

The use of Electrodialysis in the recovery of ammonium nitrate from the aqueous waste stream arising from fertilizer manufacturing

Stephen Wheston

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Supervisor:

Mr. Noel Connaughton

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Abstract

This dissertation assesses the use of Electrodialysis in the recovery of ammonium nitrate from the aqueous waste stream arising from fertilizer manufacturing. The dissertation is centred on the results of a trial plant that was operated at the Irish Fertilizer Industries Arklow plant. To give a background to the project, a brief introduction to IFI Arklow is included, describing the activities carried out on site. Following this, an account of the scope of the effluent problem at the Arklow plant, including the source of the contaminated effluent is presented. Different technologies that have been examined and trialled are discussed. Any modifications and repairs that have been made or will in the future need to be made to the Electrodialysis plant are discussed, as well as general operation of the trial plant. The main body of the text includes a presentation and interpretation of the data. The conclusion and discussion assesses the suitability of Electrodialysis in the given application and also describes future studies and potential modifications to the plant.

It should be noted that points raised and conclusions drawn are for the purposes of the dissertation, as an academic exercise. As such, these conclusions are personal, and are made based on the information uncovered during research. They are not to be taken as representing the views of IFI Arklow.

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- Thanks to Brendan Garrahan for his assistance in locating obscure textbooks and journals.
- Finally thanks to all other members of staff at Sligo IT for their efforts during the entire three years it took to complete the process.

List of Abbreviations

CAN	Calcium Ammonium Nitrate
IFI	Irish Fertilizer Industries
NET	Nitrogen Eireann Teoranta
ARU	Ammonia Recovery Unit
ICI	Imperial Chemical Industries
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention and Control
ELV	Emission Limit Value
BAT	Best Available Technology
BATNEEC	Best Available Technology Not Entailing Excessive Cost
PLC	Programmable Logic Controller
plc	Public limited company
EDR	ElectroDialysis Reversal
TDS	Total Dissolved Solids
EPA	Environmental Protection Agency

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1. Description of Plant at IFI, Arklow.

1.1 Introduction.

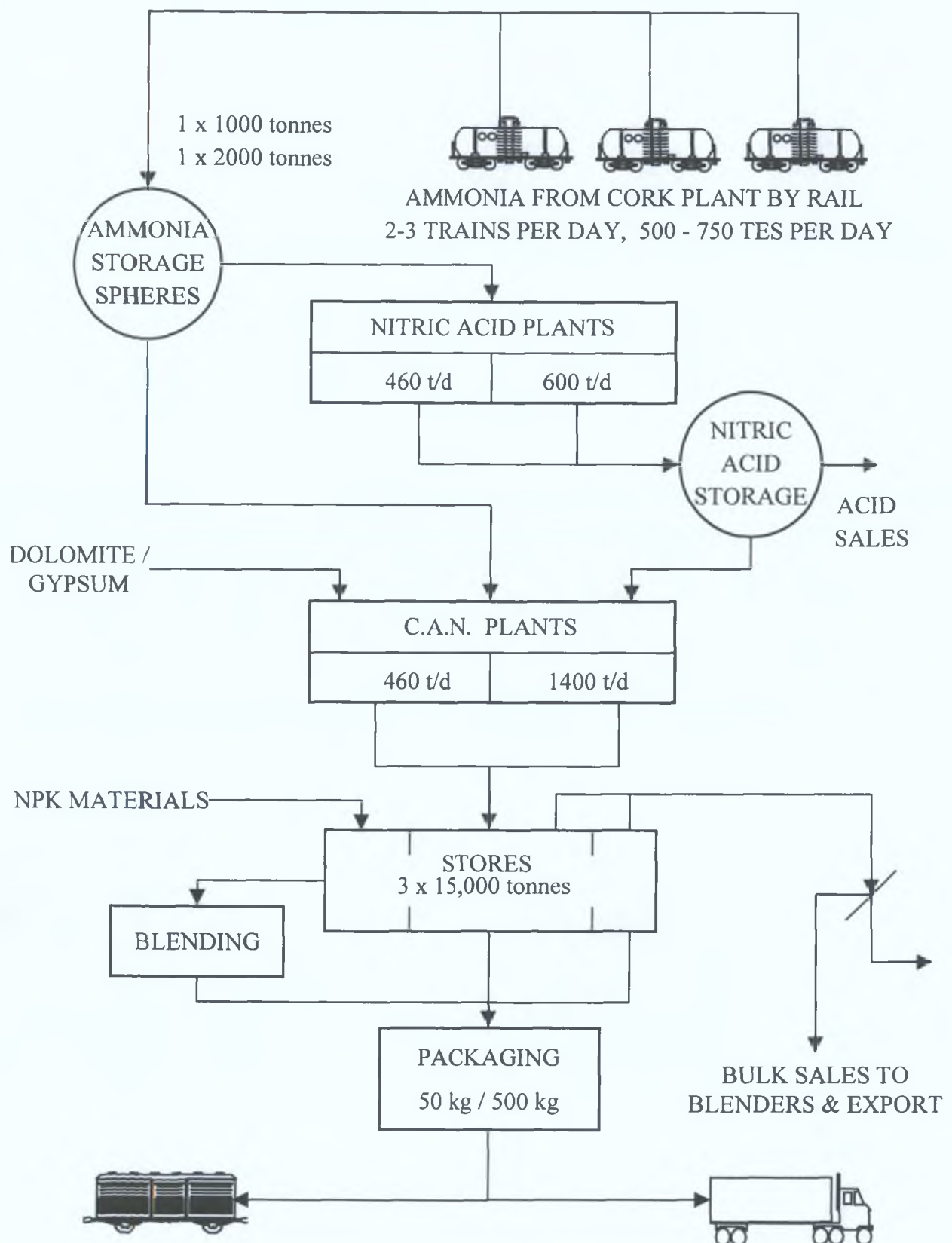
IFI Arklow is one of three factories that makes up Irish Fertilizer Industries, the other two being IFI Belfast and IFI Cork. Arklow and Cork were previously the main components of the state company Nitrogen Eireann Teoranta (NET). NET joined with ICI plc's Belfast factory Richardson's to form IFI with a 51% government holding. The Cork plant manufactures ammonia which is used at all three sites. The Cork plant also produces urea. IFI Belfast manufactures nitric acid and compound fertilizer, while the Arklow factory manufactures nitric acid and calcium ammonium nitrate (CAN) fertilizer.

IFI Arklow receives its ammonia from Cork by train, two to three trains are received each day carrying in total about 600Te of ammonia. This ammonia is stored on site in storage spheres with a total capacity of 3000m³. About half the ammonia goes to the nitric acid plants where it is oxidised at about 900°C over a platinum-rhodium catalyst to produce nitrogen dioxide., This nitrogen dioxide is reacted with water in an absorption tower to produce nitric acid. There are two nitric acid plants on site, one capable of producing 460Te/day and the other capable of producing 600Te/day. There is a small nitric acid sales outlet that accounts for less than 1% of all nitric acid produced.

The vast majority of nitric acid is sent to the CAN plants where a neutralisation reaction between the nitric acid and the ammonia takes place to produce ammonium nitrate. This ammonium nitrate is mixed with either ground limestone or ground gypsum to produce calcium ammonium nitrate (CAN). The product needs to be dried, cooled and sorted to the correct size range before it is coated to stop it from setting during storage either in bulk or in the bag.

Fig. 1: IFI ARKLOW FACTORY FLOWSHEET

IFI ARKLOW FACTORY FLOWSHEET



1.2 History of Effluent Quality

Over the years there have been many projects that have helped reduce the quantities of nitrogen in the effluent emissions from IFI Arklow. The chart below (Fig. 2) gives an account of the improvements that have been made over recent years. The data is presented as the average daily mass discharge of nitrogen given in tonnes. The data is reported in the IFI year, which runs from October to September.

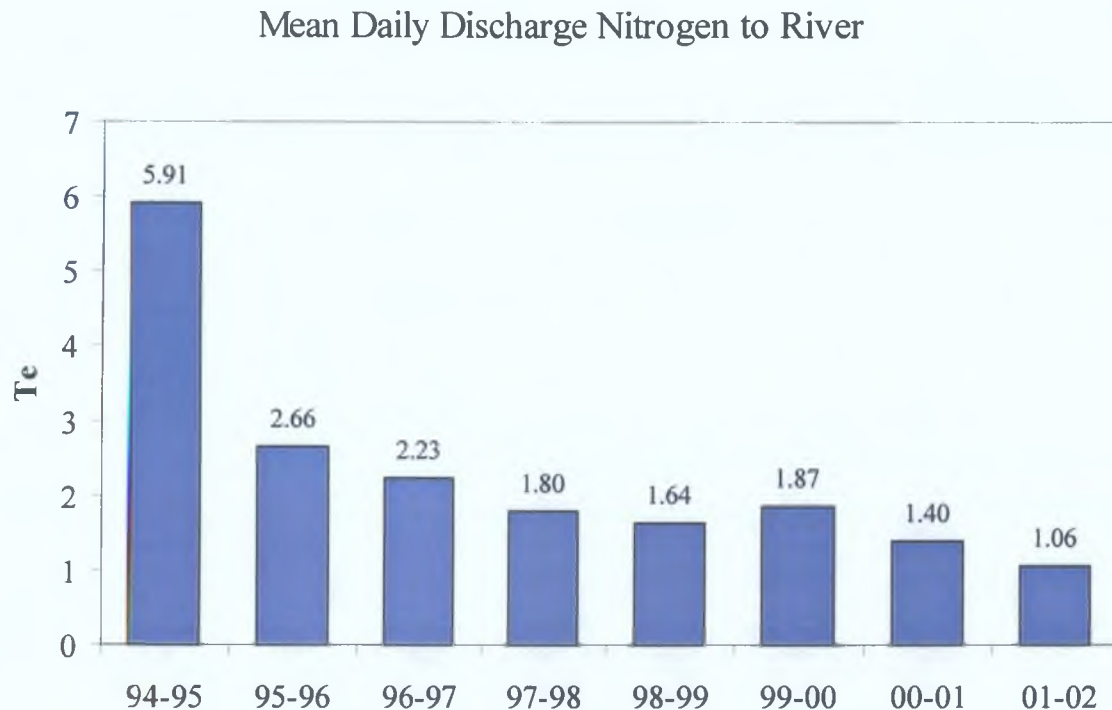


Fig. 2: Mean Daily Discharge of Nitrogen to Receiving Water

As can be seen from Fig. 2, in 1994-95, up to six tonnes a day of nitrogen was being discharged to the river. The improvement seen in 1995-96 is due to the introduction of the Ammonia Recovery Unit (ARU), further details on this plant is presented later. From 1995 to 2001, continual improvements have occurred, brought about mainly by improving housekeeping and operational practices. One such action was banning the use of water hose pipes on the fertilizer plants for cleaning operations. It had in previous years been acceptable practice to wash spilled fertilizer to drain. This practice was stopped and in its place a system of dry cleaning was introduced where spilled fertilizer is collected dry and when no contamination of the spilled fertilizer has occurred it can be recycled into the plant in a controlled manner. Product that has become contaminated is, on safety grounds, not suitable for return into the process. There will be further discussion on the safety issues associated with the recycling of contaminated fertilizer. All contaminated product is stored in a dedicated rejects store and is sold in bulk for export, where manufacturers can use it to manufacture liquid fertilizers.

As well as housekeeping initiatives some minor projects have been introduced. An example of one of these projects was the recovery of the seal water from the vacuum pumps on the small fertilizer plant (CAN1). This seal water which is used to maintain the vacuum in the plant contains large quantities of free ammonia and used to go straight to drain. Following the introduction of this project the water was sent to the Ammonia Recovery Unit where the ammonia was recovered by air stripping and returned to the plants. The cleaned water could then go direct to drain.

From Fig 2, it can be seen that the only disruption to the downward trend in nitrogen emissions occurred in 1999 - 2000. This relates to the commissioning of the CAN3 plant. During commissioning operation was not steady and there were associated losses to drain. The CAN3 (or CAN2B) plant is a granulation plant, which was installed as a direct replacement for the prilling plant that had to be closed for environmental reasons. The reason the prilling plant had to be closed is due to the nature of the activity. Prilling fertilizer is generally an environmentally unfriendly operation. Liquid calcium ammonium nitrate at high temperature is sprayed from the top of a tower (45m) against a counter current flow of air being drawn by large fans (~ 1,000,000m³/hr). As the liquid calcium ammonium nitrate cools it forms a prill, smaller prills and any dust formed will become entrained in the upflowing air and exit the plant at the prill tower fans. In the order of 200Te/yr of particulate (as Nitrogen) was emitted from the tower in this manner. Due to the nature of CAN, it is not possible to scrub the air because the limestone will tend to settle out and cause problems, although some trials into scrubbing were carried out. Ultimately, it was decided that a new plant was needed, using a different process. The new plant that was chosen was a granulation plant, CAN3. When commissioning a new plant there is a certain amount of time needed to troubleshoot any problems found. During the first few months of commissioning CAN3, there was quite a large number of plant stops and starts. Added to this, these stops were often unplanned shut downs when there was not enough time to empty all process vessels before stopping. As a result, there were some tank overflows. These events which took place during commissioning are responsible for the increase in emissions reflected in the 12-month average during 1999 - 2000.

Following successful commissioning of the CAN3 plant, there were some benefits to the nitrogen effluent emissions. As stated above, there were large air emissions from the old prilling plant (~200Te/yr particulate as nitrogen), due to the size of the particles most of these air emissions fell out on the site and following rainfall were eventually washed into the site drains adding to the nitrogen effluent burden. There was also a requirement to frequently wash out a number of process vessels on the prilling plant without the facility to recover the washings. On closing the prilling plant these emissions were removed. It had been envisaged that there would have been a greater direct reduction in effluent nitrogen emissions as a result of removing the prilling plant. This level of reduction was not achieved, however there certainly was some direct reduction.

The last entry on the chart is for IFI year to date 2001 - 2002, which shows the nitrogen emission level dropping below 1.1 tonne per day. This is in part due to reductions in April and May brought about by operation of the Electrodialysis plant.

1.3 EPA Licence Limits.

The original licence held by IFI Arklow was licence number 31 granted in January 1997. As has been described above due to air emissions, it was necessary to replace the prilling plant with a modern granulation plant. To operate the site in its changed configuration it was necessary to apply for a new licence. In March 2000 Licence 495 was granted. All IPC licences cover emissions to water; specific limits are given for all relevant parameters. As well as limits for mass and concentration, to ensure continual improvement there are often future limits that must be met. The chart below (Fig. 3) shows the different licence limits for nitrogen effluent emission that were imposed on IFI Arklow under the IPC regime. This chart gives the daily emission allowed, which may be breached by not more than 1.2 times for no more than two in ten days. As well as the daily limit, the current licence limit given in licence 495 also states that the monthly average must be below 350kg. Therefore the final effluent treatment design must be capable of removing about 800kg of Nitrogen (based on average emission of 1200kg/day).

