytes in the cell and the effect of flowrate on limiting current density.

The table below summarises the more important results of the experiments conducted thus far. The results are presented and discussed in greater detail in Section 7.

Parameter	Minimum	Maximum	Average
Current efficiency (%)	90 (Exp. 3)	100 (Exp. 2)	98
Ammonium nitrate concentrations at start (mg/ℓ)	3 300	10 040	-
Ammonium nitrate removal (%)	30,1 (Exp. 6, not completed)	98,8 (Exp. 6)	96 (approx.)
Operating voltage (V)	3,8	8	6
Operating current (A)	0,5	16	10
Specific power consumption (kWh/kg)	1,63 (Exp. 4)	3,48 (Exp. 8)	Depends on current density
Operating temperature (° C)	20	45	28
Electrolyte flowrates (ℓ/min)	2,5 (minimum operating flowrate)	5,0	3,85
Membrane life (hours)	-	-	55

As can be seen from the table, current efficiencies exceeding 98 % could be achieved for the removal of over 96 % of the ammonium nitrate in a pure solution (see Section 9.1). The operating voltage of the cell varied according to the electrolyte concentrations, temperature and current density but would be between 4 and 10 volts during normal operation. The specific power consumption (kilowatt-hours per kilogram of ammonium nitrate removed) varied according to the current density during processing but normally lay between 1,5 and 3,5 kWh/kg. These figures include only the power consumed by the electrolysis process and not pumping or other power needs (see Section 9.2).

The effects of temperature, flowrate, pH and concentration on limiting current density could not be accurately determined from the experimental data because of equipment limitations on the maximum current flow. Future experimentation should be conducted with nitrate concentrations below 500 mg/ℓ for the determination of these effects (see Section 7.2). The water transport number could not be accurately determined because electrolyte losses due to leaks and evaporation could not be quantified. The optimum electrolyte flowrate was approximately 3.85 ℓ/min (see Section 7.5).

The membrane life was about 55 hours. This was due the membranes being ruptured by the precipitation of calcium carbonate within the membranes. The carbonate ions are thought to result from the absorption of carbon dioxide in the air by the high pH catholyte solution. Some carbonate ion could be present as an impurity in the lime added to the catholyte (see Section 7.6.3). Cathode life with a stainless steel cathode is unknown but in 500 hours of operation, no deterioration has occurred. Similarly, the life of the DSA anode is not certain but stainless steel is not suitable for use as an anode (see Section 7.6.1).

Future work should address the quantification of factors affecting limiting current density, the reduction of damage to the membranes, the quantification of the effects of operation at elevated temperatures and the stripping of ammonia gas from the depleted effluent solution among others (see Section 8 and 9.6).

It was concluded that this process was not technically feasible for the removal of ammonium nitrate from aqueous solution unless the build-up and damage of membranes by calcium carbonate could be prevented. All other aspects of the treatment process are technically feasible.

This project was terminated when it was discovered that a new plant for the manufacture of calcium nitrate had been commissioned. In addition to this, AECI is more interested in the recovery of ammonium nitrate, even at relatively low purity, for sale to the fertiliser industry. Although ammonium nitrate can be recovered and concentrated by the electrolysis process described here, the use of evaporation, electrodialysis or reverse osmosis would be more practical. There are several effluent streams at Modderfontein that have sufficient ammonium nitrate concentration to make evaporation feasible. Concentration of these streams by evaporation and subsequent sale to the fertiliser industry will serve to reduce the nitrogenous effluent load and increase the amount of pure ammonium nitrate available for explosives manufacture.

1 INTRODUCTION

1.1 Nitrogenous effluents

The AECI Chemicals and Explosives factory at Modderfontein produces large quantities of nitrogenous effluents as a consequence of the production of nitric acid, ammonia, ammonium nitrate and explosives. The major pollutants in the various strong and weak effluent streams are ammonia, nitrate, sulphate, chloride, calcium and sodium. Table 1 gives typical levels of these ions in selected effluent streams at Modderfontein[1]. Stream S13 is the strong effluent that is dispersed by spray disposal while W5 is the weak effluent discharged from the central factory areas. W5 comprises two streams, W5A and W5B which come from the central factory areas. W6 is the effluent discharged to the Jukskei river.

The volumetric flowrates of these streams vary considerably with the season. Stream W5 includes the storm water drainage system for the central factory areas and its flowrate can exceed 500 m^3/h. The flowrate of S13 is generally more than an order of magnitude smaller than the flowrate of W5.

TABLE 1 : A typical assay of three major effluent streams at Modderfontein

Constituent	S13 mg/ℓ	W5A mg/ℓ	W6 mg/ℓ
Ammonia (as N)	810	170	83
Nitrate (as N)	1 400	170	64
Sulphate	1 940	250	330
Chloride	190	90	120
Sodium	500	165	206
Calcium	1 441	101	108

1.2 Exemption permit

The Modderfontein plant has an exemption permit issued by the Department of Water Affairs in terms of which all handling, treatment and disposal of waste water is undertaken. One of the conditions of the permit (and an objective of the "Towards 2000" quality drive within AECI) is that the factory should attempt to meet the conditions of the General Standards for effluent discharge by 1990[2]. Table 2 shows relevant effluent standards as applicable to direct discharges into fresh water sources[3]. In addition to these limits, total dissolved solids (TDS) level increases are prescribed for some regions.

AECI's present exemption permit expires at the end of 1990 and it is felt by AECI that renegotiation of the permit will be closely linked to the short term success of efforts to reduce effluent quantities arising at the factory.

TABLE 2 : General and Special Discharge limits for the Republic of South Africa

Property	Maximum allowable General	Special
Colour, odour or taste	Nil	Nil
pH	5.5-9.5	5.5-7.5
Dissolved Oxygen (% saturation)	75	75
Typical (Faecal) coli (mg/l)	Nil	Nil
Temperature (° C)	35	25
Chemical Oxygen Demand (after chloride correction) (mg/l)	75	30
Oxygen absorbed (from N/80 potassium permanganate in 4 hours at 26° C) (mg/l)	10	5
Conductivity: (mS/m at 25° C)		
1. Above that of intake water	75	15 %
2. In respect of mining effluent	250	250
Suspended solids (mg/l)	25	10
Sodium content (above intake water) (mg/l)	90	50
Soap, oil or grease (mg/l)	2.5	Nil
Other Constituents (maximum in mg/l):		
1. Residual chlorine (as Cl)	0,1	Nil
2. Free and saline Ammonia (as N)	10,0	1,0
3. Nitrate (as N)	-	1,5
4. Arsenic (as As)	0,5	0,1
5. Boron (as B)	1,0	0,5
6. Hexavalent chromium (as Cr)	0,05	-
7. Total chromium (as Cr)	0,5	0,05
8. Copper (as Cu)	1,0	0,02
9. Phenolic compounds (as Phenol)	0,1	0,01
10. Lead (as Pb)	0,1	0,1
11. Soluble ortho-phosphate (as P)	-	1,0
12. Cyanides (as CN)	0,5	0,5
13. Iron (as Fe)	-	0,3
14. Sulphides (as S)	1,0	0,05
15. Fluorides (as F)	1,0	1,0
16. Zinc (as Zn)	5,0	0,3
17. Manganese (as Mn)	0,4	0.1
18. Cadmium (as Cd)	0,05	0.05
19. Mercury (as Hg)	0,02	0.02
20. Selenium (as Se)	0,05	0.05
21. Sum of concentrations of cadmium (as Cd), Chromium (as Cr), Copper (as Cu),Mercury (as Hg) and Lead (as Pb).	1,0	-
22 The waste water or effluent shall contain no other constituents in concentrations that are poisonous or injurious to:		
- humans, animals, fish other than trout, or other forms of aquatic life, or that are deleterious to agricultural use	Applicable	-
- trout or other fish, or other forms of aquatic life	-	Applicable

1.3 Previous research

Previous research of effluent treatment processes has included bacterial denitrification, algal denitrification, solar evaporation, reverse osmosis, pasture irrigation, electrodialysis and evaporation. See Section 2.3.

1.4 Electrolysis of ammonium nitrate

A new electrolytic process has recently been developed at the University of Natal[4]. The process uses an electromembrane and lime to demineralise aqueous effluents containing ammonium nitrate. The process produces a calcium nitrate concentrate stream, oxygen, a mixture of ammonia and hydrogen gases and a demineralised water stream.

Calcium nitrate is used for dusting deciduous fruits. This application provides a potential market for the concentrate while the gaseous streams may be recycled to the main factory complex. The demineralised effluent may be recycled for use as low quality process water.

1.5 Research agreement

Consultation between the Pollution Research Group at the University of Natal, the Water Research Commission and the Environmental Services Department at Modderfontein resulted in an agreement, in terms of which the technical feasibility of nitrogenous effluent treatment by electrolysis was investigated.

The initial development was undertaken during early 1988 in the Department of Chemical Engineering at the University of Natal. After the commissioning of a small test rig further work was done both at the University and later, at Modderfontein.

The scope of the experimental work was to investigate the parameters which affect process performance, efficiency and equipment life.

2 PRINCIPLES OF TREATMENT OF GENERAL EFFLUENTS AND AMMONIUM NITRATE EFFLUENTS

2.1 Minimising effluent production

Before consideration is given to the processing of effluents, a factory or manufacturing complex should ensure that a maximum effort is made to reduce or eliminate effluent arisings wherever possible.

Methods for reducing effluent production[5] include:-

2.1.1 Recycling

Effluents should be isolated from each other. An effluent can often be recycled if it is captured before it is contaminated by other streams.

Cascading is another form of recycling in which the same water is used to perform several successive tasks. This reduces overall water consumption and the overall effluent volume. For example, condensate can be used as wash water or as cooling tower make-up water.

2.1.2 Conservation

Wash water should be used sparingly and recycled as much as possible in order to produce smaller volumes of more concentrated effluents which may be more economically processed.

2.1.3 Control

Most important of all is that the sources of pollutants should be identified and efficiently controlled. Production teams should be given incentives for minimising effluent production from their particular sections.

2.2 Effluent treatment and disposal

Once effluent production has been minimised, consideration can be given to the treatment and disposal of effluents by using one of the following options:-

2.2.1 Conversion of the effluent into saleable or reusable products

Conversion of the effluent into saleable or reusable products is often financially viable because the income generated by sales or by savings due to recycling can offset the cost of processing the effluent.

2.2.2 Deactivation or conversion to inert substances

Conversion to inert substances is an expedient route in the P.W.V.S. region for sulphate containing effluents. Sulphuric acid is relatively cheap so its recovery is often uneconomical. Effluents are limed to correct the pH and the calcium precipitate is separated and dumped.

This category of treatment includes biological processing in which the nutrients are the undesirable constituents of the effluent. The nutrients are broken down and released as metabolic products such as carbon dioxide, oxygen, nitrogen and a sludge (excess biomass) which is usually dumped or burned.

2.2.3 Chemical treatment

Chemical treatment of effluents can be used to remove toxic or harmful constituents from effluents. Often, however, such treatment results in an increase in the total dissolved solids (TDS) content of the effluent stream.

2.2.4 Indirect or diffuse discharge to the environment

Indirect discharge to the environment is a term which encompasses methods which release pollutants to the environment in such a way that they can be absorbed without causing damage to the environment. AECI uses this method at Modderfontein where nitrogenous effluents are sprayed as liquid fertiliser over pasture land.

2.2.5 Direct discharge to the environment

Direct discharge to the environment is legal only when the concentrations of, or quantities of, pollutants in the effluent do not exceed the limits prescribed by the Water Act of the Republic of South Africa. In extreme cases, the Department of Water Affairs may issue an exemption permit in which terms for the treatment and disposal of effluents will be clearly defined.

2.3 Options applicable to nitrogenous effluents

Some of the options discussed in the preceeding section are applicable to the treatment of aqueous effluents containing ammonium nitrate. Some of these options have been or are being investigated by AECI and most have been found to be unsuitable. A brief summary follows.

2.3.1 Concentration processes

If ammonium nitrate can be recovered from the effluent in a relatively pure and concentrated form it can be recycled back to the plant or sold for fertiliser manufacture. The following processes have been considered:-

Electrodialysis (ED) and electrodialysis reversal (EDR)6. Concentrations of up to 250 g/ℓ (as ammonium nitrate) have been achieved with batch mode operation[7]. Higher concentrations may be possible with further development.

Reverse Osmosis (RO)8. Typically, single stage water recovery varies from 75 to 90 % with feed concentrations of about 100 mg/ℓ (as N). Expensive multi-stage series-taper systems would be required to increase the water recovery and the concentration of the reject stream.

Ion Exchange (IX). Ion exchange can be used to sequentially remove both ammonia and nitrate from an effluent stream but will merely replace them with other dissolved species. If acids and bases are used for regeneration, effluent will be demineralised but the waste regeneration liquor will contain both the ammonium nitrate removed from the effluent and the co-ions of the acid/base pair used for regeneration.

Thus, the concentrate formed by IX treatment will be a 1 : 1 mixture of ammonium nitrate and the co-ions (on a molar basis). This concentrate will be neither saleable nor reusable as a source of ammonium nitrate without further processing unless nitric acid and ammonium hydroxide are used as the acid/base pair.

Evaporation. AECI is familiar with the technology of evaporation for ammonium nitrate concentration because evaporation is widely used as a concentration process at Modderfontein. However, evaporation is energy intensive and is therefore not economical for ammonium nitrate concentrations below about 70 g/ℓ (as N)[9].

While some of the effluent streams at Modderfontein are suitable for evaporation and excess steam is available, most of the effluent load is found in streams which are too dilute for economical evaporation.

In all of the aforementioned concentration processes, a filtration step will be required to remove particulates which could foul membranes or heat-exchange surfaces. In addition, the potential hazards associated with concentrating ammonium nitrate with unknown organic or inorganic contaminants must be evaluated.

2.3.2 Diffuse or indirect discharge to the environment

At present, some of the strong effluents at Modderfontein are disposed by spraying them over pasture land. The factory is situated in an estate of 60 square kilometres. Most of the estate is periodically irrigated with effluent.

The quantity of effluent exceeds the nitrogen requirement of the pasture land and excessive irrigation over a number of years has led to an accumulation of ammonium nitrate in the soil[10].

The need for rehabilitating the affected pastures has reduced the area of land available for effluent discharge. In addition the extensive piping network which is used to distribute the effluent for spraying is old and severely corroded in places.

The present method of spray disposal at Modderfontein is therefore inadequate because it is expensive to operate and because the land presently under irrigation has insufficient capacity for assimilating the amount of nitrogenous waste produced at the factory.

2.3.3 Biological processes

Both bacterial and algal processes have been developed for the removal of ammonium nitrate from aqueous effluents.

The bacterial denitrification system[11] is similar to that used for the treatment of domestic sewage. The ammonium ions are oxidised to nitrate aerobically and this is followed by anaerobic denitrification of the effluent. Since the effluent contains little or no carbonaceous material, some form of carbon energy source is required. The treatment requires long residence times and this means that large bioreactors are needed.

The algal denitrification system[12] is capable of assimilation of ammonium nitrate. However, algae preferentially assimilate the ammonium ion over other forms of inorganic nitrogen. Levels of ammonium ion which are high enough to cause concern for water potability are also high enough to inhibit the uptake and reduction of nitrates by algae. Long residence times and the requirement for maximum exposure to sunlight mean that large surface areas of long residence times are required.

Experimentation in the use of water hyacinth for nitrogen removal has been conducted in the U.S.A.[13]. In addition to the removal of nitrogen from the waste water by harvesting of hyacinth, bacterial films on the plant's root structure allow aerobic denitrification to occur.

3 DESCRIPTION OF THE ELECTROLYSIS PROCESS

The Pollution Research Group at the University of Natal has developed an electrochemical process which will enable the recovery of chemicals and water from ammonium nitrate effluents[14].

The process also produces oxygen, an ammonia-hydrogen gas mixture, and a calcium nitrate concentrate, which can be evaporated and prilled to produce solid calcium nitrate. The ammonia-hydrogen gas mixture can be recycled to an ammonium chemicals plant.

The electrolysis cell is represented in Figure 1.

The cell operates as follows:-

The ammonium nitrate containing effluent is passed through the catholyte compartment and an alkali solution of a sparingly soluble hydroxide (for example, lime) is passed through the anolyte compartment.

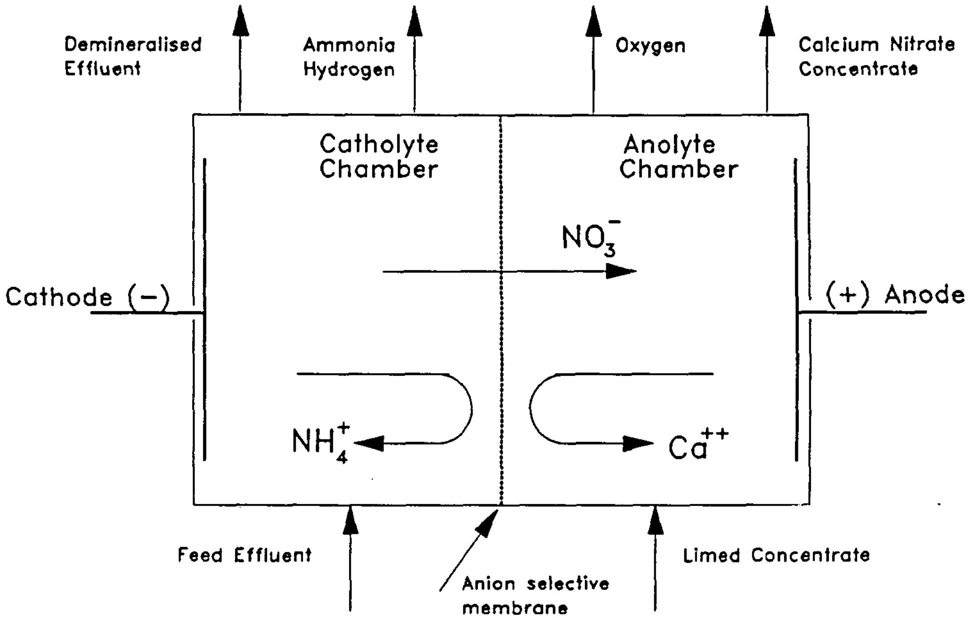

FIGURE 1 : Electrolysis Cell

When a current is passed through the cell, two electrode reactions occur. The reactions that occur depend upon the pH of the electrolyte.[20]

IN BASE:

At the cathode:-

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \qquad E^\circ = -0{,}828V$$

At the anode:-

$$4OH^- \rightarrow O_2(g) + 2H_2O + 4e^- \qquad E^\circ = 0{,}401V$$

IN ACID:

At the cathode:-

$$2H^+ + 2e^- \rightarrow H_2(g) \qquad E^\circ = 0{,}000V$$

At the anode:-

$$2H_2O \rightarrow 4H^+ + O_2(g) + 4e^- \qquad E^\circ = 1,229V$$

The gaseous products of these reactions are evolved from the electrolyte compartments. Note that even though the electrode reactions in acid (pH = 0) and in base (pH = 14) are different, the same gaseous products are produced at the same electrodes. The ionic products of the electrode reactions each undergo a chemical reaction in their respective compartments.

In the catholyte, ammonia gas is formed:-

$$OH^- + NH_4^+ \Leftrightarrow NH_4OH \Leftrightarrow NH_3(g) + H_2O$$

The equilibrium position of these reactions is determined by pH and temperature. Figure 2 shows the equilibria which exist in an ammonia/ammonium system at various pH values. At low pH values the predominant species is the ammonium ion. As the pH of the solution is increased ammonium hydroxide is formed and dissociates with the evolution of ammonia gas. In the catholyte, the pH and the temperature must be controlled such that the equilibrium lies toward the evolution of ammonia gas. In this way the effluent is depleted of ammonia species.