Fig. 3: Nitrogen Emission Limits set out in IPC Licence

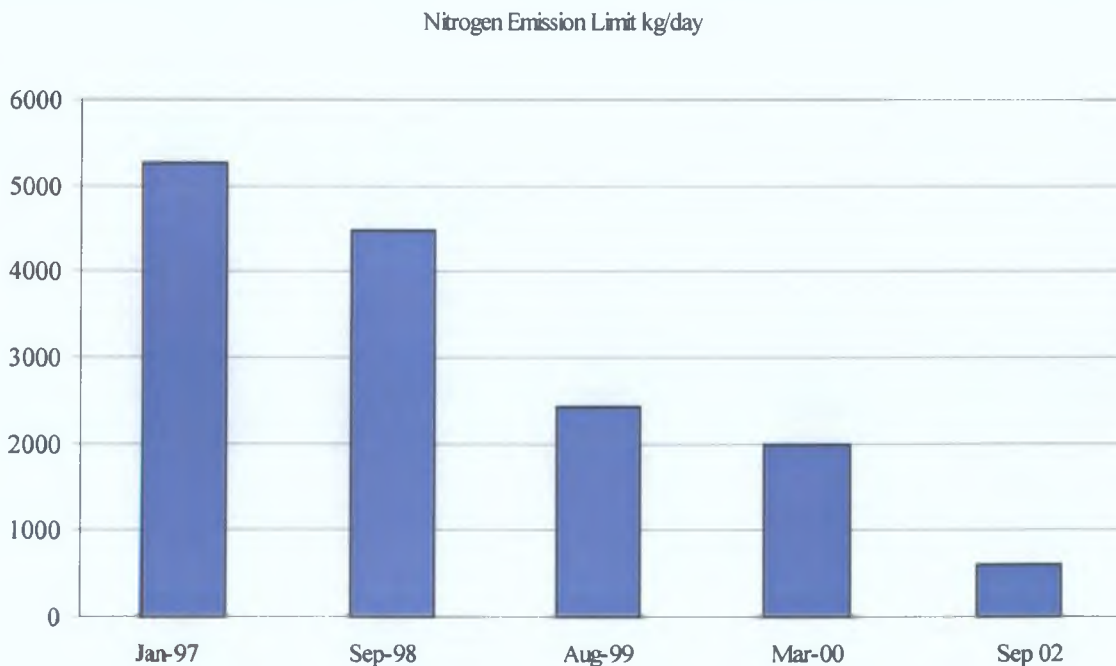


Figure 4 is a copy of schedule 2(i) from Licence 495, relating to effluent limits. As can be seen, IFI was required to comply with the first ELVs from the time of granting of the licence until the 31st August. From September 1st 2001, new tighter limits applied, these new limits could not be met by continued improvement of operations and housekeeping, it was therefore necessary for IFI to consider the installation of some form of effluent treatment. However, the treating of liquid effluent from a fertilizer plant is a very specialised area and is always specific to the site and the process. Because of this, IFI Arklow embarked on a review of current technologies in use as well as site investigations of these technologies in operation. Where possible, pilot plants of the different technologies were operated on site. This is the background to the operation of the Electrodialysis plant, to assess its effectiveness at treating liquid effluent generated at the Arklow site.

Fig. 4: Copy of Schedule of Emissions to Water from IPC Licence

Schedule 2(i) Emissions to Water

Emission Point Reference No.:	EFF1		
Name of Receiving Waters:	Avoca River		
Location :	Final effluent discharge through riverbed diffuser (Grid reference E32292, N17469)		
Volume to be emitted:	Maximum in any one day :	6,850 m ³	
	Maximum rate per hour :	285 m ³	

Parameter	Emission Limit Value			
	mg/l		Kg/day	
Temperature	30°C (max.)			
PH	6-9.5 (Until August 31, 2001) 6-9 (From September 1, 2001)			
Toxicity	10 Tu			
	Daily Mean	Monthly Mean	Daily Mean	Monthly Mean
BOD	20	-	137	-
COD	100	-	684	-
Suspended Solids	150	-	1026	-
Total Phosphates	2.0	-	14	-
Sulphates	80	-	547	-
Chlorides	300	-	2052	-
<i>Until September 1, 2001.</i>				
Total Ammonia (as N)	230	150	1000	600
Total Nitrates (as N)	230	150	1000	600
<i>From September 1, 2001.</i>				
Total Ammonia (as N)	60	45	300	175
Total Nitrates (as N)	60	45	300	175

1.4 Sources of Nitrogen in Site Effluent.

The specific parameter of interest with regard to effluent generation and licence control at the Arklow site is nitrogen. The route of generation of this contamination of site effluent with nitrogen was given in the literature review and will be recapped here:

Although it is possible for certain nitric acid plants to produce acid that is in the range of 99% concentrated, the standard plant will produce acid of up to 70%, containing 30% water. The nitric acid is sent to the CAN plants for product formation, the 30% water remains in the process and needs to be evaporated out to produce ammonium nitrate of about 96%, suitable for granulation. The ammonium nitrate passing through the system needs to be continually dosed with ammonia to keep the pH high and reduce the risk of decomposition, which could result in a fire or an explosion. Therefore the water that is removed by evaporation and condensation usually has high levels of free ammonia as well as ammonium nitrate. The free ammonia is removed by an air stripper that produces some ammonium nitrate, which is recycled to the CAN plants. The effluent that passes out of the air stripper has no free ammonia but does still have some ammonium nitrate present in the order of 5g/L. The air stripping plant at IFI Arklow is the Ammonia Recovery Unit (ARU). A description of how this plant works is given in section 2.81 of the literature review under the section air stripping.

As given in Figure 4, it can be seen that the bottom line with regard to nitrogen emissions is the monthly mean figure, which is the average daily emission, taken over a month. There is a limit for both concentration and mass but for a project like this it is more appropriate to focus on the mass emission figure. In effect, this meant that it was necessary for IFI Arklow to reduce its monthly mean figure to 350kg.

The average mass emission of nitrogen at this point was 1200kg. Previous site audits have been carried out to estimate the different sources of introduction of nitrogen to the site effluent. As a result of modifications to the process, another audit was carried out in 2000 to establish the current sources of nitrogen loss. Again this audit attempted to weight the contribution of the different sources to the overall site burden. As expected, the main source of nitrogen was from the ARU effluent.

Table 1: Site Flow and Mass Balance of Nitrogen from 2000 Audit

**Table 5.2
Site Flow and Mass Balance**

North Site		l/m	m³/d	mg/l N	kg N
1	North Bulk Handling		55	1048	57.8
2	NA5 Boiler Blowdown	360	518	56	29.0
3	NA5 Cooling Tower	60	86	10	0.9
4	Culture Box	2	3	10	0.0
5	NA5 Effluent Pit		90	84	7.6
6	P115		10	400	4.0
7	Ammonia Stripper		0	21%	0.0
8	NA4 Cooling Tower	75	108	10	1.1
9	Acid Area Hose		50	1725	86.3
10	NA4 Effluent Pit	40	58	1725	100.1
11	Steam Drum	60	86	0	0.0
12	ARU	417	600	1295	777.0
13	CAN 1 Vac Pump Seal	135	194	375	72.9
14	Misc Hoses	60	86	10	0.9
15	Canteen		4	10	0.0
	Laboratory		1	10	0.0
	Ops/Eng		32	10	0.3
	Office		3	10	0.0
16	Misc Steam Condensate	60	86	10	0.9
South Site					
1	Bulk Handling		10	496	4.8
2	Sanitary		3	10	0.0
3	CAN 2 Effluent Pit				
	Granulator Bund Area Drain		7	725	5.1
	Condensate from Jkt & AN lines	83	120	725	86.7
	Condensate Steam		24	725	17.4
	Ammonia stripper				14.0
	Fire Hose		100	10	1.0
4	Sulphuric Acid Bund Drainage	30	43	10	0.4
5	Steam Condensate	60	86	10	0.9
6	Sand Filter/Softener		90	10	0.9
Total			2553		1270
Measured			2487		2314
Estimated Base Load					1350

The estimated flow correlated extremely well with the flows calculated during the audit, which were both approximately 2500 m³/d. The estimated nitrogen load was 1270 kg/d, this was approximately 60% of the measured load, however, if allowance is made for plant shut down and concentrate overflow, then the normalised site load is approximately 1350 kg/d. This then gives a quite good correlation with source estimates presented in Table 5.2.

As can be seen from Table 1, taken from the Nitrogen Audit report 2000, it is calculated that over 700kg of nitrogen is emanating from one point source and that source is the Ammonia Recovery Unit.

1.5 Effluent Reduction Programme

There are three broad approaches that could have been taken to tackling the effluent problem at IFI.

- Replacement of the wet section.
- Treating the entire site waste stream.
- Treating single point source waste streams.

Fertilizer production involves two distinct sections or processes. The "wet section" collectively describes the process of producing 96.5% ammonium nitrate solution. This is achieved by a neutralisation reaction between ammonia and nitric acid to produce ammonium nitrate. A number of evaporation steps then remove most of the water from the ammonium nitrate solution to produce 96.5% ammonium nitrate. In the "dry section" ammonium nitrate is mixed with ground limestone / dolomite to produce a granule which is then dried and sorted by size before cooling and applying coating products that prevent caking during storage. The vast majority of effluent generated during fertilizer manufacture using old technologies occurs in the wet section as a result of contaminated condensate from the evaporation process. Due to advancements in technologies a modern wet section produces virtually no effluent waste. Therefore replacement of the old wet section with a modern "clean" wet section would result in the elimination of waste nitrogen at source. However, having spent £13 million on a new dry section in 1999, there was no budget for a new wet section and the waste would therefore have to be abated using end of pipe technology. Replacement of the wet section would have represented Best Available Technology (BAT). The area of IPPC and BAT will be covered in the discussion section.

Following the exclusion of replacement of the wet section, the focus shifted to what type of end of pipe treatment could be chosen. The first point would be whether the end of pipe treatment would treat all of the site effluent or focus on one / two major sources. This is to a certain extent governed by whether disposal or recovery would take precedence. Ammonium nitrate is a potentially explosive compound and great care needs to be taken when operating a process that uses ammonium nitrate. The ultimate worst case scenario is decomposition of ammonium nitrate followed by fire or explosion, as occurred recently at the Grande Paroisse plant in Toulouse. It has been mentioned why it is necessary to add free ammonia and keep ammonium nitrate at a high pH to prevent decomposition. The other important rule of thumb is to avoid contamination by certain species such as chlorides, organic matter and heavy metals. It is for this reason that recovery of all site effluent was ruled out because regardless

of the technology used, it would never be possible to guarantee that no contaminants would enter the process with the returning treated waste. Therefore the only technology for treatment of the site-wide effluent would be biological removal of the nitrogen. This option was examined and site visits were made to a number of installations as well as the operation of a trial plant. Ultimately however, biological treatment was ruled out because of both capital costs and operating costs associated with the massive amounts of sludge generated. Details of the trial plant operation can be found in section 3.4.

Following the elimination of a plant that would treat the entire site waste stream, the project now focused on technologies capable of treating point sources that discharge to the site effluent. The project concentrated on finding a technology that would be able to treat the waste stream coming from the Ammonia Recovery Unit. This would account for about 90% of the reduction necessary to meet the new licence limits. It would also be possible to tie in other clean waste streams (that contain only ammonium nitrate) to bring the reduction to 100% of that required. Another project introduced a series of collection tanks to collect any overflows caused by crash shutdowns of the CAN plants. These crash shut downs can be caused by a sudden major difficulty such as a power cut. The contents of these tanks are kept molten by heating and also kept at a high pH by injection of ammonia until such time as the plant is restarted and it is possible to reintroduce the ammonium nitrate into the process. It has been the case in the past that a crash shut down of one of the CAN plants can mean that effluent emissions exceed licence limits for a number of days.

Literature Review

2.1 General

This section gives a detailed review of the literature relating to electro dialysis including its various uses and technological developments. Also developments in the different technologies used to treat liquid waste in the fertilizer industry were reviewed and is presented.

Many sources were used to compile the literature review on the subject of electro dialysis. In the UCD Library, a search of the on-line catalogue was made using different keywords such as "Electro dialysis, Ammonium, Nitrate, Wastewater, Industrial". Based on the results of this search, a number of books were located in both the Belfield and Earlsford Terrace libraries. The journals in the Belfield library were also searched for relevant papers; the two journals of note found were "*The Journal of Membrane Science*" and the "*Journal of Separation Science*".

A number of relevant papers were copied from these journals.

The Library in Trinity College, Dublin was also searched and with the assistance of a member of staff, two specific books were requested (titles obtained from bibliographies of the journals). A specific paper from the *Journal of Applied Electrochemistry* was obtained from the chemistry library in Trinity. A general and specific search was carried out in the main library using the online catalog, no other publications of significance were found. An on-line search of journals in Trinity provided a number of articles.

The library in IFI contained some books on Industrial Wastewater Treatment and there was some reference made to electro dialysis in these. Perry's Chemical Engineers Handbook gave a very good ten-page description of the principle and uses of electro dialysis. Some documents produced for IFI - Arklow on the subject of wastewater treatment also made reference to electro dialysis and other methods of treating fertilizer wastewater.

The Library in ENFO was visited and while there were books and articles on wastewater, there was nothing significant with regard to electro dialysis.

With regard to the internet, a lot of time was spent searching the web using various keywords, including authors names. The main search engine used was Alta Vista, search engines within websites such as the US-EPA and Europa and the EPA were also used. A large variety of web sites were visited including as mentioned, the Europa and US-EPA websites. Within the Europa web site, the LIFE home-page gave some information on recent life funded projects to treat fertilizer wastewater. A number of university home pages were explored. Suppliers of electro dialysis equipment had good home pages with examples of the current trends in the technology and examples of installations where the process is in operation. Some Universities that are carrying out research in the field of membrane research were found. The journal Desalination had a home page with a limited copy of on-line papers. Amazon.co.uk was searched but no new books of great relevance were found.

A number of conversations were had with consultants used by IFI with regard to their experience of electro dialysis. Two of these consultants had been involved in running trials of the technology in other industries, some but not all the literature on these trials was obtained. Representatives of the company who supplied the trial electro dialysis plant to IFI-Arklow were spoken to, and some information and contacts were obtained.

2.2 Main text books used in Literature Review

Environmental Chemistry 5th edition - Stanley E. Manahan 1991 gives a very basic description of electro dialysis, describing the use of ion exchange membranes to separate ions of different charge that are moving in solution due to the application of a DC current.

Environmental Electrochemistry Fundamentals and Applications in Pollution Abatement - Krishnan Rajeshwar and Jorge Ibanez 1997. This book gives a more detailed description of electro dialysis, including the composition of the membranes and the different uses of electro dialysis, including advantages and disadvantages.

Desalination Technology, Developments and Practices edited by Andrew Porteous 1983 is a useful book. Chapter eight on electro dialysis by - W. A Mc Rae was widely referred to in a number of papers.

Very detailed descriptions of the process was found in the book; *Electro dialysis (ED) & Electro dialysis Reversal (EDR) Technology* - Floyd H. Meller, 1984.

Another very detailed book on electro dialysis was *Demineralization by Electro dialysis* - J. R. Wilson, 1960.

2.3 Theory of Electrodialysis.

Electrodialysis involves the separation and concentration of ions based on electromigration through ion exchange membranes or ion selective membranes. These ion exchange membranes act as a semi permeable barrier that allow the passage of either positively charged ions (cations) or negatively charged ions (anions) while excluding the passage of ions of the opposite charge.

When a DC potential is applied across two electrodes in an ionic solution, cations will migrate towards the negative electrode while anions will migrate towards the positive electrode. If an ion encounters a barrier on its way to the electrode it will not reach the electrode and will remain on the barrier. In electrodialysis the ion selective membrane functions as a barrier preventing the passage of either cations or anions. When a number of ion selective membranes (alternating between anionic and cationic) are placed between the two electrodes the effect is to create a channel containing solution with a high ionic content and a solution with a very low ionic content (Fig.5).

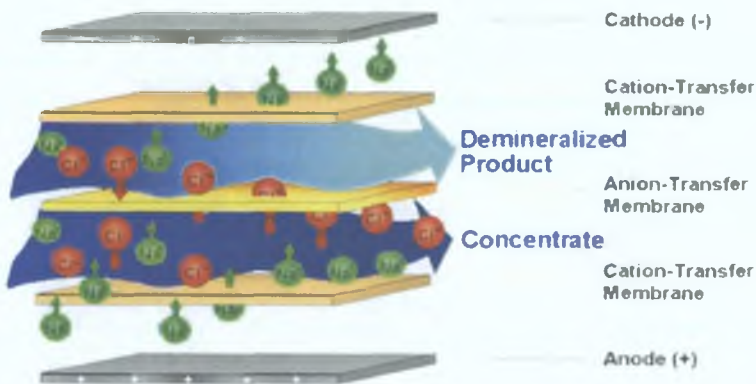


Fig. 5: Ion movement during electrodialysis process

This is the basis by which electrodialysis works, producing a concentrated stream and a dilute (demineralized) stream. In between the membranes to maintain separation and allow solution to flow there are plastic membrane spacers.

Membrane pairs consist of:

Cation transfer membrane

Demineralized water flow spacer

Anion transfer membrane

Concentrated ionic water flow spacer

Around 400 membrane pairs are sandwiched on top of each other between the two electrodes in what is known as a membrane stack. (fig.6)

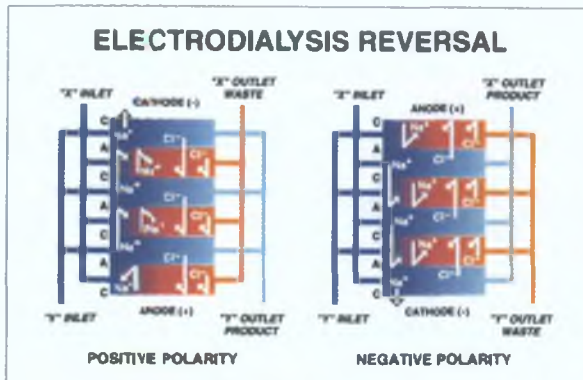


Fig. 6: Sandwich arrangement of membranes

It should be noted that water flows across not through the membranes. As the water flows across the membrane surface ions are electrically transferred through the membranes from the demineralized stream to the concentrated stream under the influence of a DC potential. It is usual to have a number of stacks arranged in series (Fig.7). The IFI-Arklow trial plant has three stacks connected in series. The concentrated stream becomes more concentrated as it moves through the stacks. It is also possible to recycle some of the concentrated stream back to the first stack to go through the process again and thus attain a more concentrated end product. This is how the plant is being operated for the IFI trial and there will be further discussion of this in the main report.

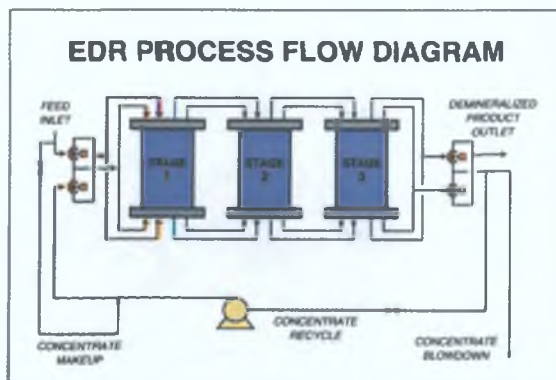


Fig. 7: Electrodesion process flow diagram

2.4 Membrane Structure.

Anion and Cation membranes are essentially resins cast in sheet form. They need to be:

- Impermeable to water under pressure
- Electrically Conductive
- Transfer only either positive or negative ions

Ion selective membranes work by affixing positive or negative charges to sites throughout the membrane matrix. Anion membranes use mostly quaternary ammonium ions, which repel positive ions and allow negative ions through. Cation membranes use sulphonate groups that repel negative ions and allow positive ions through.

Areas of development with regard to membranes are:

- Temperature
- Same charge selectivity
- Fouling
- Bipolar membranes

2.4.1 Temperature

Traditionally membranes used in electrodialysis were only tolerant to about 40°C. Recent developments have produced membranes capable of operating at temperatures up to 60°C (Laboratory of Electrochemical Thermodynamics, Membranes and Electrodes Home Page - Department of Chemistry Universite Libre De Bruxelles). Obviously it is also necessary to have spacers between the membranes that will operate (maintain rigidity) at these high temperatures.

Membranes that can operate at higher temperatures are particularly important when it comes to industrial applications. Industrial waste streams are often of a high temperature and a membrane that can withstand this high temperature removes the need to use heat exchangers. More important is the need to keep viscous solutions molten, for example, the treating of sugar solutions in the food industry. High temperature will also prevent the precipitation of salts in the system when treating high concentration saline solutions.

Operating at a higher temperature can also have benefits with regard to reduced running costs. A membrane stack at a higher temperature will have a lower resistance and thus require less power.

In Ch. 8 *Desalination Technology Developments and Practices* (1983), Mc Rae makes reference to a paper presented by E. P. Geishecker at the 5th Annual Meeting, National Supply Improvement Association, San Diego, California, July 1977. This paper described the performance of a typical electrodialysis plant removing brine.

While operating the plant at 26.7°C, the feed had TDS of 3500ppm and the dilute stream was 350ppm. 908m³ was able to pass through the plant in 24 hours. Reducing the temperature reduced the flow and increased the TDS of the dilute stream. While operating the plant at 37.8°C increased the product flow to 999m³/day and the dilute stream quality and electrical energy usage were not substantially affected compared to operating at 26.7°C. This is a clear indication that it is preferable to operate the electro dialysis plant at higher temperatures.

As well as having membranes that can withstand high temperatures, if operating the system at high temperature it is also necessary to have membrane spacers that can withstand this high temperature. (Further discussion, see spacers)

A paper written by Gurmukh D Mehta for the Journal of Membrane Science, Elsevier Scientific Publishing Company, Amsterdam (1982) considers the possibility of using Reverse Electrodialysis in conjunction with a saturated solar pond to produce electrical power. The power is produced directly by transport of ions through the membranes. To prevent precipitation of the salt it is necessary to keep the system at a high temperature. Membranes capable of operating at high temperatures are therefore needed and tests were carried out using BGU DC membranes capable of withstanding 75°C. These were successful at temperatures over 70°C but there were some problems with leaks in seals and glue joints (these also need to be able to withstand high temperatures). Other membrane manufacturers produce membranes capable of withstanding high temperatures such as Ionic's Type 103-QZL-386. Operating at this higher temperature has an added benefit because by the equation $W \propto T^2$, there will be an increase in power output. Also, electrical resistance of the stack will decrease by 2% for every °C increase in temperature (Meares, P., 1976).

2.4.2 Same charge selectivity

As stated earlier, the electro dialysis can be described as the use of ion exchange membranes to separate ions of different charge that are moving in solution due to the application of a DC current. A recent development in electro dialysis technology is the use of membranes that can not only distinguish between ions of different signs but can also selectively allow the passage of a particular ion within a solution that contains a mix of same charge ions. There are specific chemical adaptations to the structure of the membrane that allows it to distinguish between ions of the same charge. A basic variation is a membrane that simply distinguishes between monovalent and divalent anions, or more advanced is a membrane that can specifically distinguish between nitrate and other monovalent anions.

One of the most common applications / potential applications of same charge selective electro dialysis is the removal of nitrate from groundwater. The possible health implications of drinking water with a high nitrate concentration are widely known (Mirvish, S. S., 1990) The most common health effect regards children and infants; particularly mortality from "Blue Baby Syndrome". Recent research shows possible links between high drinking water nitrate levels and certain types of cancer (Ward et al., 1996).

The problem with regard to removing nitrate from drinking water by traditional methods such as Reverse Osmosis, Ion Exchange and conventional electrodialysis is that all other ions present in the water are also removed. Therefore attention must be paid to the fact that the other ions present in the water are not removed, as they are needed for normal physiological function of the human body. To overcome this problem, a form of specific ion selective removal is required.

There is also plenty of research into the field of membranes that are selective for monovalent anions (Oldani et al, 1992). In this paper, eight different commercially available membranes and two experimental ones were studied to see which gave the optimum results for nitrate removal using electrodialysis. Optimum results were yielded using ACS anion exchange membranes but these were only selective for the removal of monovalent anions, therefore there was also some removal of chloride. Based on this work Miquel and Oldani produced a commercially available process for the removal of nitrate using monovalent anion selective membranes. The process is marketed as NITREM. This was presented to the *Research Workshop on Nitrate Contamination*, Lincon, NE, US (1988).

Another system was developed by the Chemical Science Research Institute of the Voronezh State University in Russia. This system uses a nitrate-selective anion exchange resin (Wofatit SN35L) placed in a net and fitted between the anion and cation exchange membrane in a conventional electrodialysis process. The study showed that this method is a safe and practical method to selectively and effectively eliminate nitrates from drinking water. This extract is taken from the paper entitled 'Highly effective electrodialysis for selective elimination of nitrates from drinking water' - K. Kesore, F. Janowski, V. A. Shaposhnik, *Journal of Membrane Science* 127, (1997).

There are many articles and reports on the specific future use of electrodialysis to treat groundwater and drinking water. One such paper is 'Pollution of nitrate in Moroccan groundwater: removal by electrodialysis' by A. Elmidaoui et al. *Desalination* 136 (2001). The paper gives a background to the problem of contamination of the groundwater and the added difficulty of low recharge rates due to low rainfall. A selection of commercially available membranes were tested in the laboratory for their ability to selectively remove nitrate. One of the membranes tested was the ACS membrane (mono-anion permselective membrane), it gave rejections of 90.7% NO_3^- , 88.5% Cl^- , 48.3% HCO_3^- and only 7.5% of SO_4^- . These results showed good selectivity of the anionic exchange membrane toward nitrates.

Another paper on the use of electrodialysis in specific nitrate removal in a solution of monovalent anions is 'Nitrate - Selective Anion - Exchange Membranes' by A. Eyal and O. Kedem (Weizman Institute of Science, Israel) - *Journal of Membrane Science*, 38 (1988) Elsevier Scientific Publishing Company, Amsterdam. The nitrate specific membrane developed by Eyal and Kedem was achieved by animating bromomethyl groups so that the membrane contains tertiary amino groups in addition to quaternary amino groups. This membrane is capable of removing nitrate but other monovalent anions remain in solution.

An abstract from the paper by V. K. Indusekhar, G. S. Trivedi and B. G. Shah entitled 'Removal of nitrate by electrodialysis' *Desalination* 1991 made reference to the work of Eyal and Kedem and a similar membrane with tertiary and quaternary ammonium groups was tested for selective transport of nitrate under various pH ranges.

2.4.3 Fouling

Wilson (1960) describes the process of scaling and methods of removal. An accumulation of deposits on the membranes or plant in general can cause an increase in ohmic resistance and / or the restriction of the flow of liquid. This in turn leads to the development of polarization conditions (see section on Power Consumption and Process Optimization). The two main compounds involved in scale formation are CaCO_3 and MgCO_3 due mainly to their presence in hard water. Other compounds can also cause scaling, particularly in industrial applications where FeO_3 and AlO_3 may be present. The water can be pretreated for the removal of these compounds, for example by filtration or precipitation. In the electrodialysis of seawater, calcium sulphate scale is common (Ch. 17-44 Perry's Chemical Engineers Handbook, 1984).

Scale formation can damage the surface of the membrane, it is usually detected by a voltage drop or flow rate drop. Scrubbing the membrane surface will remove scale but this is a very labour-intensive time-consuming job. In-situ rejuvenation by flushing the compartments with leaching solutions, e.g. strong acids or alkalis is a very effective method of removing scale. As mentioned above another method is to prevent scale from forming in the first place and this involves a pretreatment of the waste to remove the compounds that are likely to cause scaling. Filtration, softening and / or contact with adsorbents such as activated carbon are very useful in reducing fouling.

Spiegler, wrote the paper 'Saline - Water Conservation No. 2' *Adv. Chem. Ser.*, 38, 179 (1963). A new technology which entailed the application of very brief reverse current to reduce or eliminate scale (Israel patent 13, 242 Mar. 23, 1961) was reviewed. It did indeed reduce the level of hard scale forming on the membrane and instead, a soft sludge was formed next to the membrane, which is removed with the flowing brine. The first commercially available units using brief reverse current were developed by Ionics, this technology is known as Electrodialysis Reversal (EDR). In this process, the polarity of the electrodes are occasionally reversed, lifting the scale off the membrane and into the solution. The time between changes and the duration of the change can be tailored to the process. But it is a very effective system requiring the use of no chemicals and no down time to the plant.

2.4.4 Bipolar Membranes

The use of bipolar membranes is an area of recent development and already there are a number of industrial applications. The bipolar membrane consists of an anionic permeable membrane and a cationic permeable membrane laminated together. When this composite is orientated in such a way that the cation exchange layer faces the anode, it is possible, by imposing a potential across the membrane, to split water into H^+ and OH^- , thus producing acidic and basic solutions on the surfaces of the bipolar membranes. Bipolar membranes can be used in conjunction with other ion exchange membranes to produce acid and base solutions from neutral salt solutions.

An example of this process is given in the *Desalination Journal* 107, 1996 in a paper entitled 'Development of electrodialysis with bipolar membrane for the treatment of concentrated nitrate effluents' by Sylvie Graillon, Françoise Persin, Gerald Pourcelly and Claude Gacach. This paper deals with the waste being produced from reprocessing of nuclear fuels. An important effluent produced is Ammonium Nitrate solution. The leakage of ammonia through the membranes complicates the process. First ammonia is stripped after neutralization of the ammonium nitrate by sodium or potassium hydroxide. The caustic is then regenerated by electrodialysis using bipolar membranes to produce Nitric Acid.

2.4.5 Spacers.

Spacers form the concentrating and demineralizing flow paths within the membrane stacks. G. S. Solt in P. Mears (Ed.), *Membrane Separation Process*, Elsevier, Amsterdam, 1976, described the two basic designs in early use, they were "Tortuous Path" and "Sheet Flow". The most common construction of the spacer currently in use is the tortuous path apparatus. The path is narrow but of great length, traversing the membrane surface, giving maximum opportunity for ion transport across the membrane. The thickness of the membrane spacer gives the desired spacing between the membranes. Although apparatus of this type can function with the liquid path entirely unobstructed, it has been found advantageous to cause the liquid to flow over small "bridges" during its passage along the path. The function of the bridges is to increase mixing which aid ion transport and also to minimize polarization (pg. 220 *Demineralization by electrodialysis* – Wilson, 1960). These bridges can also be referred to as "cross straps". The other advantage of using these bridges / cross straps is that the turbulence created helps break up boundary layers and slimes at the membrane surface, thus keeping the membrane surface clean and free of any fouling. Ionics spacers are generally made of low density polyethylene (pg. 25 Floyd H. Meller *Electrodialysis and Electrodialysis Reversal* - Ionics Incorporated - 1984). The paper by Gurmukh D Mehta for the *Journal of Membrane Science*, Elsevier Scientific Publishing Company, Amsterdam (1982) considering the possibility of using reverse electrodialysis in the production of electrical power referred to earlier, discussed the importance of membranes that can withstand higher temperatures. There is the same importance in such an application that the spacers can also withstand the high temperatures, otherwise the structural integrity of the membrane stack would be compromised. In his paper, Mehta said that polypropylene spacers could tolerate the higher temperatures and were therefore preferable to polyethylene spacers.

2.5 Power Consumption and Process Optimization

Aside from pumping costs, the main area to be examined with regard to power consumption is the DC power consumed while maintaining a potential across the membrane stacks. The two primary laws of electro chemistry at work are Faradays Law and Ohms Law.

Faraday's law in relation to electro dialysis states that the passage of 96,500 amperes of electric current for one second will transfer one gram of salt. The quantity 96,500 amperes per second is called a Faraday, this is equivalent to 26.8 Amperes of current passing for one hour (96,500 / 3,600 sec). Faraday's law is the basis for calculating the amount of electric current needed in an ED / EDR system.

The equation is as follows:

$$I = F^* \times Q_d \times \Delta N / e \times n$$

Where:

- I = Direct electric current in amperes
- F* = Faradays constant
- Q_d = Flow of demineralized water through the stack (L/sec)
- ΔN = Change in normality inlet V outlet (eqv/L)
- E = Current efficiency
- n = Number of cells

(Taken from ch.3-7 EPA / NSF Verification testing plan for the removal of inorganic chemical and radionuclide contaminants by electro dialysis and electro dialysis reversal - down loaded from the US-EPA web site)

Ohm's law states that the potential of an electrical system is equal to the product of the current by the systems resistance. To determine the voltage requirements for a given system, the current is determined from Faraday's law and the resistance is determined by the components of the membrane stack and the solution under treatment, the temperature of the system will also affect the systems resistance.

Faraday's law states that one faraday will be used to transport one gram of salt at 100% efficiency. Most commercial systems would claim to operate at about 80% plus efficiency.

Ions are moved in solution through the system by pumping and they are introduced to the membrane surface by turbulence (see spacer construction) and diffusion. However the ions are transported across the membrane by electrical transport. As ions are transported across the membrane the concentration of ions in the thin layer immediately adjacent to the membrane becomes depleted. With fewer ions present the resistance in that layer increases resulting in an increased voltage, eventually the voltage exceeds the breakdown voltage for water and it is broken down to hydrogen and hydroxyl ions. When disassociation of water

molecules occurs this is known as the "polarization". The point to which the current density can be increased before polarization occurs, is called the "limiting current density". Operating a plant beyond its limiting current density causes many inefficiencies.