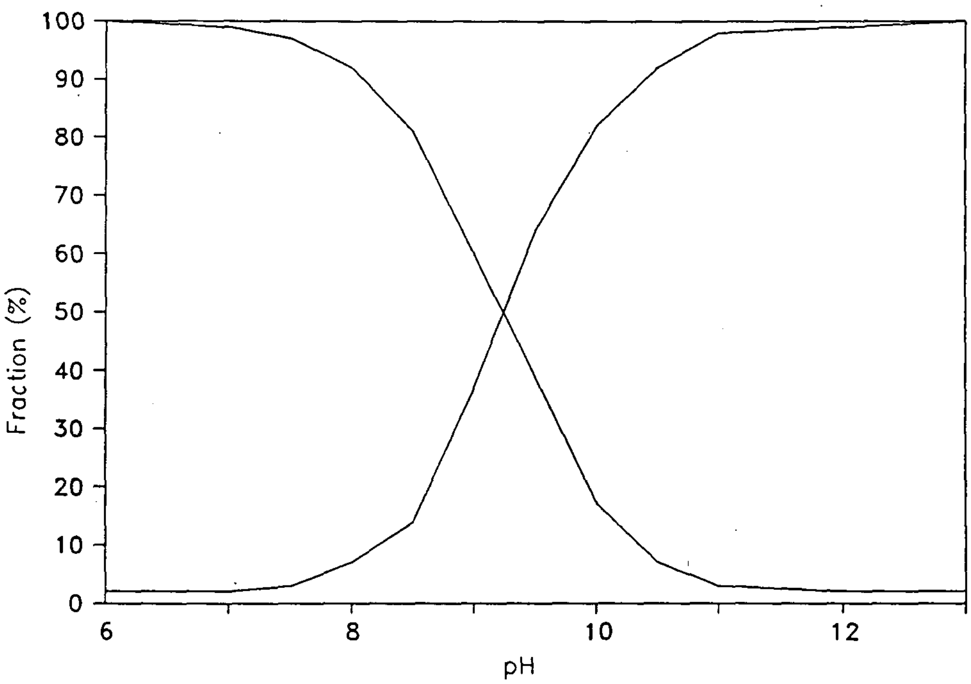

FIGURE 2 : **Fraction of Ammonia and Ammonium Ions as a Function of pH**

In acidic anolytes, nitric acid is formed from the hydrogen ions (produced by the electrode reaction) and the nitrate ions which have migrated across the membrane, In basic anolytes, hydroxide ions derived from the dissolution of calcium hydroxide are consumed at the anode directly and calcium nitrate is produced, in dissolved form, in the electrolyte.

The electrical current passing between the electrodes is carried through the anion selective membrane by nitrate anions which originate from the feed effluent. These anions move from the catholyte, thus depleting it of nitrate ions, into the anolyte where they accumulate and associate with the cations in the anolyte.

In practice, the calcium nitrate stream produced in the anolyte chamber is recirculated with the addition of make-up lime. A concentrated calcium nitrate stream is formed and may be further concentrated by evaporation and subsequent spray drying or prilling to produce granules.

4 PROCESS OPERATION AND ASSOCIATED PRINCIPLES

4.1 Modelling of the potential difference across the cell

The purpose of being able to model the potential drops which cannot be directly measured is to identify the processes which consume the most power in the cell. Electrical power consumption will be a major operating cost for this electrolysis process and the optimisation of power consumption is therefore important

4.1.1 Electrode potentials

Electrochemical equilibrium is dynamic in nature at a reversible electrode.[17] This means that the reaction proceeds in both directions simultaneously and the forward and reverse reactions proceed at equal rates. The formation and neutralisation of ions occurs at the interface between the electrode and the electrolyte. An electrochemical double layer is formed and a potential difference is set up between the electrode and the electrolyte. The value of this potential difference is the electrode potential.

Electrode potentials for electrochemical reactions are thermodynamic quantities related to the difference in free energy between the reactants and the products at equilibrium. Consider the reaction:-

$$A + ne^- \leftrightarrow B \qquad 4.1$$

The Gibbs Free Energy for the reaction is defined:-

$$\Delta G = \Delta G^\circ + RT\,ln(a_B/a_A) \qquad 4.2$$

and the equilibrium potential for the reaction is given by:-

$$E = \frac{-\Delta G}{nF} \qquad 4.3$$

This equation also implies that under standard conditions:-

$$E^\circ = \frac{-\Delta G^\circ}{nF} \qquad 4.4$$

Substitution from equations 3 and 4 into equation 2 yields the Nernst equation:-

$$E = E^\circ - \frac{RT}{nF}\ln Q \qquad 4.5$$

which describes deviations from standard conditions.

The Standard Electrode Potentials quoted in Section 3 refer to the electrode potential at 25 °C and all participating species having unit activity. The electrode potential at any other conditions will differ according to the Nernst equation. When the Nernst equation is applied to the anodic and cathodic reactions respectively we get:-

$$E_a = 0.401 - \frac{2,303 \times RT}{F}(pH - 14) \qquad 4.6$$

for the anodic electrode potential and:-

$$E_c = -0,828 - \frac{2,303 \times RT}{F}(pH - 14) \qquad 4.7$$

for the cathodic reaction.

NOTE: Equations 2 and 3 assume unit activity for the gaseous reaction products which means that the gas pressures are assumed to be 1 atm.

If both electrodes were in contact with the same electrolyte the total electrode potential would be 1.229 V (at 25 °C) and it would be independent of pH. In the case of an electrolysis cell having its electrolytes separated by a membrane, the pH of the electrolytes can differ from one another and the total electrode potential for the cell will be given by the sum of equations 2 and 3.

4.1.2 Electrode overpotentials

When an electric current is passed through an electrode that was at equilibrium, the potential will change to a new value dependent upon the density of the imposed current.[17,19] The difference between the equilibrium value and the new value is termed the overpotential (g).

The rate at which the anodic and cathodic reactions occur at an electrode surface may be represented by an Arrhenius type rate equation which relates the rate of reaction to the reaction activation energies. The activation energy for an electrochemical reaction is affected by the magnitude and direction of the electric field in which the reaction takes place. For example, positive electrode potentials reduce the activation energy of the anodic reaction thereby increasing its rate in relation to the rate of the cathodic (reverse) reaction which is retarded by the same effect.

The difference between the rates of the anodic and cathodic reactions is the net rate of reaction and this is equivalent to the current density. An increase in the current density therefore requires an increase in the strength of the electric field across the region in which the reaction takes place. This increase in electric field strength is seen as an increase in the overpotential of the electrode.

When there is no adsorption on the metal surface and the process of charge transfer between reacting species is the rate determining step, the current density may be related to the overpotential by the Volmer equation:-

$$i = i_o\left\{\exp\frac{\alpha z F \eta}{RT} - \exp\frac{-(1-\alpha) z F \eta}{RT}\right\} \qquad 4.8$$

where i_o is the exchange current density. This is a kinetic constant which refers to the rate of the anodic and cathodic reactions at equilibrium. α is a value, $0 < \alpha < 1$, called the charge transfer coefficient which represents the effect of the electric field strength on the activation energy of the reaction. The two exponential terms represent, respectively, the rates of the anodic and cathodic reactions relative to one another.

Once the overpotential exceeds about 0,1 V the ratio of reaction rates usually exceeds 50:1 and the smaller term may be ignored. This makes it possible to approximate the overpotential as a function of current density according to the Tafel equation which has the form:-

$$\eta = a + b \ln i \qquad 4.9$$

For anodic processes with $\eta > 0,1V$:-

$$a = -\log i_o \frac{2,303RT}{(1-\alpha)nF} \qquad 4.10a$$

$$b = \frac{2,303RT}{(1-\alpha)nF} \qquad 4.10b$$

and for cathodic processes with $\eta < -0,1V$:-

$$a = \log i_o \frac{2,303RT}{\alpha nF} \qquad 4.11a$$

$$b = -\frac{2,303RT}{\alpha nF} \qquad 4.11b$$

It is important to note that the Tafel equation is an approximation and is not accurate at low overvoltages. In addition, at high current densities, the generation of gases at the electrode and the diffusion of reacting species to and from the electrode may become rate limiting.

The kinetic quantities ,i_o and α, in the Volmer equation are specific both to the electrochemical reaction that occurs and to the electrode surface composition. If these quantities are not known for the electrodes in use they may be estimated from the Tafel equation by measuring the overpotential and current density for a range of concentrations.

4.1.3 Electrical conduction losses

When an electric current flows in a solution, the flow of charge consists of a flux of charged species, cations and anions, in the solution.[18] The proportion of current carried by each species depends upon its ionic charge, its concentration and its ionic mobility. If we ignore the effects of diffusion due to concentration gradients and flow of the electrolyte solution relative to the electrodes the current density in the direction of the potential gradient may be expressed:-

$$i = \sum_i -z_i U_i C_i F \Delta P \qquad 4.12$$

where:

z_i is the charge carried by ion species i,
U_i is the ionic mobility of species i,
C_i is the concentration of species i and
ΔP is the potential gradient in the direction of current flow.

Equation 4.12 is analogous to Ohm's law with the specific conductivity κ defined by:-

$$\kappa = \sum_i |z_i| F U_i C_i \qquad 4.13$$

The equivalent conductivity is defined:-

$$\Lambda_{eq} = \kappa / C_{eq} i \qquad 4.14$$

If a reliable relationship between the concentration and equivalent conductivity is available for the species concerned then κ may be predicted from knowledge of the concentration of the electrolyte.

Ionic conductivities may be defined as:-

$$\lambda_i = |z_i| F U_i \qquad 4.15$$

As the solution is diluted further the degree of dissociation of species in solution increase and the equivalent conductivity of the species increase to a maximum value at infinite dilution. At this point, the equivalent conductivity of each ion is independent of the other ions according to the Kolrausch law of independent migration of ions. These limiting ionic conductivities (λ_i^o) may therefore be added to give the equivalent conductivity of the electrolyte at infinite dilution:-

$$\Lambda^o = \sum_i \lambda_i^o \qquad 4.16$$

An empirical model, for example, the Kolrausch square root law, may be used to predict Λ_{eq} from this limiting equivalent conductivity:-

$$\Lambda_{eq} = \Lambda^o - A\sqrt{C_{eq}} \qquad 4.17$$

where A is a constant. This equation is not accurate for all ionic species however and is generally only applicable up to 0,1N solutions. Theoretical models such as the Onsager equation are also only accurate over a limited range.

Direct measurement of conductivity is the most accurate method of determining the conductive potential drop in the electrolytes. κ is the specific conductivity that is measured by a conductivity probe. The potential drop (E_R) across a volume of electrolyte due to the resistance to flow of a current (I) in the electrolyte may therefore be expressed as:-

$$E_R = \frac{Il}{\Lambda_{eq} C_{eq} a} \qquad 4.17$$

where a is the cross sectional area of current flow and l the length of the current flow path.

Conduction losses occur in both electrolyte compartments of the cell. The equivalent conductivities and concentrations of the two electrolytes differ but the dimensions of the compartments are identical in this case. Conduction losses across the membranes may be directly measured in the cell during operation.

4.2 Polarisation

Polarisation of water occurs at the membrane surface (on the catholyte side) when the rate of diffusion of anionic species through the boundary layer between the bulk solution and the membrane surface is too slow to transport the current.

When polarisation occurs, water molecules are split, at the membrane surface, to give hydrogen and hydroxide ions. The hydroxide ions which are formed in this way, carry the current through the membrane.

Polarisation therefore results in reduced current efficiency due to the unwanted transport of hydroxide ions through the membrane. Polarisation also causes an increase in the operating voltage of the process. Both the increased voltage and reduced current efficiency cause an increase in the power consumption of the cell.

4.3 Limiting current density

The current density at which polarisation starts to occur is called the limiting current density (LCD). The value of the LCD in any system depends upon the concentrations and ionic mobilities of the species in the solution. Ionic mobility is, in turn, affected by the physical size of the ion, its charge density, temperature and the strength of any interactions between it and other species in the solution.

Since LCD is affected by the concentration of the electrolytes, the value of the LCD will obviously change during batch mode operation. In practice, it is desirable to operate at a current density just below the LCD so as to retain current efficiency and minimise the membrane area. Efficient process control will therefore necessitate a model which can predict the LCD from data such as temperature and concentration.

4.4 Current efficiency

Each of the anion species present in the catholyte is capable of carrying a portion of the total current flowing through the membrane. The portion carried by a particular species depends upon its mobility in the solution, its mobility in the membrane structure and its concentration in the electrolytes.

The current efficiency, η, with respect to a particular ion may be expressed as:-

$$\eta(\%) = 100 \times \left(\frac{\text{charge transferred by specified ion}}{\text{total charge transferred}} \right)$$

In the electrolysis of a pure ammonium nitrate solution, the only anion other than the nitrate ion that will be present in significant quantities is the hydroxide ion. This ion is produced by the cathode reaction and also as a result of polarisation at the membrane surface, in the case where the LCD is exceeded. When hydroxide ions carry current through the membrane the current efficiency for nitrate removal is lowered.

At currents below the limiting current, maximum current efficiency for nitrate removal will be achieved by controlling the catholyte pH in the neutral to slightly basic range. In this pH range, however, the evolution of ammonia gas is not favoured (Figure 3).

4.5 Water transport

Water (or solvent) transport in a membrane process occurs when the membrane is not totally impermeable to the solvent. The solvent can move through the membrane under the influence of concentration gradients or may be carried through as water of hydration attached to the moving ions.

The Water Transport Number (n_w) is defined as the number of equivalents of water per equivalent of ions that pass through the membrane. Water transport number can be used to compare the performance of membranes and to detect damage, such as rupturing, of the membrane.

4.6 Effects of temperature

As temperature increases, ionic mobility increases. This effect allows the LCD to increase too.

Operation at elevated temperatures is therefore advantageous because it allows further reduction in the membrane area. Maximum permissible temperatures will be determined by the materials of construction and the downstream processing requirements.

Since ohmic heating occurs during processing, facility for cooling the electrolytes may be required.

4.7 Effects of electrolyte concentrations

The relationship between ammonium nitrate concentration and conductivity is effectively linear for concentrations between 0,01 and 10 g/ℓ. At higher concentrations the relationship is non-linear because of activity effects and at concentrations below this range, the conductivity of impurities and the solvent (water) becomes significant.

Conductivity gives an indication of ionic strength and therefore, the current carrying capacity of the solution. The LCD will increase with increasing ionic concentration. During operation, the ionic concentration of the catholyte will decrease as the catholyte is demineralised. The LCD will consequently decrease during operation.

The concentration gradients which exist across the anion exchange membrane can affect the operation of the electrolytic cell. At the beginning of a batch run the anolyte is usually a saturated solution of calcium hydroxide. The catholyte is a solution of ammonium nitrate.

As the run progresses, the concentration gradients change. In the catholyte, the nitrate concentration decreases, the hydroxide concentration increases and the total ammonia concentration decreases as ammonia is released. In the anolyte, the nitrate and calcium concentrations both increase and the hydroxide concentration remains approximately constant. The calcium nitrate formed in the anolyte is extremely soluble and the concentration of calcium nitrate in the anolyte builds up to very high levels (for example: 250 g/ℓ as calcium nitrate).

The disadvantage of this is that if the rejection of cations by the membrane is not total, some of these calcium ions may move into the membrane under the influence of the concentration gradient.

If these calcium ions, while in the membrane, come into contact with anions with which they form sparingly soluble compounds, the solubility products for these calcium compounds may be sufficiently exceeded for crystallisation to occur. The resultant growth of crystals within the membrane could damage it by cracking the ion exchange resin. Typically, such anions would be hydroxide, sulphate or carbonate anions. The carbonate and sulphate anions should not be present in the system but may occur as impurities in the lime which is added to the anolyte.

The anolyte and catholyte solutions usually have a pH of about 12,5 and 10,5 respectively. Both solutions will therefore absorb carbon dioxide from the atmosphere and form carbonate anions. During processing, the electrolyte tanks are normally closed but they are opened during sampling and contact of the solutions with the atmosphere is possible.

4.8 Effects of electrolyte flowrates

4.8.1 Boundary layer thickness

If the thickness of the laminar boundary layer adjacent to the membrane surface is reduced, the difference in concentration of the depleted species between the membrane wall and the bulk fluid will decrease. (See Figures 3 and 4).

This means that the concentration at the membrane surface will increase resulting in an increase in the LCD.

The boundary layer thickness is affected by the design of the cell, the design of any turbulence promoters used, the texture of the membrane surface itself and the bulk fluid Reynolds Number. While the fluid's characteristics will not change significantly during processing, the flowrate can be controlled and will have an effect on the performance of the cell.

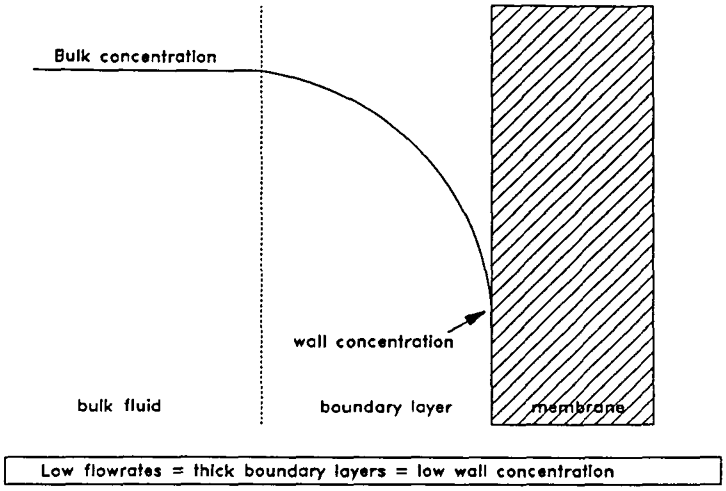

FIGURE 3 : Boundary Layer Thickness at Low Flow Rates

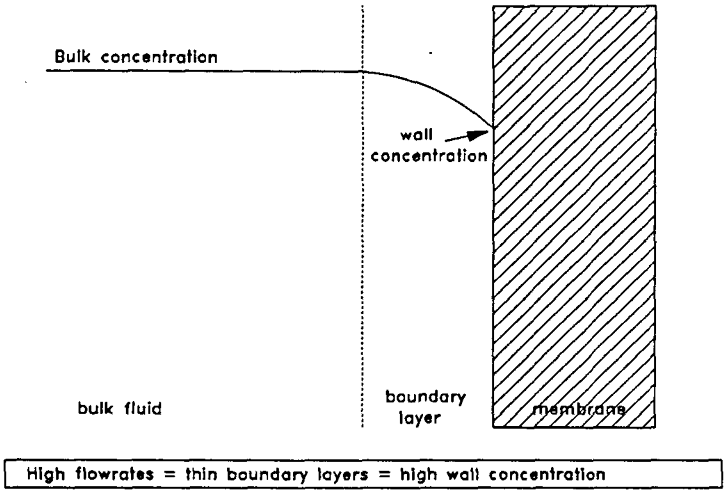

FIGURE 4 : Boundary Layer Thickness at High Flow Rates

4.8.2 Gas removal

The electrolyte flowrate and the cell design also affect the removal of gaseous electrolysis products. During normal operation, oxygen is produced at the anode surface and hydrogen at the cathode surface. The rate of production of gas depends upon the total current flowing, so at low electrolyte flowrates, the gas produced in the cell will occupy a greater proportion of the compartment volume than at higher flowrates. Since the degree of turbulence at low flowrates is lower, the bubbles of gas tend to coalesce more.

These larger bubbles tend to obscure some of the mass-transfer area of the cell, thereby increasing the current density in the remaining liquid and increasing the operating voltage. The operating voltage fluctuates as the bubbles periodically vent from the cell compartments.

At higher flowrates, the bubbles are smaller and more evenly dispersed in the electrolyte as a result of the greater turbulence. The bubbles also comprise a smaller portion of the combined volumetric flow and are flushed out of the cell more readily.

4.8.3 Pressure drop

The cell used for these experiments is an experimental unit produced by Portals Water Treatment and was designed for testing electrodialysis applications (see section 5.2.6). It has electrolyte compartments which lie in the horizontal plane and are 1,6 mm thick. The cell stack incorporates pressed plastic sheets which are used to form the flow distribution manifolds within the stack (very similar to a plate type heat exchanger).

As the flowrates through the cell increase, the pressure drop across the cell increases too. This results in higher pumping costs and a greater possibility of leaks from the cell which cannot sustain higher pressures.

4.8.4 Choice of flowrate

The electrolyte flowrates that are chosen for processing must therefore trade off the advantages of increased LCD and better gas removal against the disadvantages of higher pumping costs and more leakage.

4.9 Adaptability to variations in effluent characteristics

The electrolysis process can treat a wide range of ammonium nitrate concentrations but its tolerance of certain types of impurities is low.