There is also a limit on the voltage that can be applied to a membrane stack, this is determined by the membrane stack size and temperature of the stream. If this voltage is exceeded, current can travel laterally through an adjacent membrane to the concentrated stream manifold and this will generate enough heat to damage the membranes and spacers.

The analysis of power consumption can be split into two stages; these are "ohmic" and "nonohmic". Ohmic analysis assumes proportionality between current and voltage e.g. the higher the voltage the higher the current, in fact however, resistance increases significantly with increasing current densities. Attempts have been made to refine ohmic analysis by inclusion of polarization and other factors leading to nonlinear current voltage curves which gives the nonohmic calculation of power consumption. When voltage across the stack is raised, the current at first increases roughly proportional to the voltage; eventually, further voltage increments cause only small current increases. A computer model for non-ohmic optimization of an electro dialysis stack was developed by Belfort and Guter; in this system, the total resistance of the stack is made up of ohmic and non-ohmic elements.

(Much of the above is based on text from Ch. 17-39 42 Perry's Chemical Engineers Handbook, 1984 and pg. 29-35 Floyd H. Meller Electro dialysis and Electro dialysis Reversal - Ionics Incorporated - 1984, as well as Demineralization by Electro dialysis - J. R. Wilson 1960).

2.6 Uses of Electro dialysis.

The uses of electro dialysis can be broken down into three general categories:

- Water treatment
- Wastewater treatment
- Demineralization of products in chemical, food and drug industries.

2.6.1 Water treatment

Much of the following is taken from Ch. 8 *Desalination Technology Developments and Practices* (1983) by W. A Mc Rae. Reference has been made earlier in the document to the use of electro dialysis in the removal of Nitrate from groundwater or drinking water. There are many papers on this subject and examples of uses. However a common application of electro dialysis treating drinking water is in straightforward desalination of salt water for consumption or use in irrigation. This occurs mostly in the Middle East countries where there is a shortage of drinking water and an abundance of saltwater. There are two types of saltwater separation; seawater, but more commonly brackish water. Brackish water is more

saline than potable water but much less concentrated than seawater and is generally to be found in arid regions of the world. This system is often dual function in that the main product stream is clean potable water, but the other stream contains very highly concentrated brine which can be easily manufactured into table salt by flash evaporation or any other method.

Most of the seawater applications of electro dialysis are large installations. Boris Pilat wrote a paper for Desalination 139 (2001) entitled 'Practice of water desalination by electro dialysis'. In this paper Pilat writes about the potential advantages of using electro dialysis for small applications, the ideal example being onboard yachts. This has been the preserve for many years of reverse osmosis but he feels that electro dialysis has many advantages in this situation. The main advantages are:

- Electro dialysis requires less pretreatment (no chemicals no cost)
- Greater capacities can be treated
- Electro dialysis can run continuously without service for longer

The third type of water treatment using electro dialysis is the production of high purity and ultra high purity water for use in a process. The ultra high purity process may only use electro dialysis as primary treatment, this ultra pure water is used in the pharmaceutical and electronics industry. The high purity water can be used as cooling water or boiler feed water, which minimises the possibility of any scaling taking place inside the boiler.

2.6.2 Wastewater treatment

The most common application of electro dialysis in wastewater treatment is in the treatment of waste streams from the metal plating industries. There are many papers on the subject:

'Electrowinning / Electrostripping and electro dialysis processes for the recovery and recycle of metals from plating rinse solutions' from the *Journal of Separation Science and Technology*, 32 1997 by Wane H. Smith and Trudi Foreman. A number of trials treating simulated plating rinse solution were set up. The conclusion was that electro dialysis along with the other two methods were viable methods for the removal and recycling of metals from a tin-zinc plating bath rinse solution. One shortcoming of the electro dialysis system was the need to occasionally scrape off the zinc powder that formed on the cathode.

Joon-Bo Shim, Won-Zin Oh, Byung-jik Lee, and Hyun-Soo Park looked at 'Electro dialysis of Vanadium (iii) and Iron (ii) ions from a simulated decontamination solution' - *Journal of Separation Science and Technology*, 34, 1999. This examined the possible use of electro dialysis in the treatment of waste streams generated in the nuclear industry. The

control of pH in the system was important to ensure that the vanadium was in a complex capable of passing through the membrane.

Ch. 5 Environmental Electrochemistry Fundamentals and Applications in Pollution Abatement - Krishnan Rajeshwar and Jorge Ibanez 1997, gives an account of the use of electro dialysis in the removal and recycling of metal ions.

- Rinsing wastewaters from electroplating processes can be desalted and reused while the concentrate is recycled into the plating bath.
- Also hydroxide ions produced at the cathode can be used to precipitate and remove insoluble radioactive metal ion hydroxides.
- Sulphate ions become concentrated during the electrolytic deposition of copper on printed circuit boards and undergo undesired side reactions. They can be removed by electro dialysis, and sulphuric acid is produced on the anode of the cell, while the hydroxide ions produced on the cathode are used to neutralize the plating solution.
- Silver ions are concentrated from spent photographic fixing solutions by electro dialysis and sent to an electrolytic cell for metal recovery.

A number of other works are referenced in this book with regard to metal removal using electro dialysis, two of them are:

S. Itoi, I Nakamura, and T. Kawahara, 'Electrodialytic Recovery Process of Metal Finishing Wastewater', *Desalination* 32, 383 (1980).

S. Wedman, 'Electrodialysis for the Controlled Precipitation / Removal of Neodymium (iii) and Thorium (iv) Species from HCl feeds', 8th Int. Forum Electrolysis Chwm. Ind., The Electrosynthesis Co., Lake Buena Vista, FL, (1984).

The use of electro dialysis in the fertilizer industry is a future application, one example is the treating of wastewater at the Dyno Nobel chemical manufacturing complex in Louisiana. In this case electro dialysis is used to treat a fertilizer wastewater stream containing ammonium nitrate. (Report paper P. Ryan senior chemical engineer IFI Arklow 2001)

Another example of future potential use in the fertilizer industry is taken from an abstract published by *Desalination* vol. 70 1988. The abstract is from a paper entitled 'Pilot investigation on the treatment of fertilizer manufacturing process effluent using lime and electro dialysis reversal' by J. J. Schoeman, I. J. M. Buys, I. B. Schutte and H. Macleod. The paper was mainly concerned with phosphate removal and it was found to be very effective reducing the concentration from 3800 mg/L to 50 mg/L. It was also mentioned that nitrate and ammonium were removed in the process. The trial also showed virtually no evidence of scaling on the membranes.

2.6.3 Demineralization of products in chemical, food and drug industries.

The use of electrodialysis in the food industry is becoming common place. An example and description of the process was found on the home page of Amerida the American branch of the French separation process company Eurodia. (<http://www.amerida.com/html/tec.html>). One of the examples was Dairygold in Mitchelstown, Ireland where the waste byproduct of cheese manufacture "whey" is demineralized and forms part of an infant feed product. Demineralization of whey is a common application of electrodialysis, another example of this application was found on the same website, the plant is located in New Wilmington, PA, USA.

The Amerida website gave an account of a recent presentation of the use of electrodialysis in the pharmaceutical / fine chemical industry - which was presented at the 13th Forum on Electrodialysis in the Chemical Industry, Clearwater Beach, FL, November 1999. Until recently, the use of electrodialysis in the chemical / pharmaceutical industry was not common. This was mostly due to limitations in the chemical resistance of membranes and spacers, recent developments have produced membranes and spacers that are capable of withstanding many chemical streams. The use of monovalent selective membranes and membranes durable at elevated temperatures (as discussed previously) is considered to have been most important in facilitating the use of electrodialysis in the chemical / pharmaceutical industry.

Some examples are as follows (Taken from Amerida web site):

Clariant-France - The removal of Nitric Acid from Glyoxal. This system comprises two membrane stacks with an effective cell area of 243m², the plant operates in batch mode and has been in operation for 10 years.

Smith-Kline Beecham (UK) - Recovery of an organic salt produced during the manufacture of Penicillin. The plant has an effective cell area of 560m² and has been in operation since 1997.

A recent paper in the *Separation Science and Technology Journal*, 34, 1999 entitled 'Separation of Sodium Formate and Pentaerythritol by electrodialysis' by B. G. Shah, G. S. Trivedi, P. Ray and K. Adhikary gives another example of the potential use of electrodialysis in the chemical industry. During the manufacture of pentaerythritol, sodium formate is formed, which needs to be separated from the mixture of reaction products. Pentaerythritol is a polyhydric alcohol and is mostly used in the manufacture of paints and varnishes. An experimental electrodialysis stack was constructed and experimental work was carried out. The feed was treated at different concentrations, the current passing through the stack was varied and different potentials across the stack were tested. It was concluded that when using interpolymeric ion-exchange membranes, sodium formate can be separated from pentaerythritol, the optimum voltage was 25V.

An older application of electrodialysis in the food industry is the deacidification of fruit juices. A paper on possible advances in this process was presented by H. Voss for the *Journal of Membrane Science*, 27 (1985) entitled 'Deacidification of Citric Acid solutions by electrodialysis'. In this paper, Voss looked at two different methods and compared their efficiency. One system used the traditional cation and anion exchange membranes while the other used a bipolar membrane and anion exchange membranes. The system using the bipolar membrane process was found to be most attractive with regard to current efficiencies, consumption of sodium hydroxide and by-product formation.

Table 2: Summary of the various applications of Electrodialysis:

Water Treatment	Wastewater Treatment	Product Formation
Brackish water desalination	Rinse water from plating electronics industry	Cheese whey / milk / soy demineralization
Seawater desalination	Photographic developer regeneration	Food / Sugar desalination
Nitrate removal from drinking water	Industrial effluent treatment	Tartaric wine stabilization
Water purification for low flow applications		NaCl / Acid removal from organic product
Cooling tower / Boiler feed water		Conversion of organic salts into acid and base
		Deacidification of fruit juices
		Recovery of proteins from blood plasma
		Salt production from sea water
		Desalting amines

2.7 Developments in Electrodialysis:

Most of the developments in electrodialysis relate to the specific treatment of new waste streams or new products that can make use of electrodialysis in the formation or purification stage. Some examples of these have been given above. Many of the recent and ongoing developments have been dependent on the development and use of membranes and spacers that can withstand extremes in temperature and pH. In the area of water treatment, the use of

same sign ion selective membranes is an area of research that has been previously discussed, as has the use of bipolar membranes.

Electro-electrodialysis is a process and development in electro dialysis that has not as yet been discussed. There are a number of papers detailing the potential uses of electro-electrodialysis. A definition of the process is as follows: "Electro-electrodialysis displaces acids by permselective transport of the acid's anion through an anion-exchange membrane and electrolysis of the proton. An electrolyzer equipped with an anion-exchange membrane serves as the main electro-electrodialysis apparatus" - S. Cattoir, D. Smets, A. Rahier 'The use of electro-electrodialysis for the removal of sulphuric acid from decontaminated effluents' - *Desalination* 121 (1999). Two other papers obtained on the potential use for electro-electrodialysis were:

'Concentration of Formic Acid Solution by electro-electrodialysis ' - G. S. Luo F. Y. WU - *Separation Science and Technology*, 35 (2000).

'Concentration and purification of wet industrial phosphoric acid by electro-electrodialysis ' - D. Touaibia, H Kerdjoudj - *Journal of Electrochemistry* 26 (1996).

2.8 Other treatment methods used to treat the waste streams generated in fertilizer manufacture.

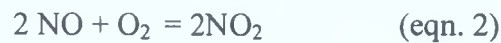
- Air Stripping
- Biological denitrification
- Reverse Osmosis
- Ion exchange

When dealing with the waste from the manufacture of fertilizers, the parameters of interest are Nitrogen, Phosphorous, and Potassium. In the case of IFI, nitrogen fertilizers are exclusively manufactured, although some blended products are produced by mixing the nitrogen fertilizer with other compounds such as potash and diammonium phosphate. This dissertation is focussing on the removal of nitrogen in the form of ammonium nitrate and will therefore focus on treatment technologies in use for the removal of nitrogen, although some reference will also be made to the removal of other nutrients.

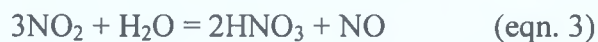
The source of water pollution from the manufacture of fertilizer originates with the reaction water that is formed when ammonia is oxidized by combustion to produce NO₂. (eqn. 1) During the combustion of ammonia other oxides of nitrogen are also produced but this is not important in this context.



The nitric oxide produced during combustion is further oxidized by "secondary air" to produce nitrogen dioxide (Needed for the absorption process in the formation of nitric acid, as nitrogen dioxide is soluble whereas nitric oxide is not). (eqn. 2)



The nitrogen dioxide produced is absorbed in water (as well as reaction water it is also necessary to add some process water) to produce nitric acid, nitrous oxides produced in the process are bleached by the secondary air. (eqn. 3) The end result of this process is the production of 70% nitric acid (the 30% being water).



The nitric acid produced is then reacted with ammonia (eqn. 4) to produce ammonium nitrate.



(Equations taken from European Fertilizer Manufacturers' Association 1995 BAT guidance notes for the production of Nitric Acid and also the 1995 BAT guidance notes for the production of Ammonium Nitrate)

The 30% water (from 70% nitric acid) remains in the process and needs to be evaporated out to produce ammonium nitrate of about 96% suitable for granulation. The ammonium nitrate passing through the system is continually dosed with ammonia to keep the pH high and reduce the risk of decomposition, which would result in a violent explosion. Therefore the water that is removed by evaporation and condensation usually has high levels of free ammonia as well as ammonium nitrate.

In some arid countries it is not necessary to treat the waste coming out the process. Instead, it is neutralized and sold to farmers who spread it on the land where it has a dual function in irrigation and enrichment. In most countries however it is necessary to dispose of the waste and due to tighter emission standards, treatment of the waste prior to disposal is necessary. The use of different technologies are in place and are under investigation at various locations

by fertilizer manufactures. There is a lot of literature on this subject, but because this area is peripheral and not central to the topic of the dissertation it will only be covered in brief.

2.8.1 Air Stripping

As detailed above, the wastewater emanating from a fertilizer plant tends to have a large quantity of free ammonia in solution. This is often removed by a process such as air stripping, the resultant waste steam will generally need further treatment before being discharged. In the process, the wastewater containing the ammonia is sprayed down a tower which has a counter current flow of air. The ammonia is stripped out of the water and continues to follow the path of the air which passes through a solution of acidified ammonium nitrate solution. This impinges the ammonia out of the air to form ammonium nitrate (continually acidified). The air stream now stripped of its ammonia continues through the tower to strip out more ammonia. The acidified ammonium nitrate solution is continually bled out and returned to the fertilizer production plant.

2.8.2 Biological denitrification

One of the traditional methods of removing nitrogen from wastewater is biological denitrification and this is used in the fertilizer industry. In this process micro-organisms convert ammoniacal nitrogen to nitrate nitrogen and in a separate process other micro-organisms convert nitrate nitrogen to nitrous oxide and nitrogen gas and therefore remove the nitrogen from the wastewater. However, due to the nature of the wastewater and the process it is not always ideal. The main problem is that for the most part, fertilizer waste is exclusively nutrient based NPK, and there is no carbon source. Therefore it is necessary to add a carbon source so the micro-organisms are able to break down the nutrients. The usual feed sources are methanol or molasses. The second problem is the production of sludge, so even though the nitrogen has been removed there are tonnes of sludge to be disposed of. The sludge produced would be very good quality with no aromatic, pathogenic or heavy metal content so it would be ideal for spreading as a fertilizer and may be sold with a slight profit for this use. However, if no market is found the cost of landfill disposal will have to be borne. From an efficiency point of view, the removal of nitrogenous compounds is wasteful, because energy was consumed fixing atmospheric nitrogen to produce ammonia, and if at all possible this energy should be conserved by recycling the ammonia back into the process thus minimizing the energy needed in ammonia production. Reverse Osmosis and Ion Exchange are methods of treating the waste by recycling it back into the process.

An example of the use of biological treatment in the removal of nutrients from fertilizer manufacturing waste can be found at Norsk Hydros' plant in Rostok Germany. Details given below are taken from a report by P. Ryan and M. McEvoy of IFI. The plant has capacity to make liquid fertilizer from its concentrated waste streams and the biological plant therefore only treats the site spillage waste and other low strength waste streams. If the concentrated waste streams were sent to the biological plant it would need to be many times bigger. The ratio of molasses consumption per tonne of nitrogen removed was ten to one.