4.9.1 Solid impurities

Solid impurities will tend to block the flow distribution manifolds in the cell and should therefore be removed by filtration prior to processing.

4.9.2 Organic impurities

Organic impurities such as waxes, oils and solvents must be avoided because they can irreversibly foul or damage the membranes. If such impurities are present and cannot be removed from a particular stream then that stream should not be processed.

4.9.3 Ionic impurities

Both ammonium and hydrogen cations can be reduced to form gases which are released from solution. Cations other than these, such as calcium or sodium, will remain in the catholyte without being reduced. The requirement for electrical charge conservation means that as nitrate ions are transported through the membrane, hydroxide ions must be formed to maintain the charge balance.

If the cationic impurities are those which form sparingly soluble metal hydroxides (for example magnesium, lead, aluminium, iron and nickel) the hydroxides will precipitate according to solubility product criteria. This will depress the pH of the catholyte and impede the release of ammonia gas from the catholyte solution.

4.10 Membrane and electrode life

In many electrolysis and electrodialysis applications the ion exchange membranes are expected to last for 1 to 2 years of operation[16]. The electrodes, in particular the expensive coated anodes (see sections 4.8.2 and 5.2.6) are expected to last for several years[15]. The actual membrane life at which the process ceases to be economically viable depends upon the value of the products and the cost of the membranes.

4.10.1 Membrane life

In order to maximise membrane life the membrane must be resistant to attack by the chemical environment in which it is to be operated. For the treatment of nitrogenous effluents by electrolysis, a membrane with the following properties is required:-

1 The membrane must be resistant to solutions of pH 2 to pH 13.

2 Resistance to attack by nitrate, ammonia, and calcium ions is essential

3 Low water transport number is desirable.

4 High nitrate selectivity and high cation rejection is desirable.

5 Resistance to temperatures up to approximately 80° C is required.

4.10.2 Electrode life

In order to maximise electrode life the electrodes must be resistant to attack by their environment.

Cathodes are usually resistant to corrosion or attack and stainless steel is adequate for this purpose.

Anodes are susceptible to corrosion by electrochemical oxidation. For this particular application, the anode is required for oxygen production. Proprietary mixtures of platinum group metal oxides are usually used for these applications because they are noble and resistant to attack, hence the term "dimensionally stable anode" or DSA. Since the mixtures are very expensive, they are usually applied as thin coatings to a specially prepared titanium base. Titanium is used because if the coating is damaged, the exposed titanium metal becomes passivated under anodic conditions and will not corrode[15]. The passivation is caused by a layer of non-conductive titanium oxide which builds up on the exposed (bare metal) surface under anodic conditions and insulates it from the solution.

5 EXPERIMENTAL APPARATUS

An experimental rig was designed to test the effects of the parameters discussed in the previous section on the operation of the process.

5.1 Apparatus design

The rig was designed for batch operation. Batch operation is required for several reasons:-

i) The electrolyte flow path in the cell is short (112 mm) and the electrolyte velocity recommended by the manufacturers is relatively high (0,08 m/s or higher). This means that the space time in the electrolyte compartments will be less than 1,4 seconds during normal operation. The actual electrolyte residence time will be less than this because the gases evolved at the electrodes occupy space in the compartment. Treatment on a once-through continuous basis would require either a longer residence time or a much higher current density.

ii) Treatment on a continuous basis would mean that the catholyte undergoes a continuous depletion of ionic strength as it passes through the cell. An analogous situation is the continuous change in composition experienced by a stream undergoing a reaction in a plug flow reactor. This depletion would be accompanied by corresponding changes in the conductivities of the electrolytes and the current density would vary along the electrolyte flow path.

iii) Batch operation can be achieved with lower residence times and current densities so that the concentration change across the cell is incremental. This means that the current density may be assumed constant at all points in the active area between the electrodes and the effects of concentration, temperature and flow velocity on the limiting current density may be determined. Variation of the current efficiency for varying concentrations and current densities may also be measured more accurately during batch mode operation.

The simplified flow diagram (Figure 5) depicts the system. The catholyte (effluent sample) and anolyte (lime solution) tanks supply pumps which recirculate the electrolytes by means of bypass lines. The recirculation aids mixing.

5.1.1 Feed

Feed to the cell compartments is bled from the bypass lines. A rotameter on each feed line allows measurement of the flowrate.

5.1.2 Filtration

The anolyte feed is filtered to prevent undissolved lime from clogging the anolyte compartment. The cake of lime which forms on the filter provides adequate contact for saturation of the feed stream with lime.

5.1.3 Recycle

After processing in the cell, the two electrolyte steams are returned to the tanks. The gases generated by the electrolysis process are also returned to the tanks from where they are vented.

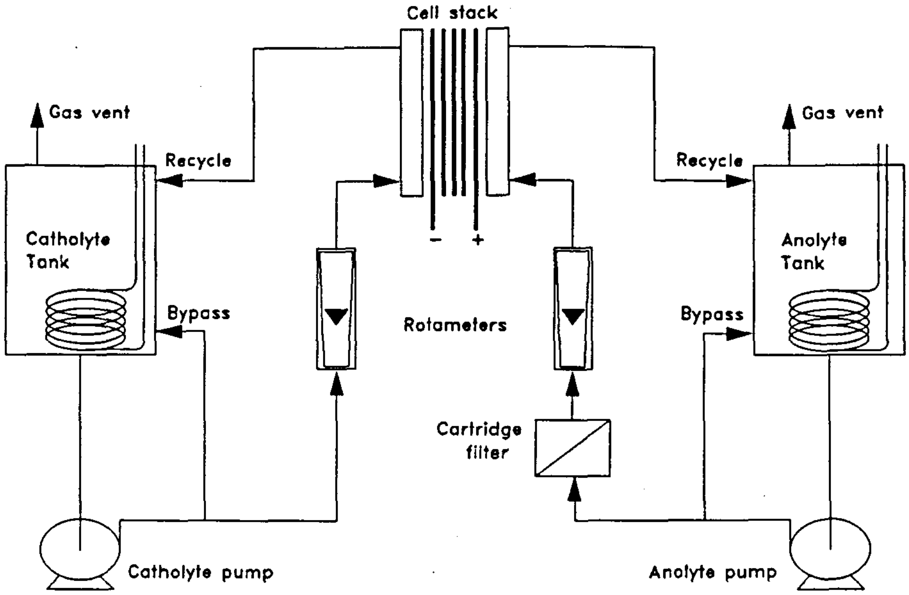

FIGURE 5 : Flow Chart for Batch Type Electrolysis Process

5.1.4 Cooling

Both tanks are fitted with tubular stainless steel cooling coils which are used for regulating temperature by removing the heat generated by the flow of current through the electrolytes.

5.1.5 Power supply

Power is supplied by means of a d.c. regulated power supply which can be used in either controlled voltage or controlled current mode. The power supply has maximum output of 25 V at 30 A with 10 % ripple

5.1.6 Electrolytic Cell

The electrolysis cell used for this investigation was made up from an experimental electrodialysis cell supplied by Portals Water Treatment. The cell has an active area of 0.0125 m^2. It was supplied with a stainless steel (Type 304) cathode and a coated niobium anode which proved to be defective. A DSA anode supplied by Electrocatalytic was used. Two types of membrane, namely Ionics 103QZL and Permaplex SB, were tested. Detailed specifications for the cell and the membranes may be seen in Appendix 3 while specifications for the other equipment are provided in Table 3.

5.2 TABLE 3 : Equipment fitted to electrolysis rig

Item	Quantity	Parameters	Description
Pump	One	0,75 kW	Speck centrifugal pump for catholyte circulation
Pump	One	0,4 kW	Speck centrifugal pump for anolyte circulation
Tanks	Two	45 ℓ	Electrolyte tanks (constructed from PVC)
Filter	One	260 mm	Wound fibre cartridge filter for filtration of anolyte
Rotameters	Two	Metric 14G, Stainless steel float	Glass rotameters for measurement of electrolyte flowrates
Power supply	One	25 V, 30 A, d.c.	Rectron regulated direct current power supply for electrolysis cell
Cell	One	0,0125 m^2, DSA anode, Stainless steel (304) cathode	Portals Water Treatment experimental ED cell modified for electrolysis
Cooling coils	Two	Stainless steel (304) 12mm O.D. Tubing, 4 m long	One coil per tank for temperature regulation of the electrolytes

6 EXPERIMENTAL PROGRAMME

The purpose of the experimental program was to investigate the effects of the parameters discussed in Section 3.

6.1 Experimental method

Two types of experiment were conducted. The method for the first type was as follows:-

1. The tanks were filled with the electrolyte solutions and the volumes noted.
2. The electrolytes were circulated at relatively high flowrates (approximately 4 ℓ/min).
3. Samples of the electrolyte were taken at regular intervals for later analysis of conductivity, pH and nitrate concentration.
4. Simultaneously, the current-voltage relationship for the cell was measured, the Amp-hour counter reading was recorded and the temperature of both electrolytes was measured.

5. The power-supply was adjusted and make-up lime was added to the anolyte when necessary.
6. The experiment was allowed to run to completion, that is, until the nitrate ions concentration was reduced to about 0,5 g/ℓ.

The method for the second type of experiment was as follows:-

1. The tanks were filled with electrolyte solutions and the volumes noted.
2. Samples of the electrolyte were taken at the beginning and the end of each experiment.
3. Current-voltage relationships were measured for the cell at each of several flowrates.

6.2 Results

The results available from Type 1 experiments were:-

1. Current efficiencies during processing
2. The relationship between LCD and conductivity or concentration of the catholyte solution.
3. The electrode potentials, overpotentials and conduvctive volt drops in the cell compartments as a function of current.
4. The effects of temperature on power consumption. Temperature could be adjusted during processing by regulating the cooling water flowrate.
5. The effects of various electrolyte concentrations on performance.
6. Membrane and electrode life.
7. Water transport numbers and water loss from the system.

The results available from type 2 experiments were:-

1. The relationship between LCD and concentration.
2. The relationship between LCD and flowrate.
3. The effect of flowrate on power consumption.
4. The effect of flowrate on gas production.

At the time of writing this report, the full experimental program had not been completed. Consequently, some of the important parameters have not been completely investigated.

6.3 Measured data

6.3.1 Measurement of the following parameters were made during the operation of the rig:-

1. Catholyte and anolyte flowrates.
2. Catholyte and anolyte volumes.
3. Electrical current flow.

4. Electrical charge transfer.
5. Potential difference across; power supply output, cell electrodes, anolyte compartment, catholyte compartment and membrane.
6. pH and conductivity of both electrolytes.
7. electrolyte temperatures.

6.3.2 Sample analysis

The nitrate concentrations were analysed in samples taken simultaneously with the measurements listed above. Analyses were undertaken by the laboratory at Modderfontein for the samples from experiments 4, 5, 6, 7 and 8. Samples from experiments 2 and 3 were analysed at the University of Natal using an Orion nitrate specific electrode.

6.3.3 Calculation of experimental results

A Lotus 1-2-3 spreadsheeting package was used to calculate the results which appear in Appendices 1 and 2 from the data gathered during the experiments. The electrode potentials and conductive volt drops were calculated from pH and conductivity data respectively and subtracted from the trans-anolyte and trans-catholyte voltages to leave a value which corresponds to the overpotential,polarisation and error voltages. When there is no polarisation these values correspond closely to the electrode overpotentials which were not directly measured. See Appendices 5 and 6.

7 EXPERIMENTAL RESULTS

The raw experimental data is given in Appendix 1 along with spreadsheets which calculate the current efficiencies and specific power consumption Appendix 2 contains the Current-Voltage plots produced from data measured during the experiments. Appendix 5 contains the results of calculations for the electrode overpotentials, reaction potentials and conductive losses. Appendix 6 consists of plots of the overpotentials of the electrodes for experiments 4, 6 and 8.

Seven experiments were performed during the period from October 1988 to December 1988. Experiments 2,3,4,6 and 8 were of type 1 (as described in section 5). Experiments 5 and 7 were of type 2.

Experiments 4, 5, 6, 7 and 8 were conducted at Modderfontein with samples of contaminated condensate from the ammonium nitrate plant. The condensate stream results from cooling of the steam evolved in the ammonium nitrate reactor. Some ammonium nitrate is entrained in this vapour and contaminates the condensate. This stream has high ammonium nitrate purity. The highest concentration encountered during the experimental work was 4 300 mg/ℓ as N.

7.1 Current efficiency

Overall current efficiencies for nitrate transfer from the catholyte exceeded 90 % in experiments 2 and 3. In experiments 4,6 and 8, which had more careful current control, the cumulative current efficiencies exceeded 98 %.

Current efficiencies calculated from the increase in nitrate concentration of the anolyte were consistently lower, averaging about 90 % overall.

TABLE 4 : Current Efficiency

Experiment	Current Efficiency (%)	Ammonium nitrate at start mg/ℓ as N	Nitrate depletion (%)
2	100	10 040	96,1
3	90	8 240	97,7
4	99	3 300	30,1
6	98	4 300	98,8
8	98	3 600	93,9

The discrepancy could be caused by water transport from the catholyte to the generally more concentrated anolyte. This water transport through the membrane could give rise to inaccuracies in the calculation of electrolyte volumes.

The strength and direction of pH and nitrate concentration gradients across the membrane surface appears to have no effect on current efficiency.

(See the spreadsheets in Appendix 1 for current efficiency data and related information).

7.2 Limiting current density

When the LCD is exceeded, the polarisation which occurs in the catholyte boundary layer adjacent to the membrane surface causes an increase in the potential difference across the boundary layer. (See Figure 6).

Note: The potential difference across the boundary layer is Ohmic at current densities below the LCD and non-Ohmic above the LCD

The potential "steps" at the electrode surfaces represent the electrode overpotentials for reduction/oxidation of water at the cathode and anode respectively.

The markers in Figure 6 show the points at which the voltage probes are positioned in the cell. When the LCD is exceeded, it will show as a change in the slope of a graph of the current/voltage relationship for the catholyte chamber. The change in slope is sometimes more obvious on a current/voltage plot of the sum of the anolyte and membrane trans-potentials.

At a given flowrate, pH and temperature, the LCD will be linearly related to the activity of the nitrate ions in the catholyte solution. The nitrate ion activity is approximately equal to the nitrate concentration for the range of concentrations which were experienced during the experiments. Therefore, we can equate the LCD to the nitrate ion concentration ([c]) with a proportionality constant (k) to get:-

$$LCD = k \times [c]$$

For temperatures between 20° C and 30° C, flowrates from 2,5 to 3,5 ℓ/min and pH between 10 and 13, the value of k varies between 1 100 and 3 800 $A.m^3/kg.m^2$. (See C-V graphs for Experiments 3,6 and 8 in Appendix 4).

The data obtained to date are insufficient and further work is necessary to quantify the effects of temperature, pH and flowrate on the proportionality constant *k*.

If this can be achieved, an accurate prediction of the LCD will be possible for the range of normal operating conditions.

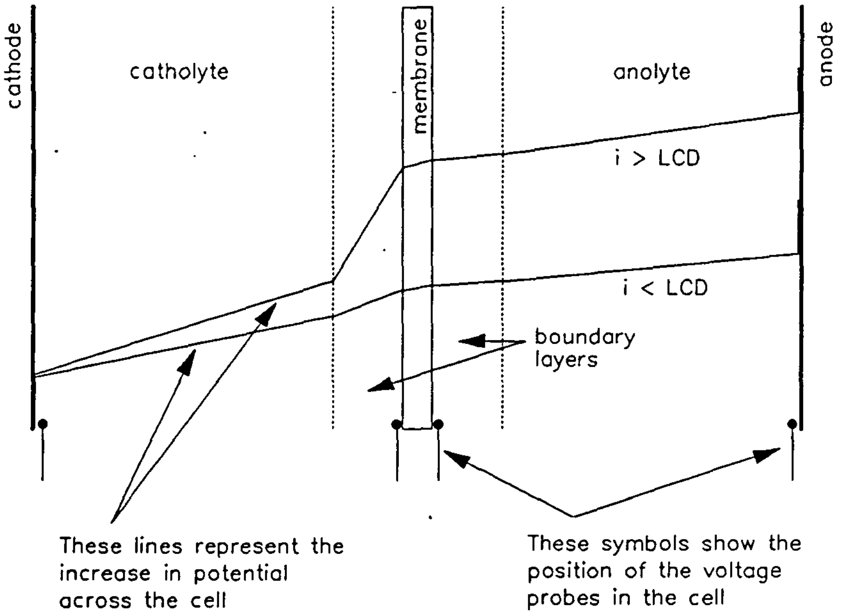

FIGURE 6 : Potential Differences Through the Electrolysis Cell

7.3 Power consumption

Specific power consumption in kilowatt-hours per kilogram of ammonium nitrate removed (kWh/kg) increases with increasing current because of the greater potential drop across the cell at higher currents. This can be seen in Table 5. The average current for Experiment 8 was higher than that used in the other experiments (see Appendix 1) and the specific power consumption is significantly higher.

Power consumption also increases at lower temperatures because of the increased potential drop caused by reduced ionic mobility in the electrolytes and the membrane. (The power consumption data is given in the spreadsheets in Appendix 1).

TABLE 5 : Power Consumption

Experiment	Power consumed kWh	Specific power consumption kWh/kg
2	1,84	1,96
3	1,45	1,71
4	0,19	1,63
6	1,51	2,07
8	2,09	3,48

The trans-anolyte and trans-catholyte potentials measured during experiments 4, 6 and 8 were broken down into their constituent parts, namely, electrode reaction potential, electrode overpotential and potential drop due to conduction of current through the electrolytes. The results of these analyses may be seen in Appendix 5.

At low current densities, the electrode reaction potentials generally constitute the greatest portion of the potential drop and hence consume the most power. These potentials are independant of the current density, thus , as the current density increases they represent less of the power consumption.

The graphs of electrode overpotentials in Appendix 6 show clearly that the anodic overpotential was lower than the cathodic overpotential during Experiments 4 and 6. The graphs for Experiment 8 however, show the opposite effect. The shape of the curves on the anode overpotential graph are inconsistent with the Tafel equation. These curves are generated by subtracting the resistive volt drop and anode potential from the trans-catholyte voltage measurement. Any inaccuracy in the prediction of these two constituent values will therefore manifest itself in the overpotential plot and this may have occurred in this case. In the graphs for Experiment 8, the three steep curves generated towards the end of the experiment definitely include the potential drop due to polarisation at the membrane surface as well as the overpotential.

7.4 Water transport and water loss from the system

During normal operation of the cell, volumes of the electrolytes in the tanks changes slowly. These changes can be attributed to the following factors:-

7.4.1 Electrode reactions

The reduction and oxidation reactions at the electrodes consume water. One mole of water (18 g) will be lost from the system for every Faraday of charge that is passed.

7.4.2 Sampling

Sampling of the electrolytes represents another loss. Each sample of electrolyte measured approximately 110 mℓ. The sample volumes had to be large enough to allow for analysis but small enough to ensure that the dissolved species withdrawn in the sample did not represent a significant loss to the system. The volume of electrolyte lost in sampling can be calculated from the experimental records.

7.4.3 Water transport

The membranes used were not totally impermeable to water and as a result, some water flows through the membrane under the influence of the concentration gradients which exist across the membrane. Since the anolyte is generally more concentrated than the catholyte, water tends to flow from the catholyte to the anolyte. The calculation of water transport numbers was made impossible by the effects of evaporation and leaks (see 7.4.4 and 7.4.5) on the volumes of the electrolytes. The loss in volume due to leaks and evaporation could not be adequately determined.

Small volume changes occur as a result of the concentration and demineralisation of dissolved solids. However, these changes are likely to be insignificant.

7.4.4 Evaporation

Evaporation of water from the electrolytes is possible especially when the process is operated at temperatures above ambient.

7.4.5 Leaks

If the clamping bolts that hold the cell together are tightened unevenly or if the flowrate is too high, the cell does not seal properly and leaks occur.

The volume of electrolyte lost to leaks and evaporation is not easily estimated. The continual loss of electrolytes causes difficulty in determining the current efficiency accurately although the electrolyte volume changes were taken into account in the computations.

7.5 The effect of flowrate on limiting current density and gas production

At higher flowrates, the gases produced in the cell are visibly more finely dispersed in the electrolytes and the potential drop across the cell is lower and more stable.

At flowrates below 2,7 ℓ/min, the potential drop begins to increase significantly and at flows below 1 ℓ/min, the potential drop fluctuates because of the effect of large gas bubbles obscuring the mass transport area. At flowrates greater than about 2,5 ℓ/min, the potential drop is stable and is almost constant. This flowrate represents a superficial flow velocity of about 0,23 m/s in the cell compartments. (See the current Voltage curves for experiments 5 and 7 in Appendix 2).

At flowrates exceeding 5 ℓ/min, the cell leaks significantly in spite of tighter clamping. The flowrate used for most of the type 1 experiments was 3,85 ℓ/min which fell in the middle of the recommended range.

The effect of flowrate on LCD could not be quantified in experiments 5 and 7 because the catholyte concentration was too high. This meant that the LCD was higher than the maximum current available from the power supply. In future type 2 experiments, catholyte concentrations below 1 g/ℓ (as nitrate) should be used. This will allow the effect of flowrate on LCD to be quantified more easily.

7.6 Membrane and electrode life

In order to determine membrane and electrode life accurately it is necessary to run the process for thousands of hours. Although this has not yet been achieved, observations made during about 500 hours of operation are presented in Sections 7.6.1 to 7.6.3.

7.6.1 Anode life

During commissioning of the test rig, stainless steel (type 304) was tested for use as an anode. Stainless steel did not prove successful because it was corroded after about 100 hours of service. When the anolyte pH dropped below pH 12 the corrosion was rapid. The pH of the anolyte drops below pH 12 when the the lime in the anolyte becomes depleted.

In addition to the corrosion of the stainless steel anode, the corrosion products, mainly iron hydroxides, fouled the membrane and caused an increase in its resistance to flow of anions.

The anode that was subsequently used was supplied by Electrocatalytic Ltd. and is of the coated DSA type. This anode shows no visible corrosion or deterioration after about 500 hours of service.

7.6.2 Cathode life

A stainless steel (type 304) cathode was used from the beginning of the project and has shown no visible corrosion or loss of mass. This type of cathode could be expected to last indefinitely in this application because it is not likely to be corroded by either the electrolysis process or the catholyte solutions.

7.6.3 Membrane life

Two types of membrane have been tested (Ionics 103QZL and PERMAPLEX SB). Both have lasted only about 50 to 60 hours before being damaged by the build-up of crystals which seem to be precipitated inside the membrane structure. These crystals have been identified as calcium carbonate but small quantities of calcium sulphate and calcium hydroxide could also be present. If the crystals are insoluble sulphates or carbonates, the sulphate or carbonate anions would probably have been impurities in the lime added to the anolyte or, in the case of carbonates, could have resulted from contact of the alkaline electrolytes with carbon dioxide in the air.

During operation the pH of both electrolytes is high (usually above pH 10,5) and exposure to the air during sampling allows absorption of carbon dioxide which is partially converted to the carbonate anion in solution.

7.7 Processing rates and scale-up data

The average nitrate flux in experiments 2, 3, 4, 6 and 8 was about 1 kg/m^2.h. Fluxes varied from 0,5 to 1,5 kg/m^2.h with specific power consumption varying between 2 and 4,5 kWh/kg of nitrate ions. Specific power consumption was generally higher at higher fluxes.

The power supply voltages used during these experiments varied between 4 and 20 Volts and the current densities from zero up to 1 300 A/m^2. Current densities higher than 1 300 A/m^2 could not be tested as the electrodes and power cables could not carry higher currents without heating up significantly.

8 DISCUSSION AND RECOMMENDATIONS

8.1 Equipment design

The inline-type filter cartridges which were used to filter solids from the anolyte feed to the cell clogged up rapidly and hindered experimental work. A larger filter or alternatively, a larger pump will allow anolyte flowrate to be maintained above the minimum recommended level for longer periods.

In addition, The option of fitting the rig with smaller tanks in which the volume may be more accurately measured should be considered.

8.2 Limiting current density

Initially it was difficult to find the LCD because of inadequate experimental methods. A rough estimate of the relationship between LCD and nitrate concentration is now available. Future work should attempt to build a more accurate model for the prediction of LCD which will include corrections for the effects of temperature, flowrate and pH.

8.3 Temperature

Future work should attempt to quantify the effects of temperature on the LCD and specific power consumption of the process. The experiments conducted so far indicate that significant reductions in specific power consumption and membrane area are possible if the cell is operated at higher temperatures.

8.4 Ammonia stripping

During the course of processing the pH of the catholyte does increase but not enough to completely strip the ammonia gas from the solution. Future work should include investigation of this aspect of the effluent demineralisation. Increased processing temperatures and air sparging will increase the rate at which ammonia is released from the solution.

8.5 Membrane life

The source of the calcium carbonate crystals which are growing in and rupturing the membranes must be isolated. The short membrane life is the major obstacle to the technical feasibility of the electrolysis process for this application.

There are several methods which may be used to reduce damage caused by calcium carbonate. They are :-

8.5.1 Acid Rinsing

Carbonates can be removed from the membrane by periodically rinsing the cell with dilute nitric acid during processing.

8.5.2 Seeding

The catholyte solution could be seeded with calcium carbonate crystals. This would help to reduce the build-up of ammonium carbonate in the catholyte and thereby reduce the amount of carbonate anion available for transport through the membrane.

8.5.3 Nitrogen Purging

The absorption of carbon dioxide by the alkaline electrolytes could be reduced by purging the electrolyte tanks continuously with nitrogen.

8.5.4 Alternative Membranes or Alkalis

The use of membranes with greater nitrate specificity and greater cation rejection could help to reduce the problem. The use of an alkali in the anolyte which has a more soluble carbonate would also help in reducing the damage to the membranes. At present, calcium hydroxide is used because it is cheap and dissociates in the anolyte to give a solution of suitable pH. Most alternative alkalis would be more expensive and would require some form of pH control.

8.6 Alternative Electrode Materials

The ideal anode for the ammonium nitrate electrolysis process would be stable against attack by nitrate and ammonium ions and would have a low overpotential for oxygen generation. The DSA anode used for these experiments has shown no deterioration in its surface coating or potential drop but an alternative electrode surface with a lower oxygen generation overpotential would allow a decrease in power consumption.

The DSA coating on the anode is primarily a mixture of ruthenium and titanium oxides and transition group metal oxides and is designed for the anodes used in the chlor-alkali industry[15-16]. It is resistant to attack by chlorine and chlorides. It has a low overpotential for chlorine generation and a higher overpotential for oxygen generation. An electrode which is more electrocatalytic to oxygen generation would be a better choice for the application of electrolysis of ammonium nitrate solutions.

Titanium-iridium and tantalum-iridium oxide mixtures are more universally electrocatalytic[15] and might be more siutable for this application.

Although the stainless steel cathode is resistant to corrosion it has a higher overpotential than the anode at any given time. Proprietary coatings for improving the electrocatalytic activity of cathodes are available and should be investigated. Recent advances in this field include the use of gas permeable cathodes in the chlor-alkali industry.[21] These cathodes consume oxygen and reduce the overall electrode potential by about 850 mV which corresponds to an energy reduction of up to 30 % over the conventional membrane cell with a steel cathode. In the ammonium nitrate electrolysis cell, the oxygen produced by the anode could be used directly in an oxygen cathode and would result in the formation of water rather than hydrogen gas at the cathode.

9 CONCLUSIONS

9.1 Process efficiency

Current efficiencies for the electrolysis of effluents containing relatively pure ammonium nitrate can be expected to exceed 95 % for concentrations exceeding 1 g/ℓ (as nitrate). At lower concentrations the current efficiency may be lower depending on the pH and the concentration of other anions in the solution.

The process will remove in excess of 95 % of the nitrate ions present at current efficiencies exceeding 95 % against both high pH gradients and trans-membrane nitrate gradients of 250 g/ℓ in either direction. Operation at currents below the limiting current density is essential if high current efficiencies are to be achieved.

9.2 Process performance

The specific power consumption for removal of ammonium nitrate from solution varies between 2 and 4,5 kWh/kg of nitrate anions. The specific power consumption increases with the rate of processing. The figures quoted here do not include pumping power, they represent only the power consumed by mass transport through the membrane.

The demineralised effluent generally contains about 90 % of the ammonium co-ion as dissolved ammonia gas. If this gas can be efficiently stripped the pH of the demineralised effluent will be reduced.

The P.C.I. electrolysis cell requires electrolyte flow velocities (superficial) of about 0,45 m/s for low cell potentials and good dispersion of gaseous electrolysis products.

9.3 Temperature

There are many advantages to operation at higher temperatures. These include:-

1. Higher LCD which allows faster processing.
2. Lower volt drops across the cell which reduce the specific power consumption.
3. Lower solubility of ammonia gas in the treated catholyte. This increases the amount of gas released by the solution.

9.4 Electrodes

Stainless steel is suitable for use as a cathode but 'D.S.A.' or some other proprietary coated anode is required. The anode should be stable from attack by nitrates and high pH solutions and should have a low overpotential for oxygen generation.

9.5 Membranes

The damage caused to the membranes by the precipitation and growth of calcium carbonate crystals within them is the only factor which prevents this electrolysis process from being technically feasible for the removal of ammonium nitrate from aqueous effluent solutions. If the source of the damage can be removed or its effect sufficiently reduced, the process will become technically feasible for this application

9.6 Future research

Future research on this process should address the following objectives:-

Quantify the effects of increased temperature on process performance.

Quantify the effects of temperature, pH, flowrate and concentration on limiting current density.

Test alternative membranes and alkalis and try to remove or reduce the damage caused to the membranes by precipitation of calcium carbonate crystals.

Test alternative anode coatings in order to try and reduce the overpotential for oxygen generation.

Test alternative cathode coatings and in particular, the gaseous oxygen cathode to determine whether it will have a significant effect on power consumption.

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11.1 APPENDIX 1 : Experimental Data

11.1.1 Experiment 2

Anolyte at start : $Ca(NO_3)_2$ 220 g/l
Anolyte volume : 43 l
Catholyte at start : NH_4NO_3 58 g/l
Catholyte volume : 17 l

Charge counter : 0,0221 Ah/count

Elapsed time (h)	Charge Counter	Current (A)	Voltage		pH	Cond. (mS/cm)	Nitrate (g/l)
			supply	cell			
0	0	9,00	5,34	3,79	7,17	75,30	44,45
2h20	905	9,00	5,25	3,70	8,36	65,80	42,75
4h35	1 800	9,00	5,34	3,79	8,52	71,60	43,00
7h36	2 975	9,00	5,43	3,86	8,96	49,40	34,60
10h06	3 964	9,00	5,51	3,91	9,16	60,50	31,55
11h50	4 580	9,00	5,60	3,93	9,24	58,90	31,30
15h41	6 172	9,00	5,60	4,04	9,46	51,80	26,50
23h55	9 480	9,00	5,72	4,16	9,89	37,50	15,55
27h51	10 965	9,00	6,10	4,48	10,29	29,30	6,76
30h46	12 905	9,00	6,99	5,37	10,68	12,64	3,25
32h09	13 450	9,00	8,19	6,55	11,12	10,22	2,65
38h10	14 188	0,90	5,60	4,01	11,36	7,56	1,72

Charge transfer (Ah)	
incr.	cumul.
0,00	0,00
20,01	20,01
19,79	39,80
25,98	65,78
21,87	87,65
13,62	101,27
35,20	136,47
73,14	209,61
32,84	242,45
42,90	285,34
12,05	297,39
16,32	313,71

Charge transfer (F)	
incr.	cumul.
0,00	0,00
0,75	0,75
0,74	1,48
0,97	2,45
0,82	3,27
0,51	3,78
1,31	5,09
2,73	7,82
1,22	9,04
1,60	10,64
0,45	11,09
0,61	11,70

Nitrate removal (eq)	
incr.	cumul.
0,00	0,00
0,47	0,47
-0,07	0,40
2,30	2,70
0,84	3,54
0,07	3,61
1,32	4,92
3,00	7,92
2,41	10,33
0,96	11,30
0,16	11,46
0,26	11,72

Power consumption (kWh)	
incr.	cumul.
0	0
0.11	0,11
0,10	0,21
0,14	0,35
0,12	0,47
0,08	0,55
0,20	0,74
0,41	1,16
0,19	1,35
0,28	1,63
0,09	1,72
0,11	1,84

Power consumption (kWh/kg)	
incr.	cumul.
0	0
2,84	2,84
-19,11	6,63
0,76	1,62
1,79	1,66
13,80	1,89
1,87	1,89
1,72	1,83
1,01	1,63
3,65	1,81
6,95	1,88
5,52	1,96

Removal efficiency (%)	
incr.	cumul.
0	0
62	62
-9	27
238	110
103	108
13	95
100	97
110	101
197	114
60	106
37	103
42	100

11.1.2 Experiment 3

Anolyte at start	: $Ca(NO_3)_2$	170 g/l	Catholyte at start	: NH_4NO_3 47 g/l
Anolyte volume	: 41 l		Catholyte volume	: 18,5 l
Charge counter	: 0,0221 Ah/count			

Elapsed time (h)	Charge Counter	Current (A)	Voltage		pH	Cond. (mS/cm)	Nitrate (g/l)
			supply	cell			
0	0	9,00	4,05	3,55	7,57	64,00	36,50
4h40	1 684	9,00	4,20	3,68	9,00	59,20	35,00
9h40	3 518	9,00	4,65	4,15	9,42	52,70	27,30
15h00	5 440	9,00	4,30	3,81	9,45	44,30	15,50
22h20	7 852	7,60	4,90	4,50	9,79	34,10	11,00
27h35	9 738	6,00	4,75	4,20	10,09	25,30	7,28
37h41	12 560	5,00	4,75	4,50	10,90	12,05	4,50
44h21	13 664	3,50	4,75	4,60	12,31	7,06	2,47
51h28	14 334	1,90	4,20	4,00	12,99	9,68	1,14
52h55	14 400	1,30	3,75	3,50	13,15	8,82	0,85

Charge transfer (Ah)	
incr.	cumul.
0,00	0,00
37,24	37,24
40,55	77,79
42,50	120,28
53,33	173,62
41,70	15,32
62,40	277,72
24,41	302,13
14,81	316,94
1,46	318,40

Charge transfer (F)	
incr.	cumul.
0,00	0,00
1,39	1,39
1,51	2,90
1,59	4,49
1,99	6,48
1,56	8,03
2,33	10,36
0,91	11,27
0,55	11,82
0,05	11,88

Nitrate removal (eq)	
incr.	cumul.
0,00	0,00
0,45	0,45
2,30	2,75
3,52	6,27
1,34	7,61
1,11	8,72
0,83	9,55
0,61	10,15
0,40	10,55
0,09	10,64

Power consumption (kWh)	
incr.	cumul.
0	0
0,15	0,15
0,18	0,33
0,19	0,52
0,25	0,77
0,20	0,97
0,30	1,27
0,12	1,38
0,07	1,45
0,01	1,45

Power consumption (kWh/kg)	
incr.	cumul.
0	0
4,29	4,29
0,98	1,52
0,68	1,04
2,28	1,26
2,27	1,39
4,47	1,66
2,39	1,70
2,09	1,72
0,84	1,71

Removal efficiency (%)	
incr.	cumul.
0	0
32	32
152	95
222	140
67	117
71	109
36	92
67	90
72	89
159	90

11.1.3 Experiment 4

Anolyte at start	**: $Ca(NO_3)_2$ 0,05 g/l**	**Catholyte at start**	**: NH_4NO_3 3.3 g/l**
Anolyte volume	**: 19,5 l**	**Catholyte volume**	**: 20,5 l**

Charge counter : 0,0221 Ah/count

Membrane type : IONICS 103QZL

Elapsed time (h)	Charge counter	Current (A)	Voltage supply	Voltage cell	pH	Cond. (mS/cm)	Nitrate (g/l)
0	0	5,30	4,90	4,59	7,80	18,00	14,60
1h45	404	3,60	4,81	4,60	8,40	20,00	13,29
4h41	800	3,20	4,81	4,61	8,70	21,00	12,40
7h36	1 205	2,70	4,81	4,60	8,90	15,00	11,51
10h25	1 503	2,70	4,81	4,65	9,00	18,00	11,07
13h14	1 807	2,70	4,81	4,67	9,10	17,00	10,20

Charge transfer (Ah) incr.	Charge transfer (Ah) cumul.
0,00	0,00
8,80	8,80
8,62	17,42
8,82	26,24
6,49	32,74
6,62	39,36

Charge transfer (F) incr.	Charge transfer (F) cumul.
0,00	0,00
0,33	0,33
0,32	0,65
0,33	0,98
0,24	1,22
0,25	1,47

Nitrate removal (eq) incr.	Nitrate removal (eq) cumul.
0,00	0,00
0,43	0,43
0,29	0,73
0,29	1,02
0,15	1,17
0,29	1,45

Power consumption (kWh) incr.	Power consumption (kWh) cumul.
0	0
0,04	0,04
0,04	0,08
0,04	0,13
0,03	0,16
0,03	0,19

Power consumption (kWh/kg) incr.	Power consumption (kWh/kg) cumul.
0	0
1,23	1,23
1,76	1,45
1,80	1,55
2,68	1,69
1,38	1,63

Removal efficiency (%) incr.	Removal efficiency (%) cumul.
0	0
132	132
91	112
89	104
60	96
116	99

Elapsed time (h)	pH	Cond. (mS/cm)	Nitrate (g/l)	Nitrate arrival (eq)		Transport efficiency (%)	
				incr.	cumul	incr.	cumul
0	12,10	7,50	0,04	0,00	0,00	0,00	0,00
1h45	12,00	7,50	0,93	0,28	0,28	85,27	85,27
4h41	11,90	6,00	1,90	0,31	0,59	94,82	90,00
7h36	11,10	5,50	2,66	0,24	0,82	72,64	84,16
10h25	6,80	6,00	3,19	0,17	0,99	68,84	81,13
13h14	9,90	5,10	5,76	0,81	1,80	326,86	122,47

11.1.4 Experiment 6

Anolyte at start	: $Ca(NO_3)_2$ 6,28 g/l	Catholyte at start	: NH_4NO_3 24.57 g/l
Anolyte volume	: 16,5 l	Catholyte volume	: 38,75 l
Charge counter	: 0,02178 Ah/count		
Membrane type	: IONICS 103QZL		

Elapsed time (h)	Charge Counter	Current (Amps)	Voltage		pH	Cond. (mS/cm)	Nitrate (g/l)	Tank level (mm)	Volume (litres)
			supply	cell					
0	0	3,90	4,84	-	9,40	32,00	19,04	563	38,75
10h52	1 544	3,70	4,90	-	9,50	28,00	16,83	525	36,06
23h26	3 056	4,80	5,46	-	9,70	25,00	14,61	487	33,38
31h35	4 604	5,50	6,19	-	9,80	21,00	12,40	445	30,41
40h48	6 590	5,60	6,54	-	9,90	15,00	8,86	430	29,35
50h48	8 080	5,50	6,69	-	10,90	11,00	6,64	418	28,50
59h27	9 855	4,50	7,24	-	10,2	6,7	2,66	410	27,93
67h12	11 421	1,40	5,61	-	10,9	1,45	0,22	390	26,52

Charge transfer (Ah)	
incr.	cumul.
0,00	0,00
33,63	33,63
32,93	66,56
33,72	100,28
43,26	143,53
32,45	175,98
38,66	214,64
34,11	248,75

Charge transfer (F)	
incr.	cumul.
0,00	0,00
1,25	1,25
1,23	2,48
1,26	3,74
1,61	5,35
1,21	6,57
1,44	8,01
1,27	9,28

Nitrate removal (eq)	
incr.	cumul.
0,00	0,00
1,29	1,29
1,19	2,48
1,09	3,57
1,68	5,24
1,02	6,26
1,80	8,06
1,04	9,10

Power consumption (kWh)	
incr.	cumul.
0	0
0,16	0,16
0,17	0,33
0,20	0,53
0,28	0,81
0,21	1,02
0,27	1,29
0,22	1,51

Power consumption (kWh/kg)	
incr.	cumul.
0	0
1,59	1,59
1,79	1,69
2,26	1,86
2,05	1,92
2,64	2,04
1,87	2,00
2,62	2,07

Removal efficiency (%)	
incr.	cumul.
0	0
103	103
97	100
86	95
104	98
84	95
125	101
82	98

Elapsed time (h)	pH	Cond. (mS/cm)	Nitrate (g/l)	Nitrate arrival (eq)		Transport efficiency (%)		Tank level (mm)	Volume (litres)
				incr.	cumul	incr.	cumul.		
0	11,60	8,50	4,87	0,00	0,00	0	0	280	18,74
10h32	12,20	16,00	8,41	1,01	1,01	80	80	264	17,61
23h26	12,00	18,00	11,96	0,93	1,94	76	78	245	16,26
31h35	8,60	19,00	15,06	0,81	2,75	65	73	245	16,26
40h48	10,00	24,00	19,49	1,16	3,91	72	73	244	16,19
50h48	10,80	28,00	23,47	1,04	4,94	86	75	243	16,12
59h27	12,00	35,00	27,90	1,11	6,05	77	76	235	15,56

11.1.5 Experiment 8

Anolyte at start : $Ca(NO_3)_2$ 6,28 g/l
Anolyte volume : 16,5 l
Charge counter : 0,02178 Ah/count
Membrane type : P.C.I.