An abstract dealing with a waste of similar composition to fertilizer waste is taken from a paper for the *Hydrometallurgy Journal* entitled 'Biological removal of ammonia and nitrate from simulated mine and mill effluents' by D. W. Koren, W. D. Gould and P. Bedard (2000). Ammonium nitrate is the fuel used in blasting for a lot of mining activities and as a result, effluent is highly contaminated with ammonium nitrate. Like fertilizer wastes, there is no carbon source to speak of, so one needs to be added. In this case, methanol was used. Trials using a stirred tank reactor for nitrification and an up-flow packed bed reactor for denitrification, yielded good results with 90% removal of nitrogen.

With regard to the use of Biological treatment on fertilizer wastewater, its use is probably only feasible as a final polishing stage, down stream of other plants used to recover nitrogen from the concentrated streams. IFI Arklow is currently carrying out trials using a pilot biological plant for the denitrification of wastewater. The aim of the trial is to see:

- What strength wastewater can be treated?
- What is the maximum quantity of nitrogen that can be removed by a given micro-organism population?
- What quantity and quality of sludge is produced?
- What is the methanol / phosphate / caustic usage per kg of nitrogen removed?
- Possible investigation into other carbon sources, namely whey.

See section 3.4 for comments on the trial.

2.8.3 Reverse Osmosis

Another method that is widely used for the removal of nitrate from wastewater is Reverse Osmosis. This is where pressure is used to overcome the osmotic pressure of an aqueous solution and force water through a non-porous, semi permeable, polymeric membrane. All particulate and high molecular weight matter and the bulk of ionic species are retained on the feed side while the treated water passes through the membrane. The main process difficulties with this technology is membrane fouling, some of the species that may cause fouling can be removed using ultra filtration or some other basic cartridge filtration system.

A paper on trials carried out on reverse osmosis as a possible treatment method for fertilizer treatment was published in *Desalination* entitled 'Water and materials recovery from fertilizer industry acidic effluents by membrane process' by A. J. Karabelas, S. G. Yiantsios, Z. Metaxiotou, N. Andritsos, A Akiskalos, G. Vlachopoulos, S. Stavroulias (2001). There were two objectives to the use of reverse osmosis; the first being the production of a concentrated effluent stream that could be reused in the process and the second obtaining high quality membrane permeate water that could be used in steam production, and for improving cooling water quality. The conclusion of the report was that membrane treatment of heavily polluted fertilizer wastewater is environmentally beneficial, technically feasible and economically

attractive. The objective is the use of zero discharge treatment methods and a further long-term trial is now taking place on site.

Another reference to the use of reverse osmosis by a fertilizer manufacturer was found via the LIFE homepage on the Europa website (LIFE94 ENVIRONMENT/B/000291). A basic description of the application was found on the homepage, a more detailed description included in the final report was sent out on request after making contact with the Commission. In this report an account of a trial of reverse osmosis technology is given. The results showed that reverse osmosis was capable of removing ammonium nitrate from a waste stream but was not chosen as the final solution in this instance because the company in question were interested in retaining the Nitrate ion for use in another process. For this reason, ion exchange using just a cation exchange resin was chosen.

2.8.4 Ion exchange

Ion exchange is another method that has been used to remove unwanted ions from fertilizer effluent. Examples of this technology can be found in many parts of the world. A paper presented at the Institute of Chemical Engineers Symposium Series No. 77 by H. P. Pandya, J. C. Shah, A. D. Gadhia and V. A. Sanghan was entitled 'Recovery of ammonia from nitrogenous plant effluents by ion exchange treatment'. It details bench models and pilot plants used to recover nitrogen from fertilizer wastewater. A paper on the actual use of ion exchange in the treatment of fertilizer waste in Hungary was presented by N. Arrion at the 6th Annual Water Treatment Technology Conference ABU-QIR Fertilizer company (1988). The paper outlines the use of ion exchange in the removal of ammonium nitrate from the condensate waste stream at Petri-Nitrogen in Hungary. In this process, about 30m³/h of condensate containing about 6 g/L ammonium nitrate passes through the cation exchange resin and then the anion exchange resin to produce a very clean stream of less than 0.005 g/L ammonium nitrate. This process also produces a concentrated stream of about 200 g/L which is further evaporated and returned to the process. The quality of effluent / concentrate produced depends for the most part on the regime used in regenerating the ion exchange bed. The paper in question is complex and beyond the scope of this literature review.

One of the main drawbacks of ion exchange is the issue of safety. The cation exchange resin is regenerated using nitric acid a strong oxidizing agent. The resin itself is oxidizable under certain conditions which can lead to a fire or an explosion. A paper written by Calvin Calmon on this subject was published in the *Chemical Engineer* in November 1980. The title of the paper was 'Explosion hazards of using nitric acid in ion-exchange equipment'. Recent examples of explosions involving the use of nitric acid in the regeneration of resin beds are given. Precautions that can be taken are outlined; temperature of the resin bed and acid are critical and in almost all cases where explosions have occurred, traces of copper or some other metal ion have been found. These metal ions can catalyze any reaction rendering it violent. There is also the issue of decomposition of the ammonium nitrate in solution, again metal ions, notably chromium and copper, will catalyze this reaction and chloride will do the same.

Even more so than resin oxidation, the decomposition of ammonium nitrate is an extremely violent reaction as was witnessed recently in Toulouse (*Chemical Engineer* pg. 4 Nov 2001). 'Synergistic Catalysis of Ammonium Nitrate Decomposition' - *Journal of the American Chemical Society* (1969) by A. G. Keenan, K. Notz and N. B. Franco outlines the processes involved in the decomposition of ammonium nitrate and due to the temperature and pressures and low pH involved in ion exchange, the possibility of such an event are high.

Other methods that could potentially be used to remove nitrogen from fertilizer wastewater but will not be covered in this paper are:

- Breakpoint chlorination - Ammonia Removal
- Catalytic decomposition - Nitrate Removal
- Catalyzed hydrogen reduction- Nitrate Removal
- Reduction by active metals- Nitrate Removal
- Evaporation concentration

3. Detailed investigations into selected technologies

Following the literature review a number of technologies were examined in greater detail. In most cases this involved site visits to plants that used the given technology. In three cases trial plants were operated on site to assess the effectiveness of the technology on the specific waste stream of interest. Reasons why certain technologies were abandoned are given.

3.1 Ion-exchange

In the case of ion-exchange, an examination of the technology revealed possible safety concerns. The process uses nitric acid to regenerate the cation exchange bed. Nitric acid is a strong oxidising agent and the resin of the bed is itself oxidisable. This has led to problems and the worst case was where a plant in the US exploded after problems were experienced during the regeneration cycle. For this reason, ion-exchange was discounted as a contender. There were also issues regarding the operation of such a plant. It would be a more labour intensive plant, adding to the fixed cost of running. To observe all safety features in place at an ion-exchange plant being used to remove nitrogen from a fertilizer wastestream. A site visit to a plant in Hungary was arranged. Details of this visit are taken from a report of the site visit by Stephen Wheston in April 2001. The safety precautions used on site were to chill the cation resin bed before regeneration using chilled water, the acid itself was then passed through a heat exchanger and chilled. Contact time between the acid and the resin bed was kept to a minimum to avoid a build up of heat and a possible reaction. The system used appeared reasonable robust and reliable. There is however some concern regarding mechanical or human errors leading to a potentially dangerous situation.

3.2 Reverse Osmosis

A Reverse Osmosis trial plant was brought on site in the summer of 2001. While the tests gave positive results there were some issues of concern. The first concern related to the very high pressures that would be involved in the process, and the safety implications of this. The second concern related to possible blinding of the membranes. During the trial, there were difficulties with build up on the membrane, leading to a pressure drop and loss of performance. One of the causes of the build up was found to be ferrous material coming from the plants while running poorly (poor start-ups). The ferrous material was being removed due to the action of low pH conditions. This ferrous material was not being removed by the in-line cartridge filters. If a full-scale plant was to be built, it might have been necessary to introduce some form of pre-treatment, such as precipitation to remove this ferrous material. Unlike Electrodialysis where the water moves past the membrane and only the ions actually cross the membrane, with reverse osmosis, the water must pass through the membrane and it is therefore more prone to the effects of blockage and membrane blinding. pH was also an area that was highlighted when operating the plant, because the waste stream from the ARU is acidic and this affected the efficiency of the reverse osmosis process. The hydrogen ion was assumed to be passing the membrane and bringing with it the nitrate ion,

this gave poor results in the final effluent quality. In order for the plant to operate correctly it was necessary to neutralise the feed, this would also be necessary on a full-scale plant.

3.3 Evaporation

The evaporation process was discounted on the grounds of energy costs.

3.4 Biological Treatment

In section 2.8.2 reference is made to the site visit to a biological treatment plant being used in Germany to treat fertilizer liquid waste. However it was revealed that the quantities of nitrogen being removed were very small. A trial plant was operated on site for a period during 2001-02. Operation of the trial plant confirmed original estimates that sludge production was equivalent to nitrogen removal on a gram for gram basis, therefore removing 1000kg of Nitrogen would produce 1000kg of sludge (dry weight). This sludge would be class A, with no pathogens, heavy metals or active organic compounds and as such would be suitable for land spreading. It would however, be very difficult to find an outlet for all this sludge and ultimately it would possibly involve land filling at enormous cost.

Another observation made while operating the trial biological plant was the vulnerability of the Nitrifying bacteria. The nitrifiers are susceptible to loss of oxygen, low temperature and pH variation. Of course it was known at the outset of the trial that these micro-organisms would be susceptible to changes in these conditions, but the extent of the susceptibility was not entirely known. Due to various problems encountered with the air supply, heaters and pH correction equipment, the full extent of their vulnerability was witnessed. With a loss of temperature, the nitrifiers became dormant but no real damage was done. With the loss of oxygen or pH variation there was a pronounced negative effect. For example, on one occasion due to a failure in the caustic dosing pump, the pH in the nitrification tank dropped to below five for a number of hours. The nitrifiers were severely affected and a massive proportion of the micro-organism population was wiped out. It took a number of weeks for the plant to return to the point where it had been before the shock to the system. Obviously a full-scale plant would have alarms and back up systems, but these too can fail. The significance of these findings is that with a mechanical system, if you have a failure it may take a day or so to fit replacement parts, but with the biological plant it may take weeks before the effluent returns to the required standard. It would not be possible to operate under such conditions, where a failure in the biological plant might mean the shut down of the entire site. There is also the question as to whether or not biological removal can be regarded as BAT, when there are treatment options that will recover the waste (See discussion section). This was in the context of a biological treatment plant treating the entire site waste stream. The possibilities of using a biological treatment plant to treat a point source was also examined, and rejected for the same reasons.

3.5 Electrodialysis

The final process examined was the one that held the most potential. It is used in another similar application in the US, a site visit to this plant was arranged and reference to this is given in the literature review section 2.6.2. A further site visit was arranged to Michealstown in Cork (literature review section 2.6.3) which operates an electrodialysis plant to demineralise whey protein. This was an interesting exercise as it showed the comparison between the current plant operated at IFI Arklow and a modern installation operating in a different application. Both plants are ultimately treating what were waste streams to produce a product that has some worth. In the case of IFI, Nitrogen that was going to drain as dilute ammonium nitrate is being concentrated and recycled into the plant to produce product. For Dairygold, before the Electrodialysis plant was brought on line, the whey stream would have been sent to the wastewater treatment plant for treatment at considerable cost of operation and further cost associated with disposal of sludge. Now this whey is used to form a saleable product which is a good example of reuse of waste and conservation of energy. The major differences between the processes are first that due to the nature of the waste stream at Dairygold, it is necessary to provide a pretreatment in the form of Ion exchange. Because the waste stream at IFI is essentially very pure, there is no pretreatment required. The plants also differ in the date of manufacture and thus the development in the technology. The membrane stacks at Dairygold are far more compact, but are still capable of treating comparable volumes of waste. The plant currently in operation at IFI is a trial plant and it is envisaged that the final plant when installed will be made of the most modern components and custom designed for the process based on the results of the trial. Another difference in the two plants is the manner in which they are run. The Dairygold plant is batch operated whereas the IFI plant operates continuously. This difference is not significant, but simply reflects the difference in the application. A reasonably significant difference between the two operations is the need for routine cleaning of the Dairygold plant due to scaling. This has not been needed at IFI. However, one advantage of the Dairygold application is that due to the seasonal nature of the process, the plant is off-line for a period of months and this allows major servicing to be carried out as well as preventative maintenance and assessment of membrane condition. It will be more difficult to incorporate this level of overhaul at IFI. The electrodialysis process is acceptable on the grounds of safety, capital costs and running costs. Arrangements were made to take delivery of a trial plant. This trial plant is capable of treating the entire waste stream from the ARU and serves the function of providing a test of the technology with the added advantage of very significant removal during the trial. Findings of the trial will be presented in sections 4, 5 and 6.

4. Commissioning and Operating Electrodialysis Plant

4.1 Introduction

Before construction of a full-scale purpose built Electrodialysis plant for IFI Arklow, the opportunity was taken to trial the technology with a mobile plant capable of treating the entire waste stream produced by the ARU. This plant is reasonably old, operating since the 1980's and before coming on site, the plant had been in storage for a number of years. For this reason, it had many mechanical faults that needed to be resolved. It was also necessary to modify the process to make it suitable to treat the wastestream of interest. All modifications are outlined below.

Plate 1: Electrodialysis Plant used at IFI, Arklow



4.2 Modifications carried out to the process

A lot of time was initially spent finding and repairing leaks in the system as well as replacing all damaged instruments. The logic system that controls the plant is an old Programmable Logic Controller (PLC). There were some problems communicating with this PLC. It was necessary to make communication in order to carry out changes to the program. A number of boards within the PLC had to be replaced.

As has been explained in the literature review, membranes that are used in Electrodialysis are prone to damage at high temperatures, although the development of high temperature membranes is a current area of research. Because the plant that is being used on site is old, the membranes being used are not able to withstand temperatures above 40°C, above this temperature they buckle and leak. The waste stream to be treated at IFI is at a temperature of 70°C, therefore the first action was to install a heat exchanger. A plate heat exchanger (Fig. 9) capable of removing the quantities of heat in the process was purchased. This was then

installed by connecting to the effluent waste stream and the site process cooling water. With this configuration, it was possible to reduce the temperature to about 30°C. A thermocouple and control valve (Fig. 8) were put in line so that in the event of an increase in temperature above the set point, the valve would close and stop the flow of effluent so as to protect the membranes.

Fig. 8: Control Valve



Fig. 9: Heat Exchanger



The trial plant can be configured to run with two series of membrane stacks in parallel, but in the case at IFI Arklow, the plant was configured to run using just one bank of membrane stacks. However, it was necessary to use a recycle system to maximise recovery. Thus the plant runs a "feed and bleed" type arrangement. The flow diagram for the plant, showing the recycle used in the feed and bleed method is presented in Fig. 10 below. Without this arrangement, it would not be possible to reduce the ammonium nitrate concentration to the levels required.