Catholyte at start : NH_4NO_3 24.57 g/l
Catholyte volume : 38,75 l

Elapsed time (h)	Charge counter	Current (A)	Voltage supply	Voltage cell	pH	Cond. (mS/cm)	Nitrate (g/l)	Tank level (mm)	Volume (litres)
0	0	16,00	9,69	-	9,40	32,00	15,94	505	34,65
5h32	3 500	16,00	11,29	-	9,50	28,00	11,29	490	33,59
12h48	6 250	12,00	9,76	-	9,70	25,00	7,09	480	32,88
28h42	8 564	6,00	9,67	-	9,80	21,00	2,66	420	28,64
32h43	9 125	4,30	8,45	-	9,90	15,00	1,77	405	27,58
35h19	9 470	3,70	8,51	-	10,90	11,00	0,97	390	26,52

Charge transfer (Ah) incr.	Charge transfer (Ah) cumul.
0,00	0,00
76,23	76,23
59,90	136,13
50,40	186,52
12,22	198,74
7,51	206,26

Charge transfer (F) incr.	Charge transfer (F) cumul.
0,00	0,00
2,84	2,84
2,23	5,08
1,88	6,96
0,46	7,41
0,28	7,69

Nitrate removal (eq) incr.	Nitrate removal (eq) cumul.
0,00	0,00
2,52	2,52
2,23	4,75
2,05	6,80
0,39	7,19
0,34	7,53

Power consumption (kWh) incr.	Power consumption (kWh) cumul.
0	0
0,80	0,80
0,63	1,43
0,49	1,92
0,11	2,03
0,06	2,09

Power consumption (kWh/kg) incr.	Power consumption (kWh/kg) cumul.
0	0
3,97	3,97
3,53	3,76
2,99	3,53
3,51	3,53
2,34	3,48

Removal efficiency (%) incr.	Removal efficiency (%) cumul.
0	0
89	89
100	94
109	98
86	97
122	98

Elapsed time (h)	pH	Cond. (mS/cm)	Nitrate (g/l)	Nitrate arrival (eq)		Transport efficiency (%)		Tank level (mm)	Volume (litres)
				incr.	cumul.	incr.	cumul		
0	12,00	22,00	13,73	0,00	0,00	0,00	0,00	505	34,65
5h32	11,50	24,00	18,16	2,47	2,47	87,03	87,03	505	34,65
12h48	11,90	30,00	22,14	2,20	4,68	98,67	92,15	500	34,30
28h42	11,10	30,00	26,57	2,42	7,10	128,95	102,10	495	33,94
32h43	9,60	30,00	26,57	0,00	7,10	0,00	95,82	490	33,59
35h19	9,00	31,00	26,13	-0,24	6,86	-85,59	89,21	490	33,59

11.2 APPENDIX 2 : Current-Voltage Data

11.2.1 Current-Voltage Data for Experiment 4

Membrane : IONICS 103QZL
Flowrate : Approx. 3.85 l/min

Faradays (F)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	V_c+V_m $+V_a$	Percentage difference (%)
0,33	2	3,54	3,44	1,58	0,47	1,31	3,36	2,33
	3	4,33	4,15	1,89	0,63	1,61	4,13	0,48
	4	5,00	4,76	2,25	0,63	1,89	4,77	0,21
	5	5,66	5,35	2,64	0,52	2,18	5,34	0,19
	6	6,25	5,88	2,85	0,52	2,45	5,82	1,02
	8	7,38	6,84	3,30	0,53	2,98	6,81	0,44
	10	8,52	7,80	3,74	0,82	3,37	7,93	1,67
	12	9,59	8,81	4,04	1,08	3,72	8,84	0,34
	14	10,58	9,68	4,29	1,34	4,06	9,69	0,10
0,65	2	3,72	3,62	1,46	0,61	1,47	3,54	2,21
	3	4,63	4,46	1,98	0,62	1,83	4,43	0,67
	4	5,36	5,16	2,45	0,50	2,14	5,09	1,36
	5	6,01	5,70	2,81	0,48	2,46	5,75	0,88
	6	6,62	6,25	3,09	0,40	2,78	6,27	0,32
	8	7,77	7,28	3,45	0,42	3,36	7,23	0,69
	10	8,92	8,29	3,83	0,66	3,79	8,28	0,12
	12	10,07	9,29	4,11	0,96	4,19	9,26	0,32
	14	11,13	10,23	4,27	1,31	4,60	10,18	0,49
0,98	2	4,04	3,94	1,39	0,81	1,62	3,82	3,05
	3	4,81	4,64	1,76	0,88	1,92	4,56	1,72
	4	5,56	5,33	2,18	0,84	2,28	5,30	0,56
	5	6,31	6,02	2,63	0,73	2,63	5,99	0,50
	6	7,02	6,66	2,99	0,69	2,99	6,67	0,15
	8	8,30	7,82	3,45	0,73	3,62	7,80	0,26
	10	9,56	8,94	3,80	0,97	4,16	8,93	0,11
	12	10,82	10,05	4,10	1,26	4,68	10,04	0,10
	14	11,97	11,06	4,31	1,51	5,23	11,05	0,09

Faradays (F)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	V_c+V_m +V_a	Percentage difference (%)
1,22	2	3,93	3,84	1,37	0,86	1,57	3,8	1,04
	3	4,65	4,49	1,72	0,87	1,87	4,46	0,67
	4	5,40	5,17	2,14	0,82	2,18	5,14	0,58
	5	6,10	5,81	2,55	0,74	2,47	5,76	0,86
	6	6,75	6,40	2,96	0,63	2,75	6,34	0,94
	8	7,93	7,45	3,48	0,68	3,28	7,44	0,13
	10	9,10	8,48	3,85	0,91	3,71	8,47	0,12
	12	10,19	9,44	4,14	1,20	4,09	9,43	0,11
	14	11,28	10,38	4,40	1,49	4,47	10,36	0,19
1,47	2	4,10	4,01	1,36	0,91	1,66	3,93	2,00
	3	4,90	4,74	1,73	0,97	1,97	4,67	1,48
	4	5,70	5,48	2,16	0,98	2,27	5,41	1,28
	5	6,41	6,12	2,57	0,94	2,54	6,05	1,14
	6	7,04	6,67	2,94	0,88	2,81	6,63	0,60
	8	8,27	7,79	3,47	0,96	3,31	7,74	0,64
	10	9,45	8,83	3,91	1,09	3,80	8,80	0,34
	12	10,57	9,82	4,23	1,35	4,24	9,82	0,00
	14	11,68	10,78	4,50	1,59	4,70	10,79	0,09

11.2.2 Current-Voltage Data for Experiment 5

Current-Voltage curves for varying flowrates
Membrane : IONICS 103QZL

Flowrate (l/min)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	V_c+V_m $+V_a$	Percentage difference (%)
1,25	2	3,97	3,84	2,04	-0,08	1,67	3,63	5,47
	4	5,61	5,29	2,88	-0,14	2,53	5,27	0,38
	6	6,95	6,52	3,51	-0,20	3,19	6,50	0,31
	8	8,26	7,68	4,02	-0,06	3,72	7,68	0,00
	10	9,47	8,71	4,44	0,09	4,18	8,71	0,00
	12	10,65	9,76	4,85	0,09	4,68	9,62	1,43
	14	11,82	10,8	5,14	0,54	5,16	10,84	0,37
	16	12,88	11,78	5,46	0,35	5,68	11,49	2,46
2,02	2	3,94	3,82	1,73	-0,19	2,28	3,82	0,00
	4	5,38	5,11	2,65	-0,29	2,75	5,11	0,00
	6	6,63	6,22	3,26	-0,21	3,16	6,21	0,16
	8	7,84	7,28	3,74	-0,08	3,62	7,28	0,00
	10	9,11	8,38	4,17	0,09	4,12	8,38	0,00
	12	10,29	9,41	4,55	0,28	4,63	9,46	0,53
	14	11,42	10,40	4,94	0,25	5,20	10,39	0,10
	16	12,45	11,32	5,24	0,32	5,73	11,29	0,27
3,85	2	4,00	3,90	1,73	-0,21	2,38	3,90	0,00
	4	5,47	5,22	2,65	-0,26	2,83	5,22	0,00
	6	6,66	6,29	3,21	-0,08	3,18	6,31	0,32
	8	7,87	7,36	3,65	0,12	3,58	7,35	0,14
	10	9,09	8,45	4,04	0,38	4,03	8,45	0,00
	12	10,24	9,44	4,35	0,61	4,48	9,44	0,00
	14	11,33	10,36	4,62	0,87	4,94	10,43	0,68
	16	12,43	11,30	4,78	1,15	5,40	11,33	0,27
5,20	2	3,92	3,83	1,39	0,13	2,30	3,82	0,26
	4	5,32	5,08	2,05	0,34	2,70	5,09	0,20
	6	6,57	6,20	2,65	0,46	3,07	6,18	0,32
	8	7,73	7,24	3,20	0,53	3,49	7,22	0,28
	10	8,92	8,28	3,72	0,58	3,94	8,24	0,48
	12	10,06	9,28	4,14	0,67	4,41	9,22	0,65
	14	11,15	10,20	4,43	0,77	4,86	10,06	1,37
	16	12,27	11,15	4,81	1,05	5,33	11,19	0,36
2,02	2	3,98	3,88	1,52	0,02	2,36	3,90	0,52
	4	5,37	5,13	2,34	0,03	2,74	5,11	0,39
	6	6,59	6,22	2,98	0,10	3,11	6,19	0,48
	8	7,75	7,24	3,57	0,16	3,47	7,20	0,55
	10	8,87	8,22	3,99	0,44	3,86	8,29	0,85
	12	10,02	9,23	4,36	0,52	4,32	9,20	0,33
	14	11,15	10,16	4,65	0,74	4,77	10,16	0,00
	16	12,23	11,10	4,88	1,03	5,24	11,15	0,45

11.2.3 Current-Voltage Data for Experiment 6

Flowrate : Approx. 3,85 l/min
Membrane : IONICS 103QZL

Faradays (F)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	$V_c+V_m+V_a$	Percentage difference (%)
0	2	3,53	3,42	1,74	0,08	1,55	3,37	-1,46
	4	4,95	4,68	2,19	0,63	2,27	5,09	8,76
	6	6,06	5,65	2,6	0,63	2,93	6,16	9,03
	8	7,09	6,54	2,91	0,52	3,4	6,83	4,43
	10	8,16	7,47	3,23	0,52	3,82	7,57	1,34
	12	9,09	8,27	3,54	0,53	4,17	8,24	-0,36
	16	10,98	9,9	3,9	0,82	5,03	9,75	-1,52
	20	12,75	11,39	4,17	1,08	5,83	11,08	-2,72
1,25	2	3,42	3,32	1	0,8	1,49	3,29	-0,90
	4	4,66	4,42	1,72	0,58	2,1	4,4	-0,45
	6	5,91	5,55	2,58	0,28	2,68	5,54	-0,18
	8	6,98	6,48	3,1	0,39	3,02	6,51	0,46
	10	8	7,35	3,44	0,58	3,34	7,36	0,14
	12	8,9	8,11	3,7	0,74	3,67	8,11	0,00
	16	10,6	9,52	4,09	1,08	4,35	9,52	0,00
	20	12,02	10,7	4,35	1,48	4,85	10,68	-0,19
2,48	2	3,44	3,35	0,97	0,78	1,59	3,34	-0,30
	4	4,66	4,43	1,68	0,62	2,13	4,43	0,00
	6	5,8	5,45	2,43	0,44	2,58	5,45	0,00
	8	6,98	6,51	3,04	0,51	2,93	6,48	-0,46
	10	8	7,4	3,41	0,69	3,28	7,38	-0,27
	12	8,96	8,24	3,7	0,82	3,68	8,2	-0,49
	16	10,6	9,62	4,16	1,11	4,35	9,62	0,00
	20	12,31	11	4,54	1,46	4,95	10,95	-0,45
3,74	2	3,85	3,76	1,31	0,81	1,64	3,76	0,00
	4	5,27	5,03	2,25	0,57	2,2	5,02	-0,20
	6	6,4	6,03	2,95	0,38	2,7	6,03	0,00
	8	7,44	6,96	3,35	0,48	3,11	6,94	-0,29
	10	8,58	7,95	3,72	0,66	3,56	7,94	-0,13
	12	9,58	8,83	4,01	0,84	3,99	8,84	0,11
	16	11,46	10,43	4,45	1,23	4,73	10,41	-0,19
	20	13,07	11,77	4,8	1,69	5,24	11,73	-0,34
5,35	2	3,96	3,87	1,35	0,68	1,81	3,84	-0,78
	4	5,42	5,2	2,27	0,59	2,27	5,13	-1,35
	6	6,66	6,3	3,1	0,39	2,82	6,31	0,16
	8	7,85	7,37	3,63	0,51	3,26	7,4	0,41
	10	9,07	8,46	4,12	0,72	3,68	8,52	0,71
	12	10,24	9,48	4,48	0,93	4,05	9,46	-0,21
	16	12,21	11,2	5	1,46	4,73	11,19	-0,09
	20	13,93	12,66	5,44	1,98	5,26	12,68	0,16

Faradays (F)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	V_c+V_m $+V_a$	Percentage difference (%)
6,57	2	4,04	3,96	1,39	0,62	1,95	3,96	0,00
	4	5,68	5,48	2,43	0,7	2,38	5,51	0,55
	6	6,91	6,6	3,29	0,31	2,99	6,59	-0,15
	8	8,2	7,79	3,96	0,59	3,3	7,85	0,77
	10	9,6	9,06	4,54	0,77	3,9	9,21	1,66
	12	10,83	10,2	4,97	0,99	4,34	10,3	0,98
	16	12,98	12,12	5,63	1,52	4,95	12,1	-0,17
	20	14,96	13,87	6,23	2,02	5,06	13,31	-4,04
8,01	2	4,69	4,6	2,13	0,45	2,04	4,62	0,43
	4	6,57	6,38	3,48	0,43	2,42	6,33	-0,78
	6	8,47	8,17	4,53	0,58	3,09	8,2	0,37
	8	10,33	9,93	5,32	0,87	3,74	9,93	0,00
	10	12,78	12,25	6,3	1,33	4,65	12,28	0,24
	12	14,82	14,2	7,09	2,08	5,09	14,26	0,42
9,28	1	4,56	4,53	2,19	0,66	1,67	4,52	-0,22
	2	6,62	6,54	3,66	0,96	1,92	6,54	0,00
	4	11,42	11,22	6,47	1,79	3,01	11,27	0,45
	6	15,49	15,18	8,92	2,36	3,85	15,13	-0,33
	8	19,26	18,85	11,22	3,2	4,45	18,87	0,11
	10	23,64	23,13	13,59	4,6	4,95	23,14	0,04

11.2.4 Current-Voltage Data for Experiment 7

Current-Voltage curves for varying flowrates
Membrane : PERMAPLEX SB

Flowrate (l/min)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	V_c+V_m $+V_a$	Percentage difference (%)
0,7	2	3,76	3,68	1,83	0,41	1,42	3,66	-0,54
	4	4,83	4,64	2,26	0,68	1,68	4,62	-0,43
	6	5,96	5,65	2,82	0,81	2,01	5,64	-0,18
	8	7,14	6,71	3,20	1,10	2,34	6,64	-1,04
	10	8,20	7,68	3,58	1,31	2,73	7,62	-0,78
	12	9,25	8,62	4,15	1,25	3,14	8,54	-0,93
	16	11,12	10,23	4,28	2,34	3,73	10,35	1,17
	20	12,46	11,38	5,38	2,45	4,07	11,9	4,57
	24	13,70	12,35	4,90	2,41	4,32	11,63	-5,83
1,70	2	3,56	3,48	1,12	0,70	1,67	3,49	0,29
	4	4,52	4,31	1,68	0,79	1,81	4,28	-0,70
	6	5,27	4,97	2,17	0,83	1,92	4,92	-1,01
	8	6,05	5,64	2,63	0,88	2,11	5,62	-0,35
	10	6,90	6,37	2,92	1,10	2,36	6,38	0,16
	12	7,71	7,07	3,16	1,31	2,62	7,09	0,28
	16	9,29	8,43	3,48	1,83	3,10	8,41	-0,24
	20	11,00	9,91	4,02	2,33	3,67	10,02	1,11
	24	12,58	11,25	4,36	2,55	4,14	11,05	-1,78
2,72	2	3,52	3,44	1,10	0,55	1,81	3,46	0,58
	4	4,44	4,24	1,70	0,65	1,91	4,26	0,47
	6	5,21	4,90	2,16	0,73	2,02	4,91	0,20
	8	5,98	5,57	2,64	0,77	2,17	5,58	0,18
	10	6,79	6,27	2,95	0,89	2,39	6,23	-0,64
	12	7,58	6,94	3,33	0,98	2,61	6,92	-0,29
	16	9,05	8,19	3,87	1,28	3,02	8,17	-0,24
	20	10,56	9,48	4,34	1,52	3,53	9,39	-0,95
	24	12,06	10,74	4,85	1,90	3,99	10,74	0,00
3,85	2	3,41	3,34	1,02	0,36	1,96	3,34	0,00
	4	4,46	4,26	1,75	0,47	2,12	4,34	1,88
	6	5,32	5,01	2,29	0,48	2,25	5,02	0,20
	8	6,11	5,69	2,77	0,53	2,37	5,67	-0,35
	10	6,91	6,37	3,07	0,79	2,53	6,39	0,31
	12	7,68	7,04	3,37	0,91	2,71	6,99	-0,71
	16	9,16	8,31	3,89	1,35	3,10	8,34	0,36
	20	10,63	9,55	4,37	1,65	3,54	9,56	0,10
	24	12,05	10,72	4,73	1,95	3,97	10,65	-0,65

11.2.5 Current-Voltage Data for Experiment 8

Flowrate : Approx. 3.85 l/min
Membrane : PERMAPLEX SB

Faradays (F)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	V_c+V_m $+V_a$	Percentage difference (%)
0	2	3,81	3,72	1,64	0,25	1,84	3,73	0,27
	4	4,87	4,65	1,97	0,28	2,40	4,65	0,00
	6	5,74	5,42	2,21	0,29	2,93	5,43	0,18
	8	6,65	6,21	2,41	0,34	3,48	6,23	0,32
	12	8,40	7,74	2,72	0,50	4,54	7,76	0,26
	16	10,14	9,25	3,00	0,59	5,68	9,27	0,22
	20	11,77	10,65	3,27	0,66	6,72	10,65	0,00
	24	13,14	11,76	3,56	0,80	7,39	11,75	-0,09
	28	14,23	12,6	3,86	0,90	7,80	12,56	-0,32
2,84	2	3,30	3,23	0,79	0,38	2,09	3,26	0,93
	4	4,54	4,31	1,30	0,65	2,39	4,34	0,70
	6	5,63	5,27	1,94	0,39	2,96	5,29	0,38
	8	6,77	6,27	2,38	0,43	3,47	6,28	0,16
	12	9,06	8,29	2,80	0,57	4,94	8,31	0,24
	16	11,29	10,24	3,11	0,65	6,49	10,25	0,10
	20	13,12	11,77	3,44	0,79	7,51	11,74	-0,25
	24	14,39	12,82	3,80	0,96	8,02	12,78	-0,31
	28	15,60	13,76	4,22	1,11	8,43	13,76	0,00
5,08	2	3,67	3,58	1,06	0,39	2,14	3,59	0,28
	4	5,15	4,92	1,82	0,57	2,59	4,98	1,22
	6	6,72	6,36	2,56	0,58	3,33	6,47	1,73
	8	8,16	7,68	2,84	0,59	4,24	7,67	-0,13
	12	11,14	10,38	3,37	0,73	6,32	10,42	0,39
	16	13,59	12,56	3,98	1,01	7,63	12,62	0,48
	20	15,41	14,14	4,56	1,30	8,29	14,15	0,07
	24	17,06	15,52	5,23	1,58	8,76	15,57	0,32
	28	18,79	17,02	5,88	2,02	9,20	17,1	0,47
6,96	2	4,66	4,55	1,84	0,46	2,23	4,53	-0,44
	4	6,93	6,69	2,97	0,42	3,30	6,69	0,00
	6	9,26	8,88	3,58	0,64	4,72	8,94	0,68
	8	11,65	11,16	4,15	1,14	6,00	11,29	1,16
	12	16,10	15,30	5,48	1,78	8,16	15,42	0,78
	16	19,55	18,52	6,98	2,54	9,12	18,64	0,65
	20	23,04	21,83	8,47	4,04	9,84	22,35	2,38

Faradays (F)	Current (A)	Power Supply (V_{ps})	Cell potential (V_{cell})	Catholyte potential (V_c)	Membrane potential (V_m)	Anolyte potential (V_a)	$V_c+V_m+V_a$	Percentage difference (%)
7,41	2	5,17	5,07	2,3	0,44	2,32	5,06	-0,20
	4	8,05	7,81	3,58	0,47	3,78	7,83	0,26
	6	11,11	10,75	4,44	1,15	5,24	10,83	0,74
	8	14,65	14,15	5,3	1,91	7,08	14,29	0,99
	12	20,1	19,4	7,45	3,12	9	19,57	0,88
7,69	2	5,65	5,53	2,83	0,32	2,37	5,52	-0,18
	4	9,35	9,13	4,39	0,69	4,12	9,2	0,77
	6	13,6	13,21	5,7	1,71	5,9	13,31	0,76
	8	17,7	17,2	7,04	2,53	7,72	17,29	0,52
	11	23,94	23,1	9,44	4,74	9,07	23,25	0,65

11.3 Appendix 3 : Specifications for Electrolysis Cell and Membranes

11.3.1 Electrolytic Cell Specifications

Item	Material	Quantity
Internal manifold formers	Polypropylene	4
Turbulence promoting spacers	Polyethylene mesh	2
Anion Membrane	Ionics 103QZL or Permaplex SB	1
Cathode	Stainless steel (Type 304)	1
Anode	DSA coated Titanium	1
Facing Plates	uPVC	2
Gaskets	Natural rubber	2
Strongbacks	Coated Mild Steel	2
Securing Studs	Stainless steel	4
Nuts and Washers	Stainless steel	8

General Dimensions and Specifications

Active Area	0,0125 m^2
Compartment Thickness	1,6 mm
Recommended Flowrate	3,85 ℓ/min
Recommended Securing Nut Torque	25 N.m

11.3.2 Permaplex SB Anion Exchange Membrane Specifications

Name	Permaplex SB
Class	Anion exchange membrane
Type	Strongly basic anion permeable
Electrical resistance	2,7 to 3,5 Ohm/cm^2 with 0,5 N $NaCl$
Thickness	0,15 to 0,17 mm
Exchange capacity	1,5 to 2,0 meq/g as dry resin
Effective membrane area	0,0125 m^2

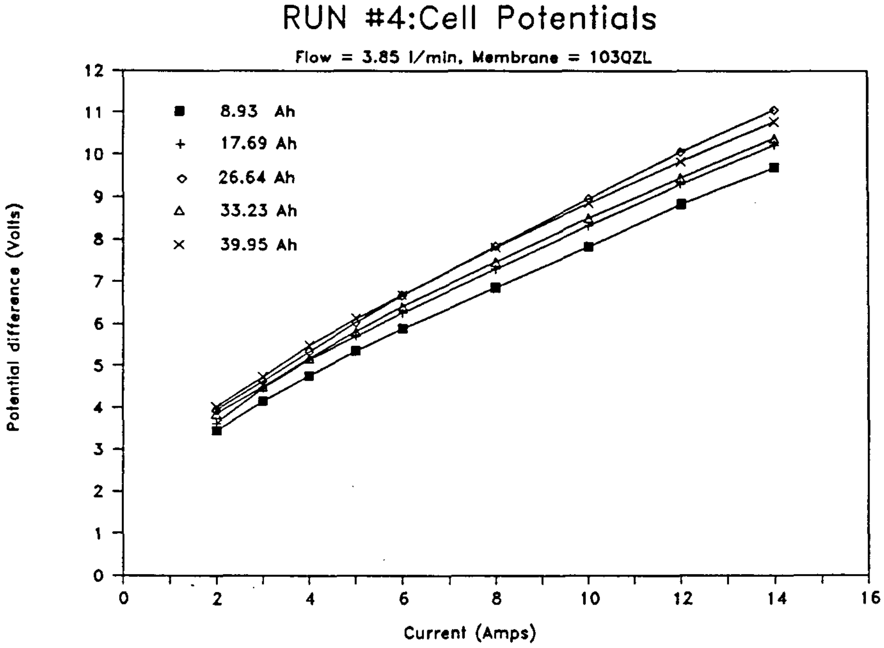
11.3.3 Ionics 103QZL Anion Exchange Membrane Specifications

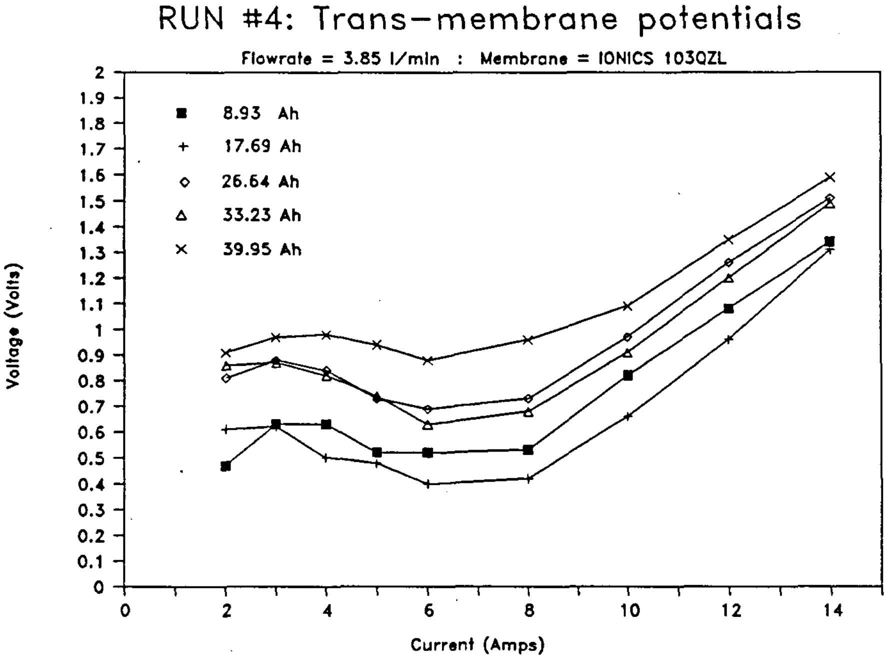
Name	Ionics 103-QZL-386
Class	Anion exchange membrane
Type	Cross-linked co-polymer of vinyl monomers with quaternary ammonium anion exchange groups.
Electrical resistance	9 Ohm.cm^2 in 0,1 N $NaCl$ 4 Ohm.cm2 in 1,0 N $NaCl$
Thickness	0,63 mm
Exchange capacity	2.1 meq/gram as dry resin
Effective membrane area	0,0125 m^2

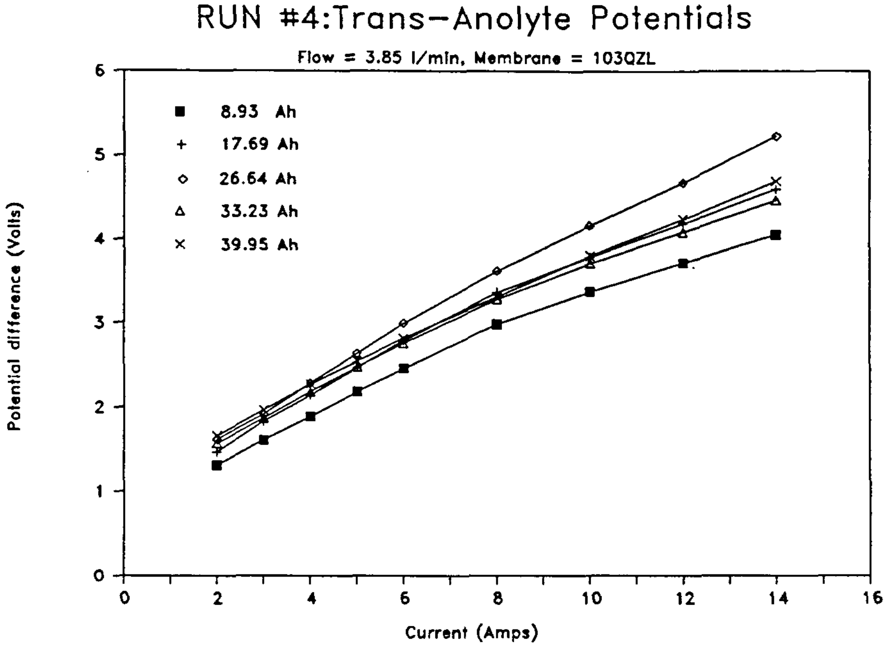
11.4 Appendix 4 : Current-Voltage Curves

11.4.1 Current-Voltage Curves for Experiment 4

Membrane Type : IONICS 103QZL

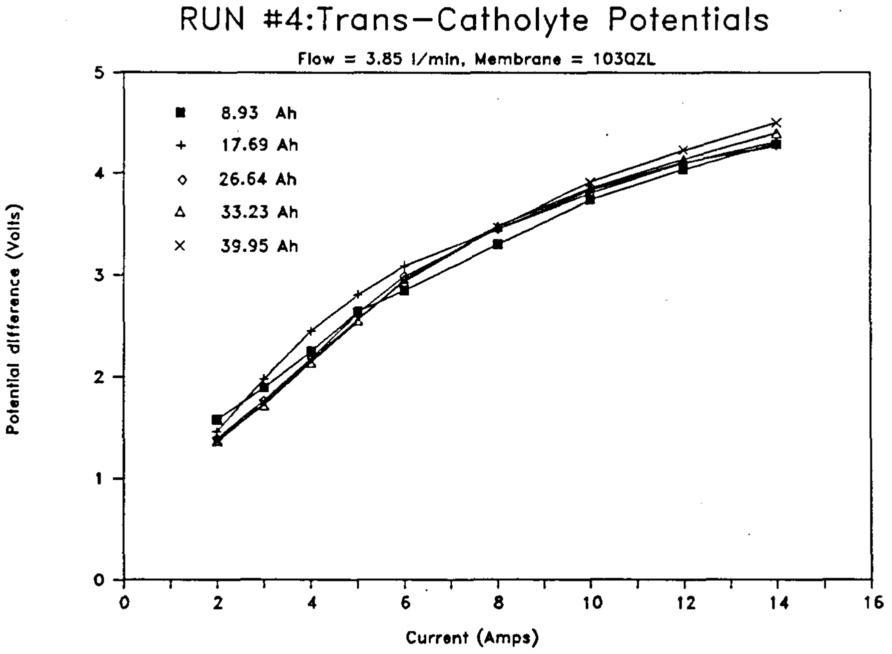






RUN #4:Trans-Anolyte Potentials

Flow = 3.85 l/min, Membrane = 103QZL

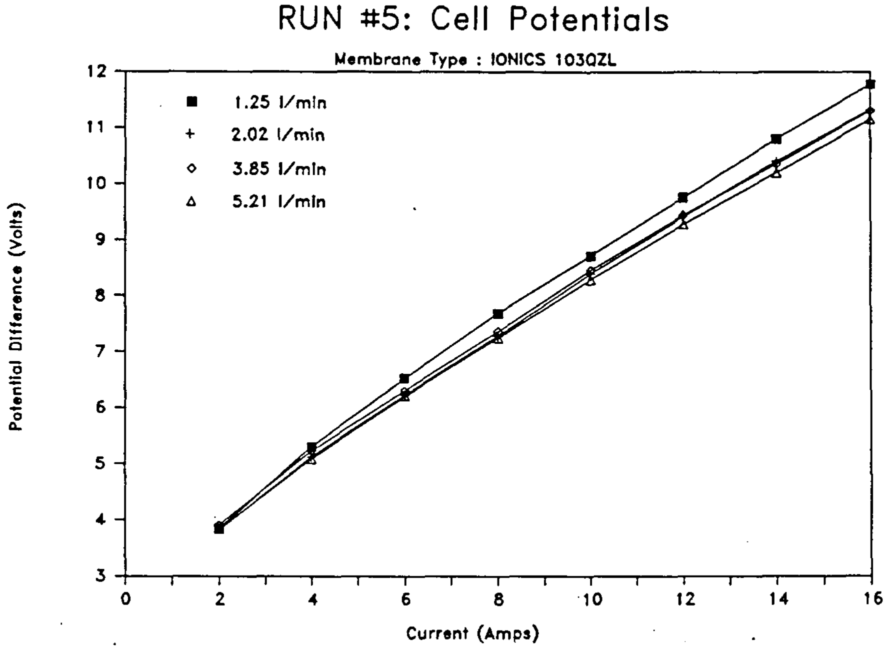


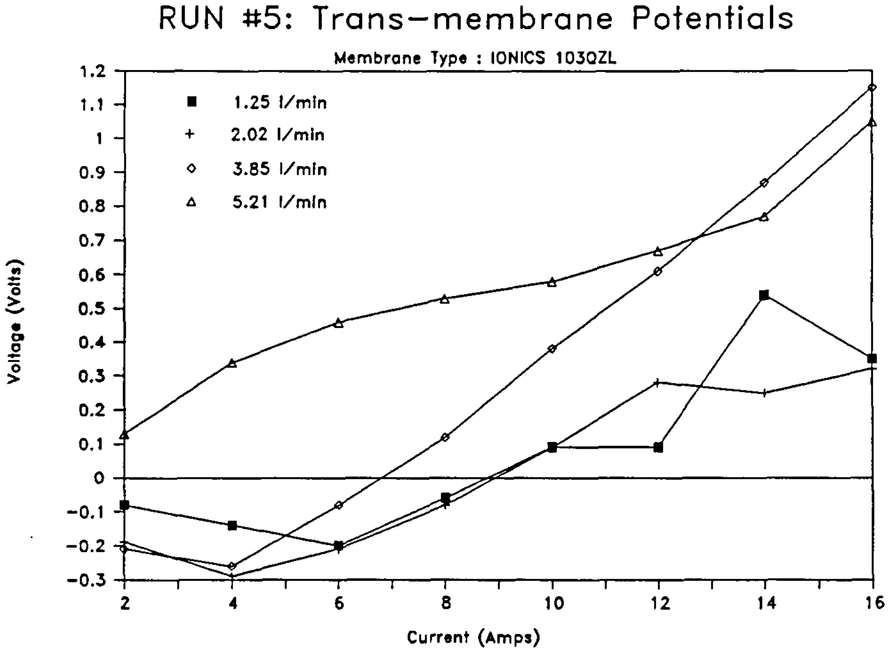
RUN #4:Trans-Catholyte Potentials

Flow = 3.85 l/min, Membrane = 103QZL

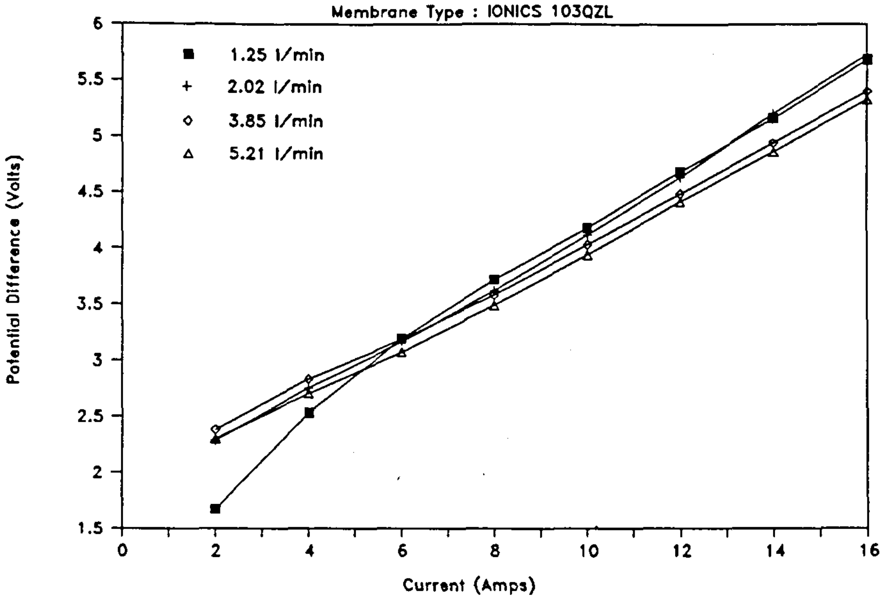
11.4.2 Current-Voltage Plots for Experiment 5