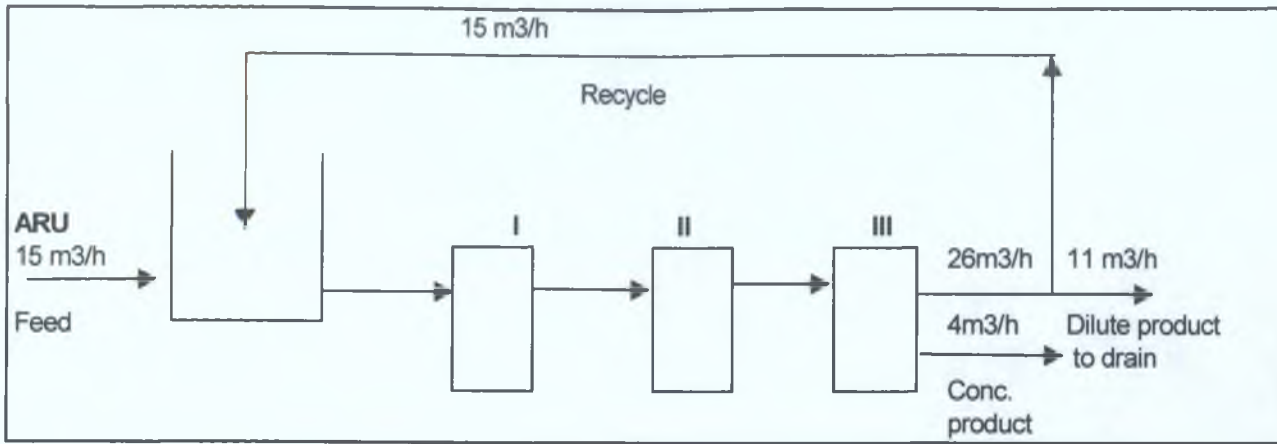


Fig. 10: Feed and bleed method of operation

The picture below (Plate 2) shows one of the membrane stacks with the protective cover removed. The protective cover is needed to prevent accidental electric shock from the stacks operating at a potential of about 350V DC. In the picture it is possible to make out the individual membranes that make up the stack. Plate 3 shows the three stacks arranged in series.

Plate 2: Membrane Stack



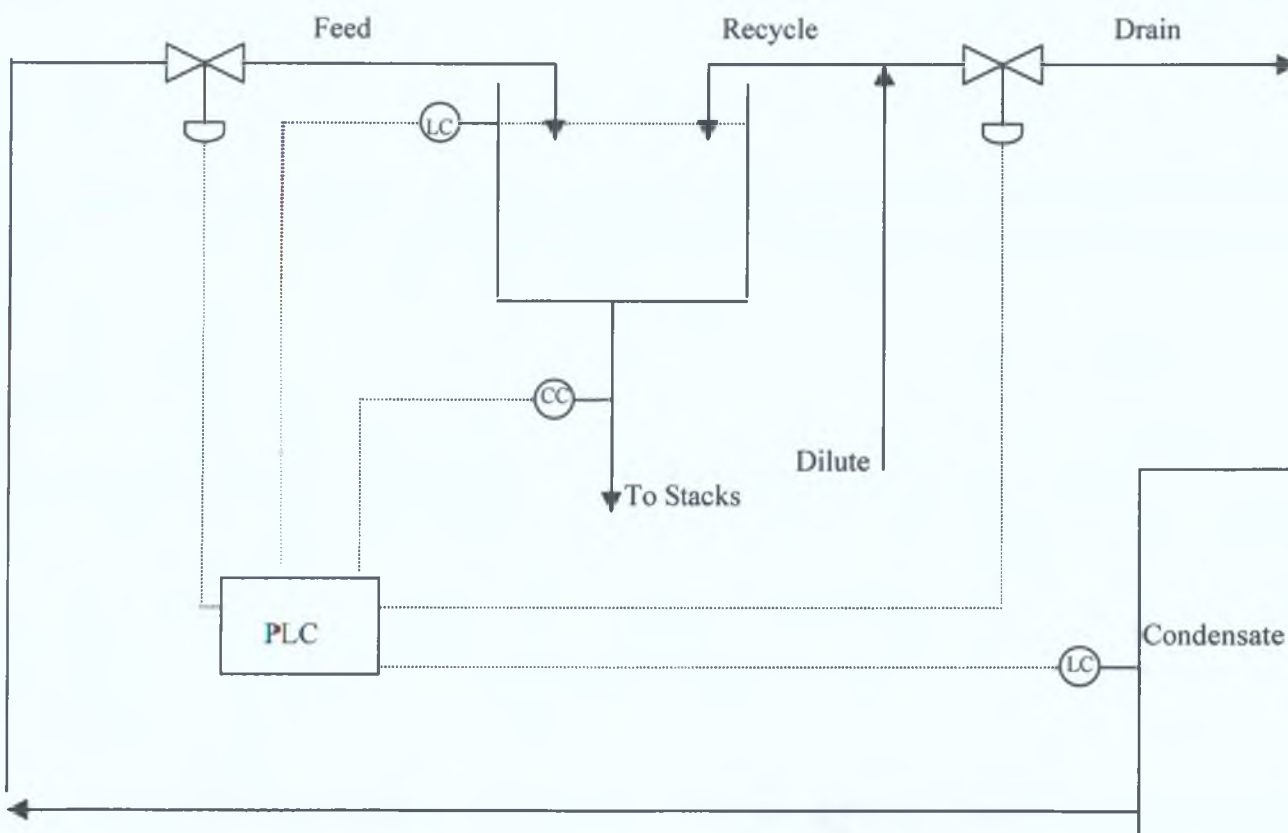
Plate 3: Membrane Stacks in series



The initial trial operations were on a batch mode running for about five hours, and these are the results that are presented in Appendix 1. In the first few weeks of operation, for safety reasons it was necessary to stop the plant after the days trial was complete. This was because the concentration of the effluent could vary in strength. If effluent of high strength entered the plant the resistance across the stack is greatly reduced and at a fixed voltage, it is possible for an increase in current to pass through the stacks. Without the use of fuses this high

current could damage the membrane stacks or even destroy the plant if a fire were to start. Fuses are used to trip the plant whenever a high current is reached. A control system needed to be designed to control the strength of effluent being introduced to the plant. This was done by installing a conductivity meter at the point where the effluent enters the stacks. This conductivity meter is part of a control loop and is linked to a control valve so as the conductivity increases the valve will begin to shut, limiting the amount of high strength effluent entering the plant. Due to the reduced feed rate, the tank level begins to fall, the PLC then closes the dilute drain valve to facilitate a greater flow rate. This reduces the conductivity of the feed going to the stacks. Below is a diagram of this control loop.

Fig. 11: Control Loop for EDR



This control system was installed and operated, and the plant has run continuously for many days without stopping. Further modifications are planned however, as on occasions, the conductivity meter does not detect the increased feed strength quickly enough and this high strength effluent is allowed to pass through the system and trip the plant. The corrective action proposed is to introduce another conductivity meter at a different point that will give earlier warning of high strength feed.

This control system is effective but is itself only a stopgap to the final solution, which is under construction. The final solution involves the installation of a 600m³ buffer tank that will collect the plant condensate and allow some mixing and dilution before the solution is pumped to the Electrodialysis plant. This has the added advantage that it will facilitate the collection of other effluent streams that contain ammonium nitrate. This project is underway, the bund for housing the storage tank is being prepared and the tank itself is being manufactured off site. It is expected that this part of the project will be completed in September 2002.

4.3 Future Modifications to the Process

One of the actions that will be carried out to improve efficiency is to reduce the time between polarity reversal. Currently reversal takes place every ten minutes. During the reversal of polarity, the concentrate stream becomes the dilute stream and the dilute stream becomes the concentrate stream. Obviously it will take a short period of time to flush out the contents of the lines with the new solution. In the case of the concentrate stream which upon reversal becomes the dilute stream; for the first couple of seconds as the dilute stream it is mixing with the residual high concentration solution in the line. Eventually the stream is made up entirely of dilute product, but until this takes place, the efficiency of the plant is greatly reduced. By increasing the time between reversals, that period of reduced efficiency during transition from dilute stream to concentrate stream will be minimised and overall efficiency increased. As is explained in section 2.4.3 of the literature review, the reason for reversal of polarity is to remove any possible built up of sediment or scale on the membranes that would affect plant performance. Because ions only travel towards one membrane for a short period of time, the possibility of scale build up is limited. If any scale does build up, reversing the polarity will force this scale into solution where it is carried away by the flowing dilute / concentrate streams. The configuration of reversal every ten minutes would be suitable for a waste stream that contains a high proportion of scaling compounds such as calcium carbonate. However in the case of IFI Arklow, apart from ammonium nitrate, the waste stream is very clean and scaling is not an issue. It was hoped that a discussion on the effect of increasing the delay between reversal could have been included in the dissertation but because of problems editing the PLC program, it has not yet been possible to carry out such action.

Another potential improvement action involves replacing any potentially damaged membranes. When an Electrodialysis plant is in storage, it is necessary to pickle the membranes in brine to avoid damage, without this they can crack and form leaks. These leaks can be in around the manifold with the result that the dilute stream can leak into the concentrated stream and vice versa. The plant in use in Arklow was not stored as it should have been and there was only sufficient brine to cover the bottom half of the membrane stack. As a result, there is potentially some damage to the membranes in the top half of the stack. However there are two series of three membrane stacks in parallel in the trail plant (only one series of three is needed for this application), the membranes in the second series were stored

in the same manner and it would be expected that the membranes at the bottom half of the stack would be in better condition. It would be possible to replace the top half of the three active stacks with the bottom half of the three inactive stacks and monitor any improvement in efficiency. This may be done in the future but this is a major job involving disassembly and reassembly of six membrane stacks. It would lead to extended downtime of the plant and would only be attempted during a period when the site is off line. Even then it may be a risky operation with the potential to introduce further problems.

5. Results

A detailed copy of all results to date is included in Appendix 1.

The following section will describe how the results from the trial were obtained, and what problems were encountered when gathering these results.

5.1 Method used to generate results

Results are given in the form of a mass balance, and the plant efficiency is then worked out on the results of that mass balance. When talking about mass, it is kilograms of nitrogen that is in question, to calculate the mass of nitrogen in the different streams two parameters are needed, one is the flow and the other in the concentration.

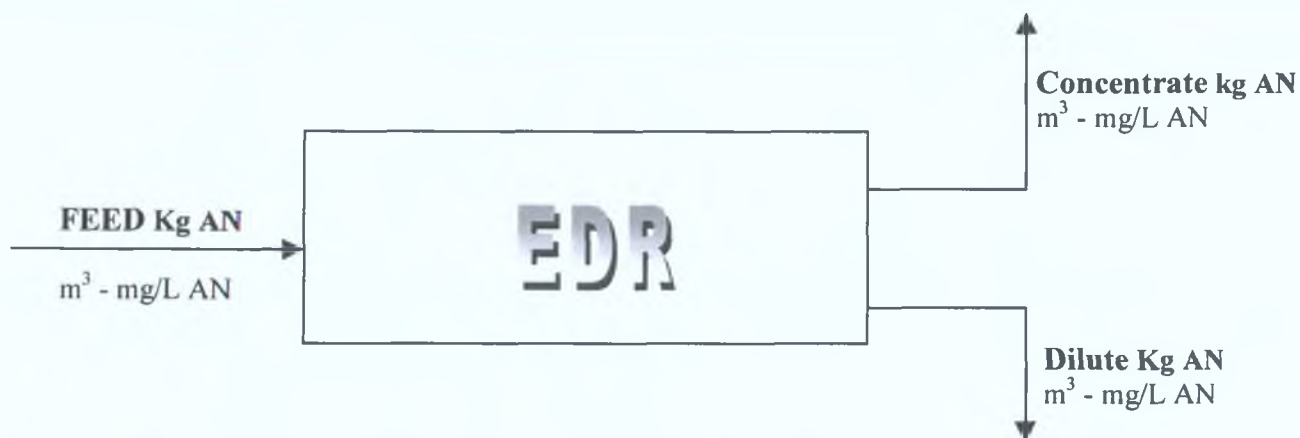


Fig. 12: Model for mass balance

The flow of effluent into the plant is measured using a portable magnetic flow meter. The flow of concentrate out of the plant is measured by an integrated flow meter. The concentrated effluent is collected in a tank and pumped in batch back to the plant, the quantity that has been pumped is known by taking note of the integrator readings on the tank. Therefore two of the three streams are measured directly, from this the flow of the third stream (dilute stream) can be calculated.

5.2 Discussion on results

Due to the time required to carry out tests and the number of samples taken it is not practical to do a chemical analysis to determine nitrogen concentration. Instead the concentration of nitrogen is determined by conductivity. There is a fixed relationship between nitrogen concentration and conductivity of the effluent solution; this was determined by experiment. Standard solutions of ammonium nitrate were made up and their conductivity was measured and a graph was constructed with the values, with the slope of the line being equivalent to the conversion factor needed to convert a conductivity reading in mS/cm into a concentration reading in g/L.

Following the installation of the control loop to control the feed strength to the plant, it was possible to run the plant continually for a number of weeks. An assessment of the impact on site effluent was reviewed. As previously stated, the current average mass of nitrogen from the site is in the order of 1200 kg per day. Based on the mass balance carried out, it was calculated that over a twenty-four hour period, the Electrodialysis plant would remove up to 800kg of Nitrogen. This would therefore mean that the site effluent should be around 400kg. This was not the case as can be seen by the chart above (Fig 13), which gives nitrogen emissions for an eight-day period. During this period, the daily average nitrogen mass emission from the site for the period was 720kg, while if mass balance calculations were to be believed, the value should have been closer to 400kg. The flow measurements are easily confirmed and agree with the site water balance. The most likely cause of inaccuracy was the estimation of ammonium nitrate concentration in the three streams. Because the feed stream into the Electrodialysis plant is taken at the point of export to the two nitric acid plants it is necessary that it contains a quantity of free acid to reduce the pH for safety reasons. As has been explained, to carry out the mass balance rather than complete analytical testing, conductivity from each of the streams is taken to be proportional to the ammonium nitrate concentration. This proportionality was worked out by preparing a series of standard solutions and measuring their conductivity. A graph was constructed with the values, the slope of the graph reflected the proportionality. The possibility that pH might be affecting the proportionality between conductivity and ammonium nitrate concentration was examined. Straight away it became apparent that pH of a solution was crucial with regard to the relationship between conductivity and concentration as can be seen from figure 14.

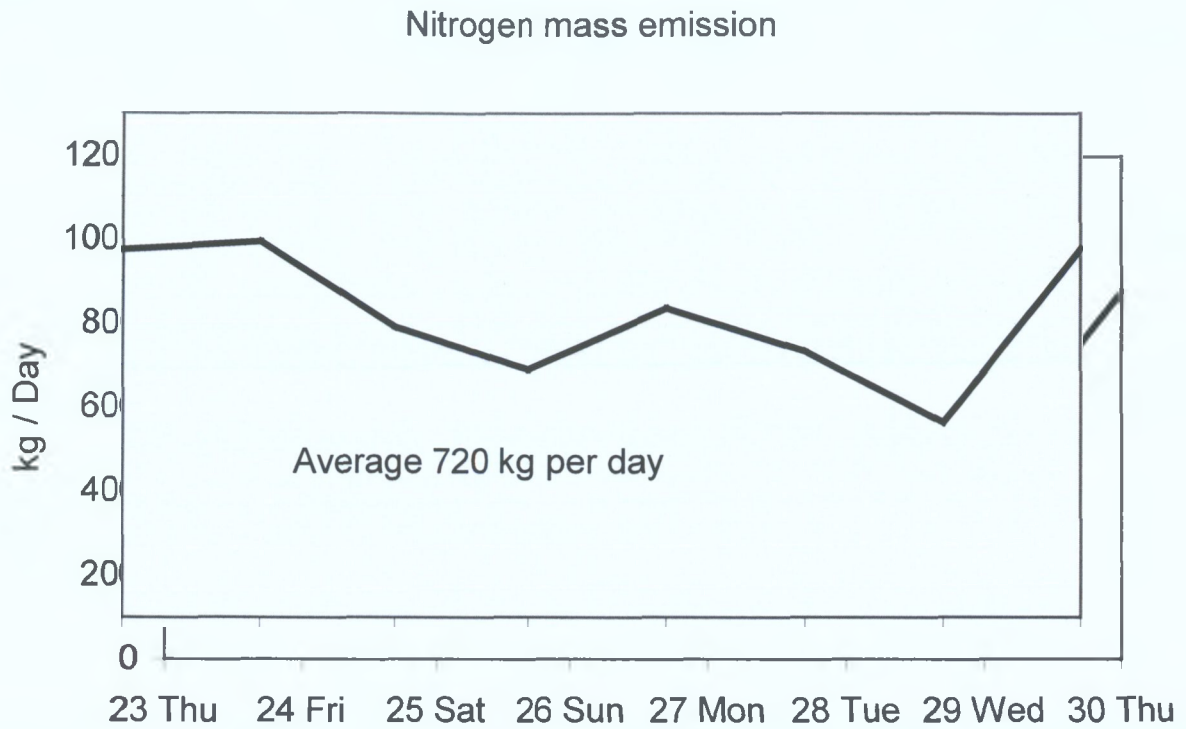
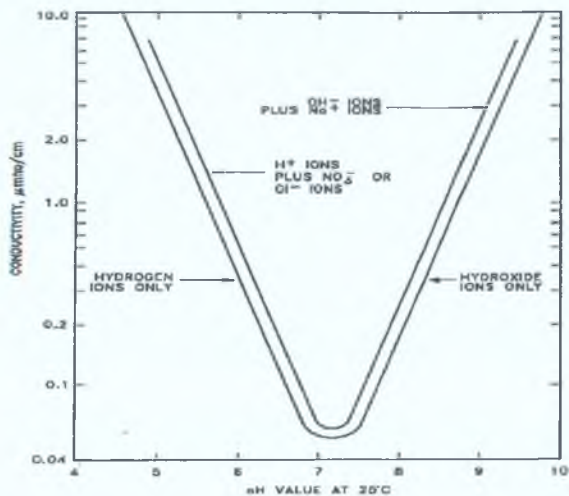


Fig. 13: Nitrogen Mass Emission from the Site with the Pilot Electrodialysis Plant in operation

slope of the graph reflected the proportionality. The possibility that pH might be affecting the proportionality between conductivity and ammonium nitrate concentration was examined. Straight away it became apparent that pH of a solution was crucial with regard to the relationship between conductivity and concentration as can be seen from the chart below.

Fig. 14: pH V's Conductivity



As can be seen from Fig. 14, the conductivity will increase greatly as the pH increases or decreases. Therefore in the case at IFI Arklow where the feed is acidic, it was clear that the conductivity would be higher at this lower pH and therefore there would be an overestimate of the ammonium nitrate concentration.

An estimate of the margin of error is given below (Table 3) which shows how much more ammonium nitrate appears present in solution for every extra gram of free acid in solution.

Table 3: Illustration of the overestimate of ammonium nitrate as a result of free acid in solution

Free acid g/L	Overestimate in ammonium nitrate concentration in g/L
1	3.6
2	7.3
3	10.9
4	14.5
5	18.1
6	21.7

The following equation is used to give the relationship between conductivity and pH as expressed in table 3. This equation was derived by experiment, by varying the quantity of free acid in standardised ammonium nitrate solution, and recording the change in conductivity.

$$\text{Ammonium nitrate g/L} = \text{Cond.} - (5.1 * \text{free acid conc. g/L}) / 1.4$$

Unfortunately it is not possible to retro-apply this equation to the results already gathered because the pH of the solutions is not known. To work out true percentage efficiencies taking free acid into account, a new series of detailed trials will need to be carried out similar to those carried out on the dates given in Appendix 1. However as well as measuring the conductivity of the different streams the pH is also needed. Both of these values can be imported into the above equation to give a true concentration of ammonium nitrate in the different streams.

Below is a summary of the results presented in Appendix 1, where percentage recovery is calculated from measurements taken every half-hour. As has been previously stated, at the time these results were being gathered, the significance of free acid in the waste stream was not realised. For this reason, there is a definite over-estimate in the total kg of Nitrogen removed, although the percentage recovery should still be reasonably accurate, based on the following:

The amount of acid entering the plant is equal to the amount of acid leaving the plant in either the dilute stream or the concentrate stream. So the three streams that need to be measured each contain a proportional fraction of acid that will elevate the conductivity reading and offset the results. On this basis, the amount of ammonium nitrate estimated in each stream would be a slight overestimation but the ratio of ammonium nitrate in the different streams should be correct.

The only problem with this rationale is that it is expected that free acid will be preferentially removed from the effluent instead of ammonium nitrate due to the size of the hydrogen ion and its ability to move easily in solution and across the membrane. If this is the case, with a higher proportion of free acid in the concentrate stream, the calculated mass of ammonium nitrate would be greater and hence this would show a greater mass of ammonium nitrate in the concentrate stream against the dilute stream and therefore greater percentage recovery.

Table 4: Percentage recovery results for trial period

Date	kg AN Inlet	kg AN Dilute stream	kg AN Conc. stream	% Recovery
07/02/2002	496.76	84.27	412.49	83
13/02/2002	404.73	26.68	378.05	93
14/02/2002	329.12	15.19	313.93	95
13/02/2002	250.00	19.45	230.55	92
18/02/2002	424.87	22.75	402.13	95
19/02/2002	332.87	35.71	297.17	89
01/03/2002	310.02	15.47	294.55	95
04/03/2002	349.02	18.36	330.66	95
05/03/2002	519.07	9.47	509.60	98

Another comment on the results relates to those results for the 7th of February, 2002. One of the first problems that was discovered in the process was a problem with the second stack in the system. When the polarity was being reversed, the voltage in this stack dropped. This gave rise to a reduction in recovery efficiency for the first trial runs. This problem was caused by a faulty fuse and was resolved. After this, the plant efficiency improved.

6. Discussion

The following discussion will focus on two areas. The first is whether or not the approach to effluent treatment at IFI Arklow represents BAT or BATNEEC. The second area of discussion will focus on cross media pollution and whether the cross media pollution implications of running an effluent treatment plant at IFI Arklow outweighs the need for operation of such a plant.

6.1 BAT v's BATNEEC

The current EPA licensing structure is the Integrated Pollution Control (IPC) Licence brought in under Section 82 of the EPA Act, 1992. The core objective of IPC is as it states, to integrate the licence to cover pollution to all media. Previous regimes used separate licences for air, water and waste, the effect of this is that one media may suffer at the expense of the other. For example, a scrubber removing a potential air emission may discharge the scrubbing solution to water with the potential to cause pollution. An integrated licence covers emissions to all media and prevents shifting of pollution between various media. If the pollution is shifted to a new media, it is important that it is to the one that will have the least environmental impact.

To control pollution under the IPC regime, the principle to be adhered to is **BATNEEC**, this stands for Best Available Technology Not Entailing Excessive Cost. IPC licensed companies are required to “prevent, eliminate or where this is not practicable, limit or reduce an emission from an activity” by means of the “provision and proper maintenance, use, operation and supervision of facilities which, having regard to all circumstances are the most suitable for the process”. The **Technology** used should be the **Best** at preventing pollution and **Available** in the sense that it is procurable by the industry concerned. **NEEC** sets out the balance between environmental benefit and the financial expense to be borne by the industry. Emission Limit Values set by the EPA are set on the basis of BATNEEC identified by the EPA, i.e. they are achievable using BATNEEC technology. The EPA has published various BATNEEC guidance notes to cover different licensable sectors.

The EC Directive 96/61/EC, Integrated Pollution Prevention and Control (IPPC) was brought in to supersede the IPC licensing structure. One of the fundamental differences between IPC and IPPC is that rather than BATNEEC, IPPC uses **BAT** or **Best Available Technology**.

Article 2 of the Directive states that BAT shall mean "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle, the basis for emission limit

values designed to prevent and, where is not practicable, generally to reduce emissions and the impact on the environment as a whole."

Annex IV outlines the special considerations which need to be taken into account when determining the Best Available Technique to treat a particular source of pollution. When looking at the various options available to treat the effluent at IFI Arklow, if possible BAT would be used. Based on the definitions given in the Directive it is thought that using Electrodialysis to treat the ARU waste stream represents BAT. Electrodialysis is a low waste technology, there is no use of hazardous substances and most importantly, the use of Electrodialysis furthers "the recovery and recycling of substances generated and used in the process and of waste". This is one of the advantages of Electrodialysis and one of the ways it meets BAT requirements, the nitrogen that would go to drain is instead recycled into the plant to create more product. But on top of this, the clean stream is now also another potentially useful waste stream. The Electrodialysis process has removed the vast majority of ions from the clean stream leaving a low TDS value. With a low TDS value this stream is potentially very useful as boiler feed water or for general process water or cooling water. It may be necessary to carry out some tertiary treatment before the clean stream would be reused, but this is an area that is under investigation and will most certainly be taken advantage of. This will reduce the quantity of demineralised water that is needed to be produced, which will save on energy and chemical usage. Other treatment methods such as biological treatment will eliminate nitrogen from the waste stream but it will replace it with a substitute waste – sludge, which will need to be disposed of. An evaporation system may have been cheaper to install and easier to operate, but would have had a greater energy requirement to recover all the nitrogen in the waste stream.

As has been mentioned in the earlier section introducing the background to the effluent treatment project at IFI Arklow, replacement of the old wet section of both CAN plants with a new modern wet section capable of providing sufficient ammonium nitrate with virtually no contaminated condensate was one of the options examined. This option would have removed enough nitrogen from the site effluent to meet our licence limits and would have met the requirements of BAT. However, it was not possible due to the excessive costs of implementation, possibly four to five time more expensive than the next best option. This sort of cost could simply not be borne by the company in its current financial position. The point to be made is that although BAT no longer has the NEEC aspect, it still does have to take into account the cost. The definition of **Available** under section 11 of article 2 is - "those (techniques) developed on a scale which allows implementation in the relevant industrial sector, under **economically** and technically viable conditions, taking into consideration the **costs** and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator". It is clear from the above definition that cost is still a valid reason for rejecting one treatment option over another, even if the one rejected may be more effective. On this basis, rejecting the replacement of the wet sections on the basis of cost is justified and the

next best option can still be considered as BAT. On these grounds, the next best option, which is Electrodialysis can be considered to be BAT.

6.2 Cross Media Pollution

This is an interesting area worthy of discussion. The principle is similar in many ways to the IPC principle, in that environmental media should not be cleaned up at the expense of polluting another environmental medium. Environmental impact will be the approach used when discussing this point. The discussion is not about which is the most suitable method for the treatment of the waste stream but rather, is the treatment of the waste stream going to have a greater environmental impact than if no treatment had been carried out?

6.2.1 Impact of IFI effluent on Avoca River

The first point to be examined is the impact of the waste stream before treatment. Currently IFI Arklow discharges 3500m³ to 4000m³ of effluent to the Avoca River each day. This effluent contains on average (prior to Electrodialysis treatment) 1200kg of Nitrogen, with a roughly 50:50 split between nitrate and ammonium, although due to a recent project which removed an ammonium rich stream, there is in the order of 50kg excess nitrate. This is significant as it makes it less likely for ammonium to exist in its unionised form of ammonia. Based on work carried out by Board na Mona in 1995, river flows have been calculated, and these flows were used to calculate what dilution effect they would have on the IFI Arklow effluent. Although dilution factors upwards of 1 in 177 have been calculated, the lowest dilution was about 1 in 60, representing a dry weather flow. The case of dry weather flow will be used because it is in this scenario that the IFI Arklow discharge would have the greatest environmental impact because of the lack of dilution. The impact of the effluent will be taken as one of direct toxicity. The subject of eutrophication is not relevant as the discharge is into a fast moving river which is flowing to the sea within 1 km of the discharge point, so there is no chance of algal blooms removing oxygen from the water and affecting fish stocks.

When working out the dilution effects of the river, it is worth noting that the IFI Arklow effluent is discharged by a diffuser across the width of the riverbed, so dilution is uniform and there would be no areas of plug flow where relatively higher concentrations may be found. Using the average concentration of ammonium nitrate discharged from site for the year 2001 and based on the above discharge rates and the river flow information, the ammonium nitrate concentration to be found during normal emissions in the Avoca River during dry weather can be calculated. Using an average concentration of 982mg/L ammonium nitrate diluted 1 in 60, the river concentration will be in the order of 16mg/L. There is no data available to the author on the toxicity of ammonium nitrate to aquatic species. But as a neutral salt it will be relatively harmless in this concentration, the EC Directive on freshwater gives a maximum admissible concentration (MAC) of 50mg NO₃ /l for nitrate.

It is of more relevance to concentrate on the ammonium fraction, and calculate what the possible ammonia concentration would be, taking pH and temperature into account. The acute lethal concentrations of unionised ammonia for a variety of fish species lie in the range of 0.2 to 2 mg/L, with trout being the most sensitive (Alabaster, J.S. & Lloyd (1982) Water Quality Criteria for Freshwater Fish. Butterworths, London). The average ammonium concentration in the effluent discharge was 173mg/L for 2001, assuming a 1 in 60 dilution for dry weather conditions the ammonium concentration in the river will be 2.8mg/L. Using a pH of 7.4 and a temperature of 15°C (estimated maximums), it can be seen that the percentage of free ammonia would be 0.66%, giving an actual free ammonia concentration of 0.02mg/L, well below the level that will be toxic to fish.

Table 5: The NH3 content (as % of total ammonia) of water at different pH values and temperature

PH	TEMPERATURE deg C				
	0	5	10	15	20
6.6	0.03	0.05	0.07	0.11	0.15
6.8	0.05	0.08	0.11	0.18	0.24
7.0	0.09	0.12	0.18	0.27	0.39
7.2	0.13	0.20	0.29	0.42	0.61
7.4	0.21	0.31	0.46	0.66	0.97
7.6	0.34	0.49	0.72	1.05	1.53
7.8	0.53	0.78	1.14	1.65	2.40
8.0	0.84	1.23	1.79	2.59	3.74
8.2	1.33	1.93	2.80	4.05	5.81
8.4	2.09	3.03	4.37	6.26	8.90
8.6	3.28	4.72	6.76	9.58	13.41
8.8	5.10	7.28	10.30	14.37	19.71
9.0	7.84	11.07	15.40	21.02	28.01
9.2	11.89	16.47	22.38	29.66	38.14
9.4	17.61	23.82	31.37	40.06	49.42
9.6	25.31	33.13	42.01	51.44	60.77
9.8	34.94	43.98	53.45	62.67	71.05
10.0	45.98	55.45	64.54	72.68	79.55

From the above it can be concluded that even before treatment, the effluent being emitted had a very small environmental impact on the river.

With regard to the environmental impact of the IFI Arklow effluent discharge, it must be pointed out that to all intents and purposes, the Avoca river downstream of the Avoca mines has been a “dead river” since mining first began in about 1750. Mining activities are dated to this period by W. Smyth (1853). Although other evidence suggests mining activities from an even earlier date, damage caused to the river through mining activities has been well documented (A Went, 1979). Studies carried out into Macro-invertebrates in the Avoca river by An Foras Forbatha in 1978 noted that flora and fauna had been almost eliminated in the river due to excessive copper and zinc contamination (Report No. WR/C 35). Some recent studies suggest that there is now a limited fauna since the closing of the Avoca mines in 1982, but the levels of contaminated leachate that still enter the river make it impossible for a balanced ecosystem to survive. The conclusion of a Board na Mona report assessing the chemical and biological quality upstream and downstream of IFI Arklow in 1994 states that: “The results demonstrate an extremely low score using species diversity indices (Trent Biotic Index, Simpson's Index). There is no evidence of biological difference in samples upstream and downstream of IFI Arklow outfall. It is, therefore, concluded that the poor biological quality of the river sediment may be due to toxic inputs from historic mining activity along the valley and in addition to possible on-going lechates from the associated tailing ponds.”

The above evidence does indicate that the Avoca River downstream of the mines is devoid of life, and as such, emissions from IFI Arklow would have a very limited environmental impact as there is no ecosystem to impact upon. It is accepted however that migratory fish probably do make the run up the river to spawn during spate conditions and as such, the river water quality needs to be of a standard that will allow the passage (not residence) of any migratory fish. On this point, migration of spawning fish will generally occur in the winter and spring when the river will be in full flow and any emissions from IFI Arklow will be greatly diluted by over 1 in 100. There are very few species, particularly on the east coast that will make the run during summer.

6.2.2 Environmental impact of effluent treatment plant at IFI Arklow

Next to be examined is the environmental impact of operating an effluent treatment plant at IFI Arklow. This will be based on the operation of the Electrodialysis plant recovering in the order of 700kg of ammonium nitrate per day. The area to be examined will be energy consumption and the associated CO₂ production.

The Electrodialysis plant uses no chemicals and the only raw material used is energy. Energy is consumed in two ways while operating the plant. The first is operation of pumps to drive the effluent through the system and the second is the power consumed to drive a current across the three membrane stacks. There is also a small quantity of energy used on miscellaneous items such as lights, heaters and electrical instruments.