Membrane Type : IONICS 103QZL

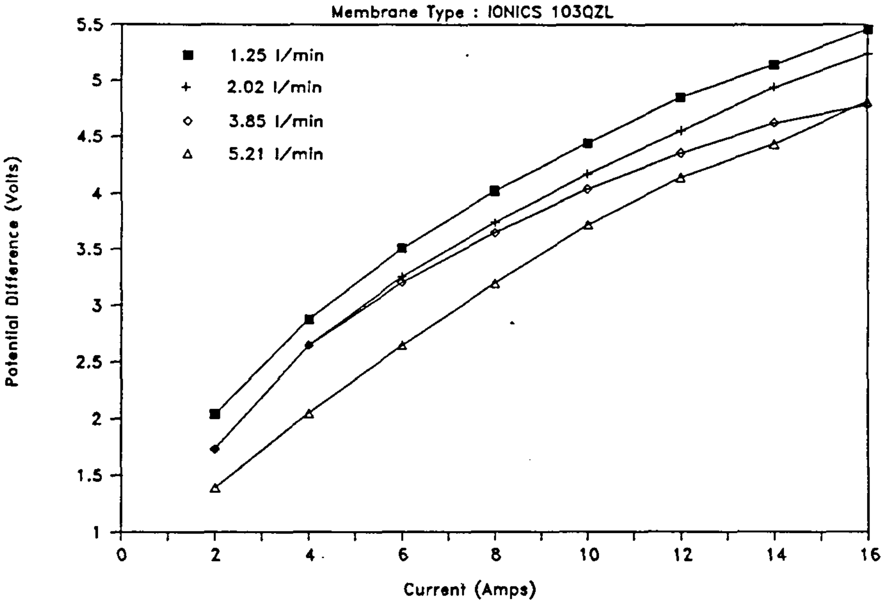




RUN #5: Trans–anolyte Potentials

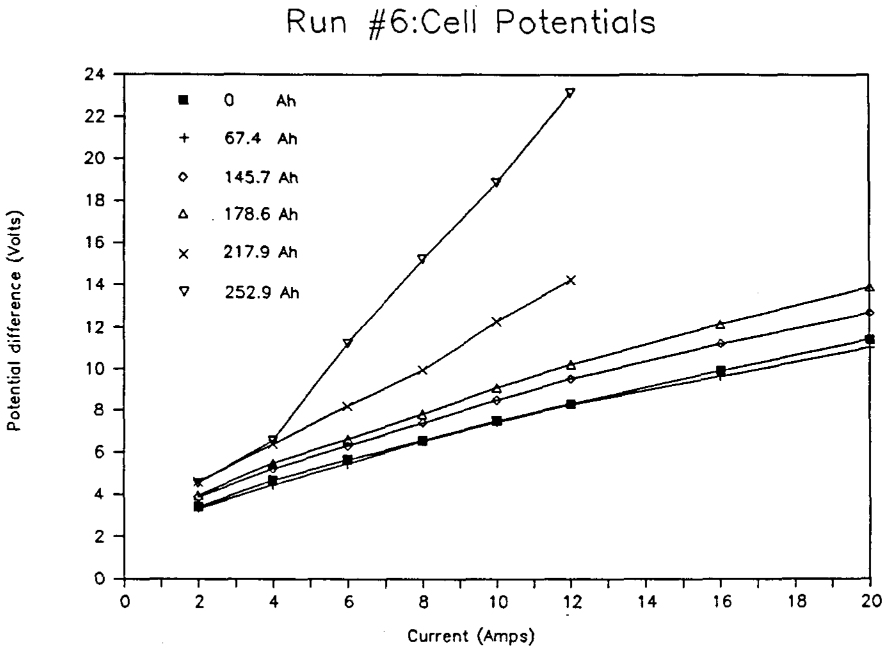


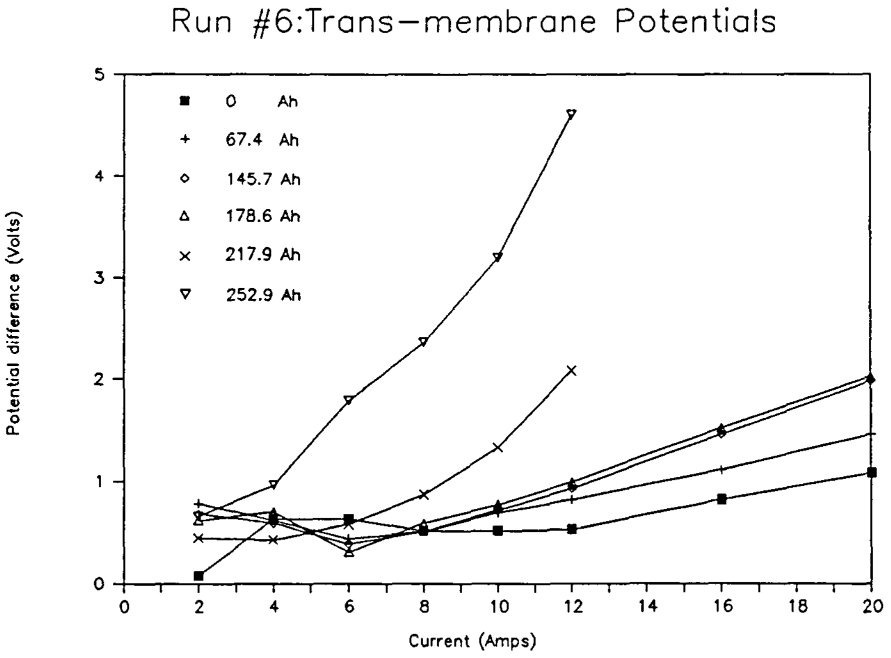
RUN #5: Trans–catholyte Potentials



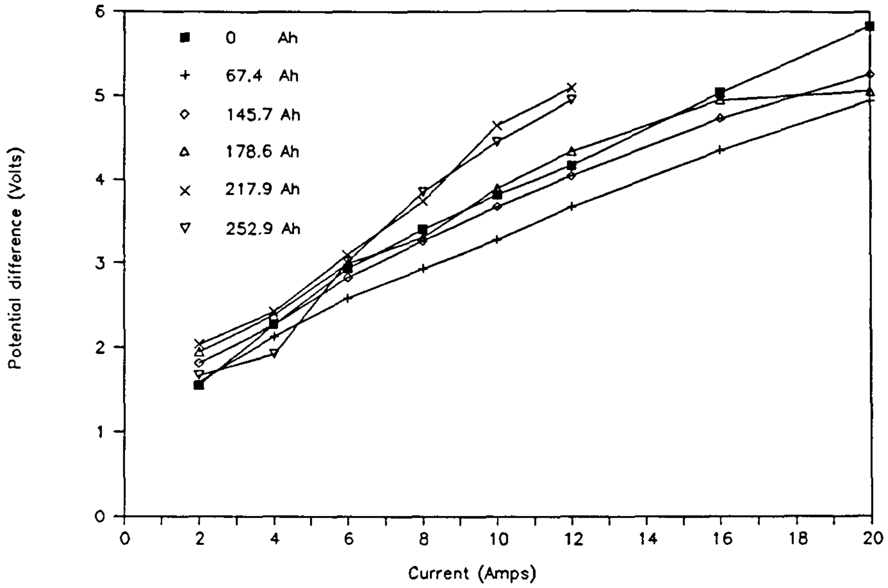
11.4.3 Current-Voltage Plots for Experiment 6

Membrane Type : IONICS 103QZL

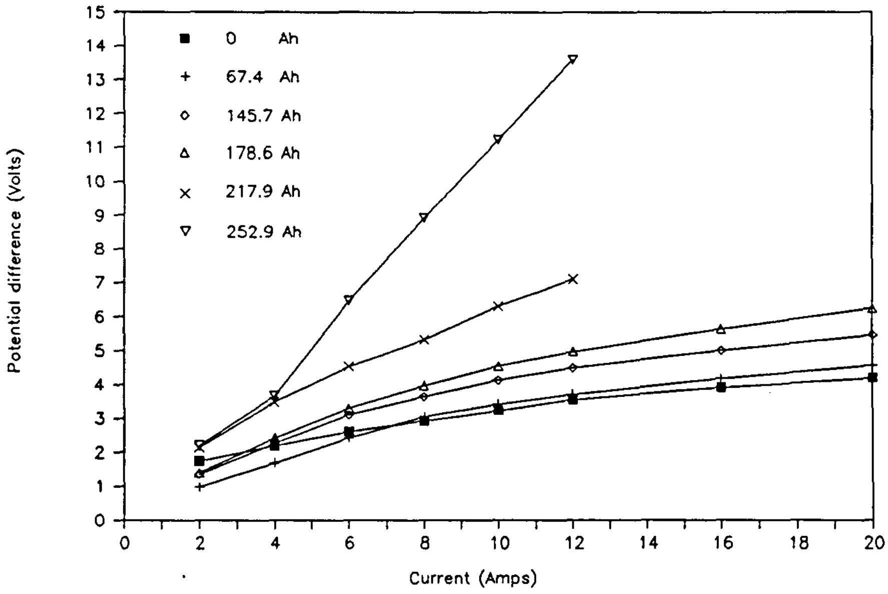




Run #6:Trans-anolyte Potentials

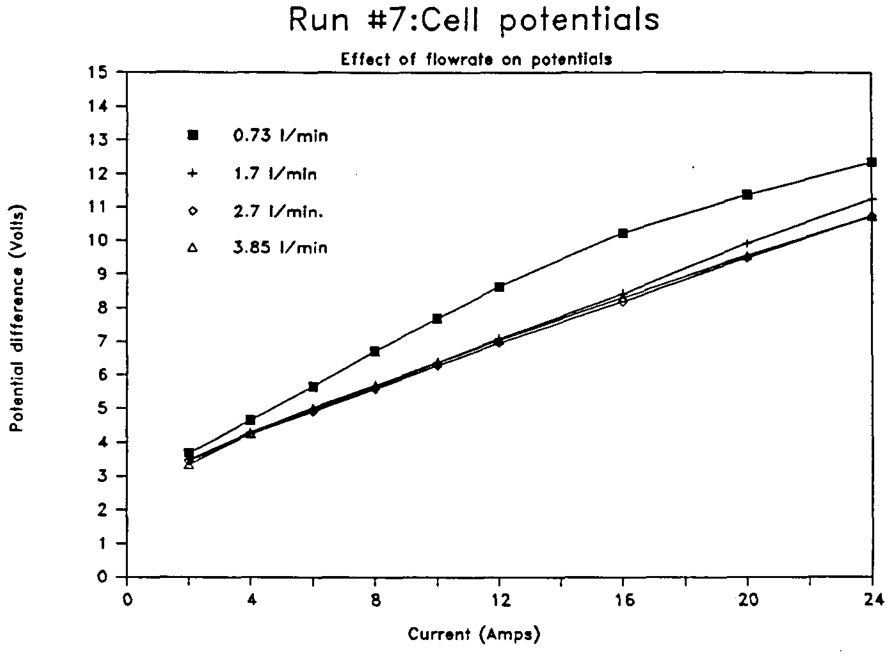


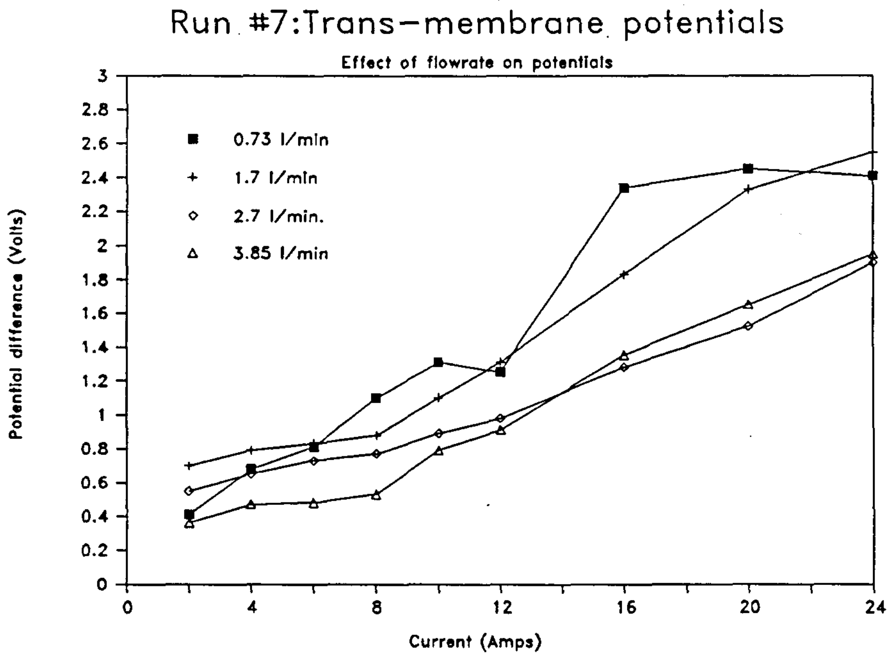
Run #6:Trans-catholyte Potentials

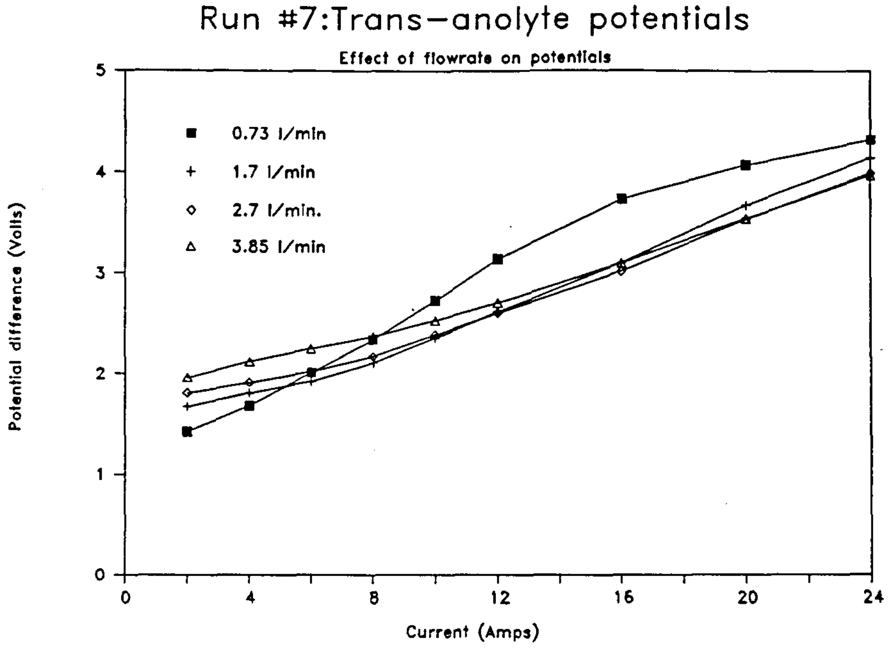


11.4.4 Current-Voltage Plots for Experiment 7

Membrane Type : PERMAPLEX SB

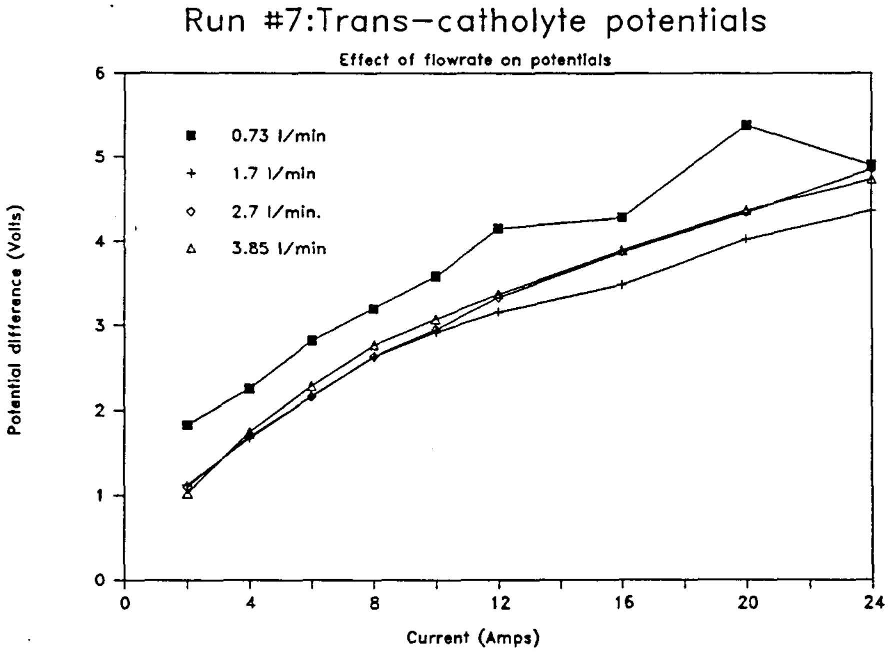






Run #7:Trans-anolyte potentials

Effect of flowrate on potentials

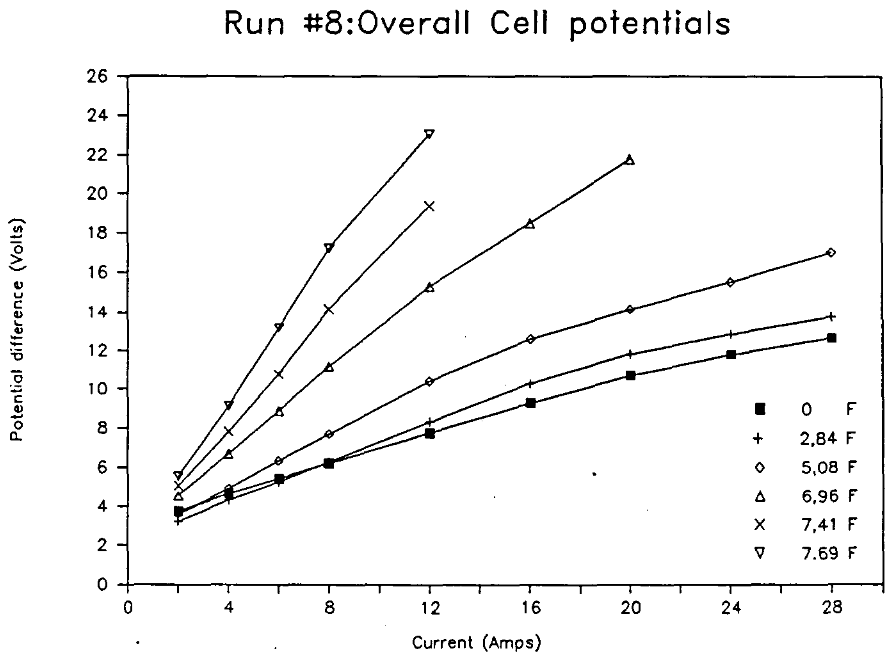


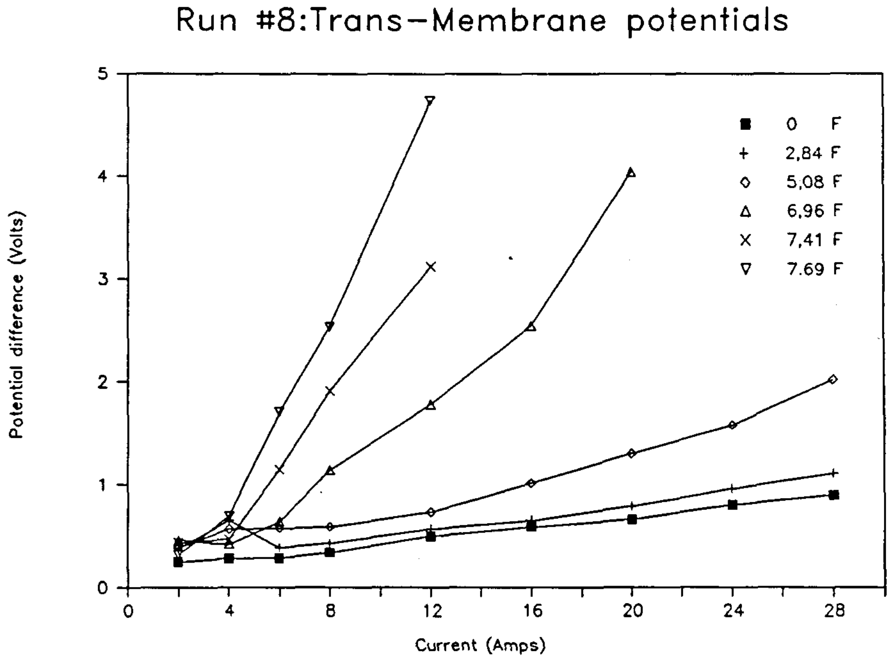
Run #7:Trans-catholyte potentials

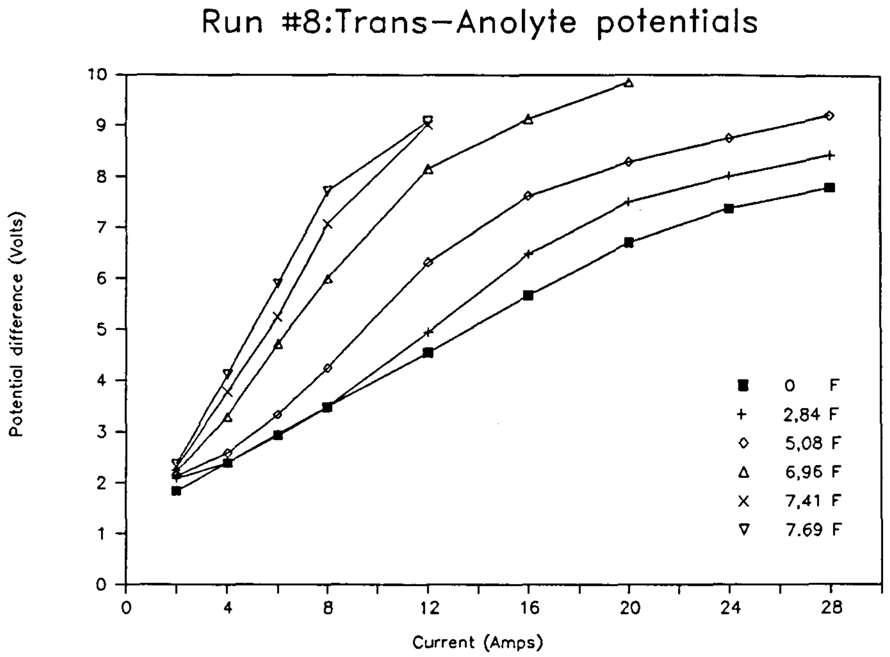
Effect of flowrate on potentials

11.4.5 Current-Voltage Plots for Experiment 8

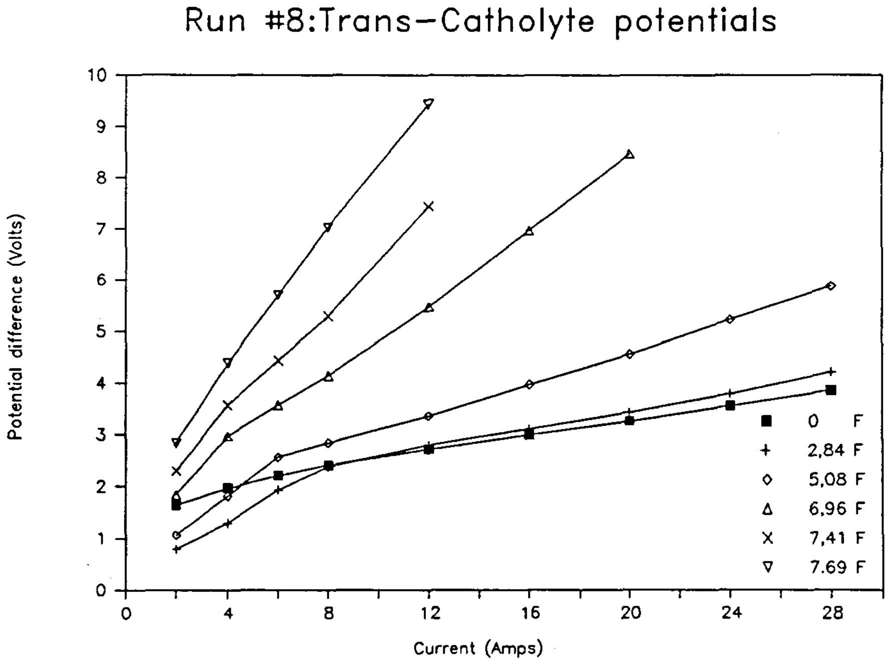
Membrane Type : PERMAPLEX SB







Run #8:Trans-Anolyte potentials



Run #8:Trans-Catholyte potentials

11.5 APPENDIX 5 : Results of Volt-drop modelling

11.5.1 Experiment 4

Charge (F)	8,80	17,40	26,20	32,70	39,40
	Cathode potentials $E_{cathode}$				
	0,73	0,71	0,70	0,70	0,69
Current (Amps)	Resistive Volt drops $\Delta V_{catholyte}$				
2	0,13	0,12	0,17	0,14	0,15
3	0,19	0,18	0,26	0,21	0,23
4	0,26	0,24	0,34	0,28	0,30
5	0,32	0,30	0,43	0,35	0,38
6	0,38	0,36	0,51	0,43	0,45
8	0,51	0,49	0,68	0,57	0,60
10	0,64	0,61	0,85	0,71	0,75
12	0,77	0,73	1,02	0,85	0,90
14	0,89	0,85	1,19	0,99	1,05
	Cathode overpotentials $\eta_{cathode}$				
2	0,72	0,62	0,52	0,53	0,52
3	0,97	1,08	0,80	0,81	0,81
4	1,26	1,49	1,14	1,16	1,17
5	1,59	1,79	1,50	1,50	1,50
6	1,74	2,01	1,78	1,84	1,80
8	2,06	2,25	2,07	2,22	2,18
10	2,37	2,51	2,25	2,44	2,47
12	2,54	2,67	2,38	2,59	2,64
14	2,67	2,71	2,42	2,71	2,76

Charge (F)	8,80	17,40	26,20	32,70	39,40
	Anode potentials E_{anode}				
	0,52	0,53	0,57	0,83	0,64
Current (Amps)	**Resistive Volt drops** $\Delta V_{anolyte}$				
2	0,34	0,43	0,46	0,43	0,50
3	0,51	0,64	0,70	0,64	0,75
4	0,68	0,85	0,93	0,85	1,00
5	0,85	1,06	1,16	1,06	1,25
6	1,02	1,28	1,39	1,28	1,50
8	1,36	1,70	1,86	1,70	2,00
10	1,70	2,13	2,32	2,13	2,50
12	2,04	2,55	2,78	2,55	3,00
14	2,38	2,98	3,25	2,98	3,50
	Anode overpotentials η_{anode}				
2	0,45	0,52	0,58	0,32	0,52
3	0,58	0,67	0,65	0,41	0,58
4	0,69	0,76	0,78	0,50	0,63
5	0,81	0,87	0,90	0,58	0,65
6	0,91	0,98	1,03	0,65	0,67
8	1,10	1,13	1,19	0,75	0,67
10	1,15	1,14	1,27	0,76	0,66
12	1,16	1,11	1,32	0,71	0,60
14	1,16	1,10	1,41	0,67	0,56

11.5.2 Experiment 6

Charge (F)	0,00	1,25	2,48	3,74	5,35	6,57	8,01
	Cathode Potentials $E_{cathode}$						
	0,67	0,67	0,66	0,65	0,64	0,58	0,63
Current (Amps)	Resistive Volt drops $\Delta V_{catholyte}$						
2	0,08	0,09	0,10	0,12	0,17	0,23	0,38
4	0,16	0,18	0,20	0,24	0,34	0,46	0,76
6	0,24	0,27	0,31	0,36	0,51	0,70	1,14
8	0,32	0,36	0,41	0,49	0,68	0,93	1,52
10	0,40	0,46	0,51	0,61	0,85	1,16	1,90
12	0,48	0,55	0,61	0,73	1,02	1,39	2,28
16	0,64	0,73	0,82	0,97	1,36	1,86	3,05
20	0,80	0,91	1,02	1,21	1,70	2,32	3,81
	Cathode Overpotentials $\eta_{cathode}$						
2	0,99	0,24	0,21	0,54	0,54	0,57	1,12
4	1,36	0,87	0,82	1,36	1,29	1,38	2,09
6	1,69	1,64	1,47	1,94	1,95	2,01	2,76
8	1,92	2,07	1,98	2,21	2,31	2,45	3,17
10	2,16	2,32	2,24	2,46	2,63	2,80	3,77
12	2,39	2,49	2,43	2,63	2,82	2,99	4,18
16	2,59	2,69	2,69	2,83	3,00	3,19	
20	2,70	2,77	2,86	2,94	3,10	3,33	

Charge (F)	0,00	1,25	2,48	3,74	5,35	6,57	8,01
	Anode Potentials E_{anode}						
	0,69	0,72	0,71	0,51	0,59	0,64	0,71
Current (Amps)	Resistive Volt drops $\Delta V_{anolyte}$						
2	0,30	0,16	0,14	0,13	0,11	0,09	0,07
4	0,60	0,32	0,28	0,27	0,21	0,18	0,15
6	0,90	0,48	0,43	0,40	0,32	0,27	0,22
8	1,20	0,64	0,57	0,54	0,43	0,36	0,29
10	1,50	0,80	0,71	0,67	0,53	0,46	0,36
12	1,80	0,96	0,85	0,81	0,64	0,55	0,44
16	2,40	1,28	1,13	1,07	0,85	0,73	0,58
20	3,00	1,59	1,42	1,34	1,06	0,91	0,73
	Anode Overpotentials η_{anode}						
2	0,56	0,61	0,74	1,00	1,11	1,22	1,26
4	0,98	1,06	1,14	1,42	1,47	1,56	1,56
6	1,34	1,48	1,45	1,79	1,91	2,08	2,16
8	1,51	1,66	1,65	2,06	2,24	2,30	2,74
10	1,63	1,82	1,86	2,38	2,56	2,81	3,58
12	1,68	1,99	2,12	2,68	2,82	3,15	3,94
16	1,94	2,35	2,51	3,15	3,29	3,58	
20	2,14	2,53	2,82	3,39	3,61	3,51	

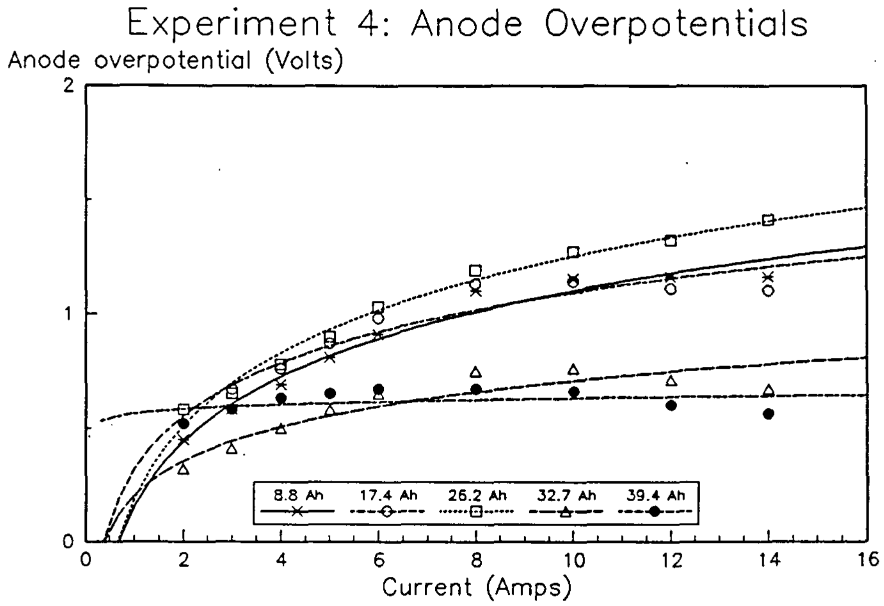
11.5.3 Experiment 8

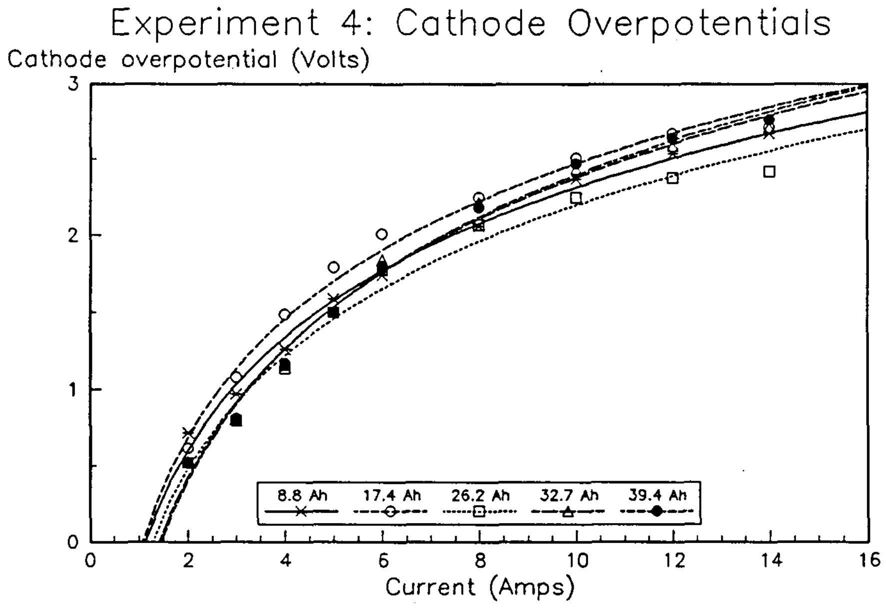
Charge (F)	0,00	2,84	5,08	6,96	7,41	7.69
	Cathode Potentials $E_{cathode}$					
	0,67	0,67	0,66	0,65	0,64	0,58
Current (Amps)	Resistive Volt drops $\Delta V_{catholyte}$					
2	0,08	0,09	0,10	0,12	0,17	0,23
4	0,16	0,18	0,20	0,24	0,34	0,46
6	0,24	0,27	0,31	0,36	0,51	0,70
8	0,32	0,36	0,41	0,49	0,68	0,93
12	0,48	0,55	0,61	0,73	1,02	1,39
16	0,64	0,73	0,82	0,97	1,36	1,86
20	0,80	0,91	1,02	1,21	1,70	2,32
24	0,96	1,09	1,22	1,46	2,04	2,78
28	1,12	1,28	1,43	1,70	2,38	3,25
	Cathode Overpotentials $\eta_{cathode}$					
2	0,89	0,03	0,30	1,07	1,49	2,01
4	1,14	0,45	0,96	2,08	2,60	3,34
6	1,30	1,00	1,60	2,57	3,29	4,42
8	1,42	1,35	1,78	3,01	3,98	5,53
12	1,57	1,59	2,10	4,10	5,79	7,46
16	1,69	1,71	2,51	5,36		
20	1,80	1,86	2,88	6,61		
24	1,93	2,04	3,35			
28	2,07	2,28	3,80			

Charge (F)	0,00	2,84	5,08	6,96	7,41	7.69
	Anode Potentials E_{anode}					
	0,52	0,55	0,53	0,57	0,66	0,70
Current (Amps)	Resistive Volt drops $\Delta V_{anolyte}$					
2	0,12	0,11	0,09	0,09	0,09	0,08
4	0,23	0,21	0,17	0,17	0,17	0,16
6	0,35	0,32	0,26	0,26	0,26	0,25
8	0,46	0,43	0,34	0,34	0,34	0,33
12	0,70	0,64	0,51	0,51	0,51	0,49
16	0,93	0,85	0,68	0,68		
20	1,16	1,06	0,85	0,85		
24	1,39	1,28	1,02			
28	1,62	1,49	1,19			
	Anode Overpotentials η_{anode}					
2	1,20	1,43	1,53	1,57	1,57	1,59
4	1,65	1,63	1,89	2,56	2,95	3,26
6	2,06	2,09	2,55	3,89	4,32	4,96
8	2,50	2,50	3,37	5,09	6,08	6,69
12	3,33	3,75	5,28	7,08	7,83	7,88
16	4,23	5,09	6,42	7,87		
20	5,04	5,90	6,91	8,42		
24	5,48	6,20	7,21			
28	5,66	6,39	7,48			

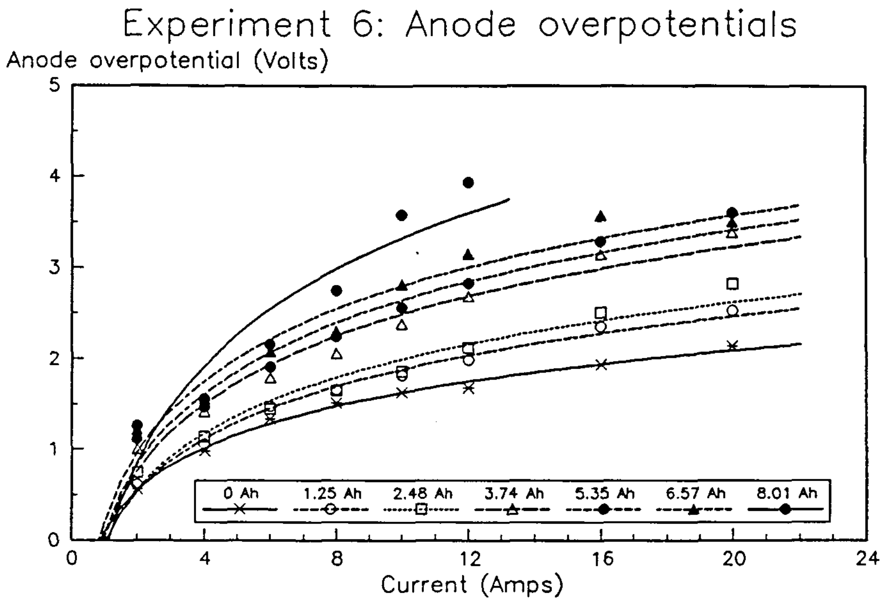
11.6 Appendix 6 Overpotential Graphs

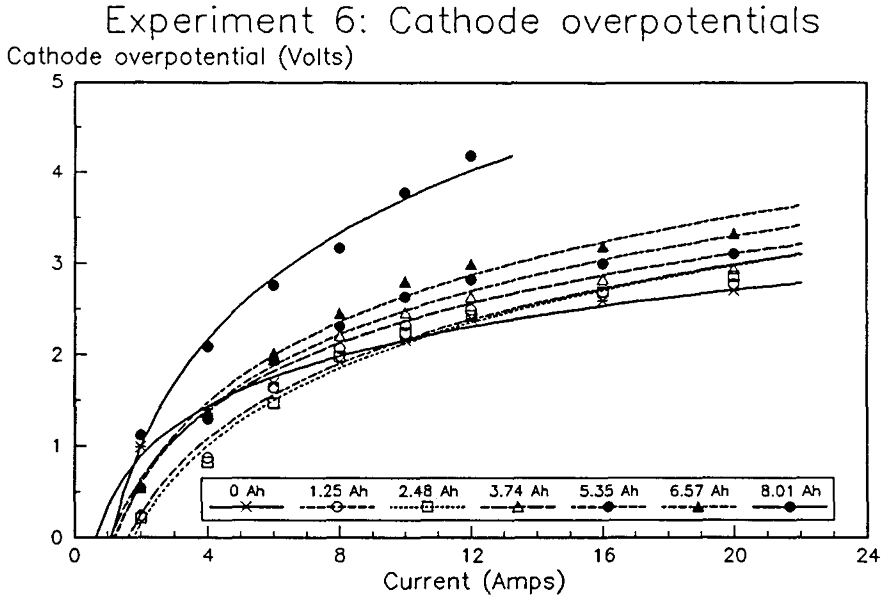
11.6.1 Experiment 4



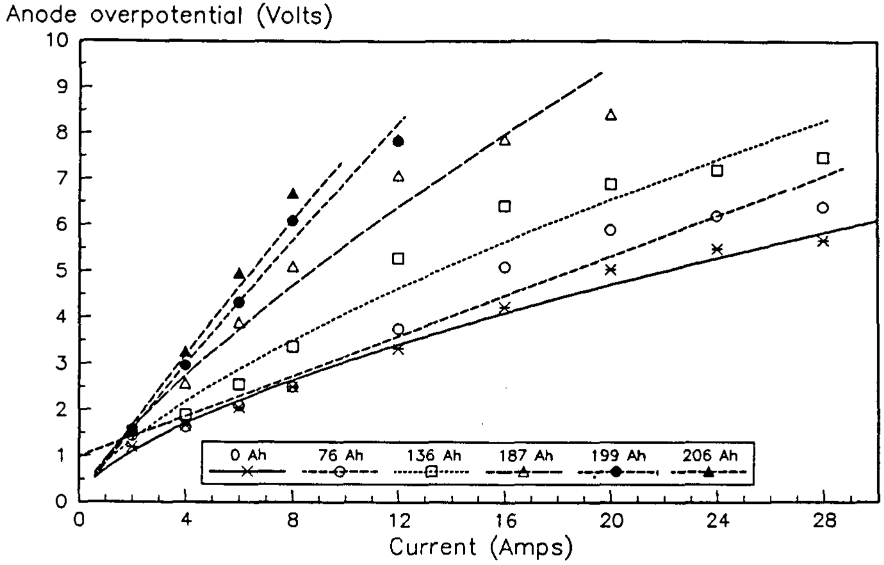


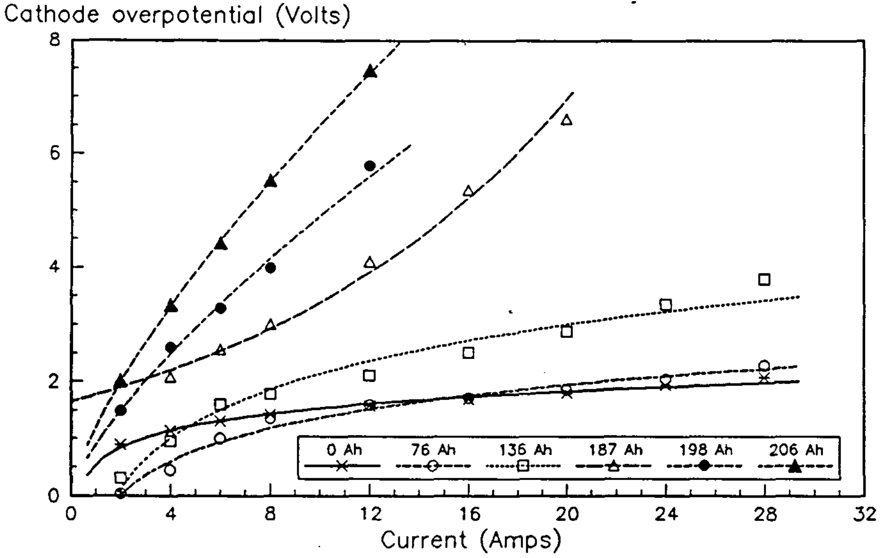
11.6.2 Experiment 6





11.6.3 <u>Experiment 8</u>


Experiment 8: Anode overpotentials


Experiment 8: Cathode Overpotentials