The following is a breakdown of the total energy consumed by the plant. It was not possible to get direct measurements of power consumption from the IFI plant (although this will be

done in the future). Instead, an example of a plant treating a similar hydraulic load and removing comparable quantities of salt has been taken (Perry's Chemical Engineers Handbook, 1984). Using this example, a total energy consumption of 700 kwatts/day was calculated. This is equivalent to 2,520,000 kJoules. To work out raw energy requirements and CO₂ production, it will be assumed that electrical energy is being produced by a gas turbine power station burning natural gas. The calorific value of natural gas will be taken as 55MJ/kg (assumed 100% methane). To produce 2520MJ of energy at 100% efficiency, 48kg of natural gas would be required. In reality, steam powered generating plants have efficiencies between 30-40%. For the example, 35% efficiency will be assumed, this therefore requires combustion of 131kg of natural gas, energy loss from distribution on the national grid is estimated at 10%, making the required mass of natural gas 144kg/day.

Burning 144kg/day natural gas (assuming 100% methane) will produce 395.9 kg of CO₂. While this in itself may not be a massive figure when taken over a year, the amount of CO₂ produced would be 145Te/year (If coal were used as the primary energy source the value will be in the order of 1250Te/year). This is not an insignificant figure when you consider that under the Kyoto protocol western countries must reduce their CO₂ levels to those of 1990, with Ireland agreeing to reduce its emissions to 13% above its 1990 figure.

It should be noted that the above example does not take into account the energy required to evaporate off the water in the concentrate stream before it is returned to the process. This is because due to the exothermic nature of the site, the current arrangement allows for the use of plant steam to evaporate off the water content of the returning stream. If however, primary energy was needed in the future, this would add an estimated further 13,000Te of CO₂ emissions per annum.

It is difficult to draw a final conclusion. It is dependent on the interpretation of the impact of the IFI Arklow effluent on the Avoca River. The data presented above indicates that the current impact is essentially negligible. This being the case, it does not make great environmental sense to emit any extra CO₂ to the atmosphere as well as use up more of the earth's limited non-renewable energy sources. On the other hand, if it were the case that lechate from mining activities were abated and the return of a viable ecosystem was eminent except for emission from IFI, it would make absolute sense to use up energy and emit CO₂, to see a return to a healthy river. It would however be more ideal if the effluent could be abated without the use of primary energy by using clean technology in the production plants.

7. Conclusions

7.1 Effectiveness of Electrodialysis in meeting new IPC Licence Limits

As has been pointed out, the use of conductivity readings to estimate ammonium nitrate concentration was affected by the free acid content in the feed stream. Also the acid enters the concentrate stream preferentially over ammonium nitrate, therefore there is an overestimate of recovered product. However from the summary results presented, it can be concluded that the process is capable of removing ammonium nitrate from the waste stream. The dilute stream that is currently goes to drain contains about 0.6g/L, a reduction from about 5g/L. Not taking into account inaccuracies related to conductivity readings, there is about a tenfold reduction in Nitrogen to drain. The quantity of nitrogen that it is necessary to remove from the ARU is in the region of 700 - 800 kg. With improvements to the process, it is still felt that this figure can be achieved. One of the most immediate improvements to the process will come from removing the excess acid in solution as will be explained as follows.

The free acid in the feed stream is affecting the calculations of the amount of nitrogen removed. But a second implication relates to the operation of the plant. As was explained in the section relating to commissioning of the plant to prevent high strength feed entering the process and tripping the plant it was necessary to install a control valve that closes as the feed strength increases to allow less feed into the system. This control valve will shut completely when the conductivity reaches 20 mSe. As part of the investigation into the effect of the acid addition causing miscalculation of ammonium nitrate concentrations, it was discovered that in fact too much acid was being added to the stream in the first place.

The control valve that doses the stream discharging from the ammonium recovery unit (ARU) with acid has on occasion, been found passing acid when in the closed position. The set point is at a pH of 2 and at this value, the valve should close. On a recent test, pH in the order of 1.3 was measured, meaning that the control valve is not functioning correctly. This has major implications for running of the Electrodialysis plant. Because the feed to the plant is highly acidic it also has a high conductivity, reaching over 20 mSe. At this point, the valve is closing and feed to the Electrodialysis plant is being stopped. When the Electrodialysis plant is not taking in this feed, it is diverted to drain and discharges with the remainder of the site effluent. The original control valve has now been replaced, but while it was in operation, the Electrodialysis plant was not treating the entire waste stream it has the potential to treat. The plant will need to run for a period of time treating all of the ARU waste stream, then another mass balance can be carried out to quantify the effectiveness of the Electrodialysis plant.

7.2 Further discussion on the issue of pH

The difficulties that the acid addition to the effluent from the ARU is causing the Electrodialysis plant has been discussed. The notion of adding acid at one point and then expend energy taking it out a few seconds later 10m down the line sounds slightly absurd. However, this was the only point at which the Electrodialysis plant could be tied in (after acid addition). Ideally the plant would treat the raw effluent from the ARU and not expend energy removing this excess acid. But some acid addition will be required for the final plant. Because the membranes are only stable in a pH range of 1-10 and above 10 there is a risk of permanent damage. It is possible during times of unsteady running of the CAN plants that there is a large quantity of rich condensate sent to the ARU. Also it is possible for the control valve controlling the pH of the absorption section of the stripper to fail. In both of these scenarios it is possible that the condensate being sent to the Electrodialysis plant may have free ammonia. Due to the sharp neutralisation curve, it is possible for the pH to quickly swing up to 10. To prevent this from occurring, there will always be a need for some acid to be added to the condensate entering the plant. This will be done in a controlled manner that does not use excess power.

7.3 Electrical efficiency

It had been hoped to include a discussion on the electrical efficiency of the plant but insufficient data has been gathered on this point to date. However electrical efficiency is an area that will receive concerted focus once all other aspects of the plant are satisfactory. Ultimately the main cost of running the Electrodialysis plant is the power required to drive the ions across the stacks as well as the hydraulic power to move the effluent through the system. The former has the larger power requirement. It will in the future be possible to optimise the recovery rate while using the lowest possible current through the membrane stacks.

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Appendix

EDR Trial 07/02/2002

Conductivity conversion factor 0.65

Continuous Results

Time		10:00	10:30	11:00	11:30	12:00	12:30	13:00	13:30	14:00	14:30	Totals
Stack Voltage												
	1	363	363	363	363	363	363	363	363	363	363	
	2	59	59	363	59	59	363	59	363	59	363	
	3	351	351	353	351	351	353	351	353	351	353	
Inlet												
temp	OC	29	29	29	29	30	29	29	30	31	31	
Q	m3/hr	8.5	9.8	10.1	9.9	11.2	10.1	10.1	9.9	10.5	10.8	50.45
C	mS/cm	11.8	17.6	17.3	16.2	16.1	15.9	15.4	13.9	13.3	13.6	
Conc	g/l	7.67	11.44	11.245	10.53	10.465	10.335	10.01	9.035	8.645	8.84	
AN	Kg	32.5975	56.056	56.78725	52.1235	58.604	52.19175	50.5505	44.72325	45.38625	47.736	496.756
Feed												
temp	OC	31	31	32	31.2	32	31.4	32.5	32.5	32	32	
Q	m3/hr	27	27	29	29	29	30	30	28	28	28	285
C	mS/cm	6	7.5	6.5	7.5	6.5	6	7.5	7.5	6	6.5	
Conc	g/l	3.9	4.875	4.225	4.875	4.225	3.9	4.875	4.875	3.9	4.225	
AN	Kg	52.65	65.8125	61.2625	70.6875	61.2625	58.5	73.125	68.25	54.6	59.15	625.3
Dilute product												
C	mS/cm	1.2	1.45	1	1.4	1.01	1.1	1.4	0.9	1	1	
Conc	g/l	0.78	0.9425	0.65	0.91	0.6565	0.715	0.91	0.585	0.65	0.65	

Batch Product Results

Initial Gauge reading 85055370

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	Gallon	Gallon	m3/h	mS/cm	g/l	Kg
1	85056090	720	2.725	22	14.3	38.97448
2	85056850	760	2.877	32	20.8	59.8396
3	85057650	800	3.028	32	20.8	62.98906
4	85058400	750	2.839	29.7	19.305	54.80786
5	85059200	800	3.028	30.5	19.825	60.03644
6	85059970	770	2.915	29.5	19.175	55.89048
7	85060740	770	2.915	26.6	17.29	50.39617
8	85061180	440	1.666	27.3	17.745	29.55565
Total		5810	21.993			412.4897

Notes: The concentrate product was pumped batchwise

EDR Trial 13/02/2002

Conductivity conversion factor 0.65

Continuous Results

Time		11:30	12:00	12:30	13:00	13:30	14:00	14:30	15:00	15:30	16:00	Totals
Stack Voltage												
	1	322	322	322	322	322	322	322	322	322	322	
	2	302	302	302	302	302	302	302	302	302	302	
	3	300	300	300	300	300	300	300	300	300	300	
Inlet												
temp	OC	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	
Q	m3/hr	9.3	9.4	10.1	9.2	9.8	9.2	9.8	9.8	9.4	9.9	47.95
C	mS/cm	12.9	13.1	11.45	13.67	13.3	13.4	12.87	12.2	13.6	13.5	
Conc	g/l	8.385	8.515	7.4425	8.8855	8.645	8.71	8.3655	7.93	8.84	8.775	
AN	Kg	38.99025	40.0205	37.58463	40.8733	42.3605	40.066	40.99095	38.857	41.548	43.43625	404.7274
Feed												
temp	OC	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	
Q	m3/hr	27	27	29	29	29	30	30	28	28	28	285
C	mS/cm	6.2	6	5.5	6	6.5	6	5.5	6	5	6.2	
Conc	g/l	4.03	3.9	3.575	3.9	4.225	3.9	3.575	3.9	3.25	4.03	
AN	Kg	54.405	52.65	51.8375	56.55	61.2625	58.5	53.625	54.6	45.5	56.42	545.35
Dilute product												
C	mS/cm	1.55	1.4	1.65	1.45	1.6	1.6	1.6	1.6	1.3	1.7	1.5
Conc	g/l	1.0075	0.91	1.0725	0.9425	1.04	1.04	1.04	1.04	0.845	1.105	

Batch Product Results

Initial Gauge reading 85063630

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	Gallon	Gallon	m3/h	mS/cm	g/l	Kg
1	85064350	720	2.725	29.3	19.045	51.90692
2	85065080	730	2.763	29.4	19.11	52.80747
3	85065800	720	2.725	30.5	19.825	54.0328
4	85066490	690	2.612	30	19.5	50.93256
5	85067210	720	2.725	30.2	19.63	53.50133
6	85067430	220	0.833	31.4	20.41	16.9972
7	85068140	710	2.688	30.5	19.825	53.28234
8	85068740	600	2.271	30.2	19.63	44.58444
Total		5110	19.343			378.0451

Notes: The concentrate product was pumped batchwise

EDR Trial 14/02/2002

Conductivity conversion factor

0.65

Continuous Results

Time		10:00	10:30	11:00	11:30	12:00	12:30	13:00	13:30	14:00	14:30	15:00	Totals
Stack Voltage	1	339.5	339.5	339.5	339.5	339.5	339.5	339.5	339.5	339.5	339.5	339.5	
	2	340	340	340	340	340	340	340	340	340	340	340	
	3	316	316	316	316	316	316	316	316	316	316	316	
Inlet													
temp	OC	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	
Q	m3/hr	10.7	10.4	10.9	10.1	9.5	9.1	9.2	9.2	9.8	8.4	8.7	53
C	mS/cm	9.5	10.2	10.2	9.8	9.9	9.1	9.05	9.2	9.2	9.4	9.3	
Conc	g/l	6.175	6.63	6.63	6.37	6.435	5.915	5.8825	5.98	5.98	6.11	6.045	
AN	Kg	33.03625	34.476	36.1335	32.1685	30.56625	26.91325	27.0595	27.508	29.302	25.662	26.29575	329.121
Feed													
temp	OC	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	
Q	m3/hr	28	28	28	28	28	28	28	28	28	28	28	308
C	mS/cm	5	4.5	4	5	4	4	4.5	4.5	4	4.5	4.5	
Conc	g/l	3.25	2.925	2.6	3.25	2.6	2.6	2.925	2.925	2.6	2.925	2.925	
AN	Kg	45.5	40.95	36.4	45.5	36.4	36.4	40.95	40.95	36.4	40.95	40.95	441.35
Dilute product													
C	mS/cm	1	0.8	0.8	0.7	0.6	0.8	0.75	0.85	0.8	0.8	0.9	1.5
Conc	g/l	0.65	0.52	0.52	0.455	0.39	0.52	0.4875	0.5525	0.52	0.52	0.585	

Batch Product Results

Initial Gauge reading

85067430

Run	Gauge reading	Quantity	Quantity	conductivity	Conc	AN
	<i>Gallon</i>	<i>Gallon</i>	<i>m3/h</i>	<i>mS/cm</i>	<i>g/l</i>	<i>Kg</i>
1	85068170	740	2.801	23	14.95	41.87788
2	85068910	740	2.801	23	14.95	41.87788
3	85069610	700	2.650	24.2	15.73	41.68104
4	85070330	720	2.725	24.4	15.86	43.22624
5	85071050	720	2.725	21.8	14.17	38.62016
6	85071790	740	2.801	21.4	13.91	38.96464
7	85072510	720	2.725	22.1	14.365	39.15164
8	85073030	520	1.968	22.3	14.495	28.53207
Total		5600	21.198			313.9315

Notes: The concentrate product was pumped batchwise

EDR Trial 13/02/2002

Conductivity conversion factor 0.65

Continuous Results

Time		09:30	10:00	10:30	11:00	11:30	12:00	12:30
Stack Voltage								
	1	340	340	340	340	340	340	340
	2	341	341	341	341	341	341	341
	3	316	316	316	316	316	316	316
Inlet								
temp	0C	30.1	30.1	30.1	30.1	30.1	30.1	30.1
Q	m3/hr	10	9.6	9.2	10.1	9.2	8.5	8.4
C	mS/cm	13.5	12.7	10.3	11.9	12.1	12.1	12.2
Conc	g/l	8.775	8.255	6.695	7.735	7.865	7.865	7.93
AN	Kg	43.875	39.624	30.797	39.06175	36.179	33.42625	33.306
Feed								
temp	0C	32.1	32.1	32.1	32.1	32.1	32.1	32.1
Q	m3/hr	28	28	29	29	29	30	30
C	mS/cm	6.5	6	6	5	5.5	5.5	5
Conc	g/l	4.225	3.9	3.9	3.25	3.575	3.575	3.25
AN	Kg	59.15	54.6	56.55	47.125	51.8375	53.625	48.75
Dilute product								
C	mS/cm	1.15	0.95	0.9	1	0.9	0.95	0.95
Conc	g/l	0.7475	0.6175	0.585	0.65	0.585	0.6175	0.6175

32.5

250

Batch Product Results

Initial Gauge reading 85073030

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	Gallon	Gallon	m3/h	mS/cm	g/l	Kg
1	85073890	860	3.255	26.3	17.095	55.65182
2	85074610	720	2.725	26.7	17.355	47.30084
3	85075340	730	2.763	27.1	17.615	48.67627
4	85075830	490	1.855	27.3	17.745	32.91424
5	85076520	690	2.612	27.1	17.615	46.00908
Total		3490	13.211			230.5522

Notes: The concentrate product was pumped batchwise

EDR Trial 18/02/2002

Conductivity conversion factor 0.65

Continuous Results

Time		10:00	10:30	11:00	11:30	12:00	12:30	13:00	13:30	14:00	14:30	15:00	Totals
Stack Vol	1	356	356	356	356	356	356	356	356	356	356	356	
	2	357	357	357	357	357	357	357	357	357	357	357	
	3	332	332	332	332	332	332	332	332	332	332	332	
Inlet													
temp	OC	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	
Q	m3/hr	10.1	9.5	9.4	8.4	9.1	7.5	8.4	8.5	8.1	8.4	8.4	47.9
C	mS/cm	12.6	12.6	16.7	14.7	13.9	12.8	17.3	11	13.3	12.6	12.5	
Conc	g/l	8.19	8.19	10.855	9.555	9.035	8.32	11.245	7.15	8.645	8.19	8.125	
AN	Kg	41.3595	38.9025	51.0185	40.131	41.10925	31.2	47.229	30.3875	35.01225	34.398	34.125	424.8725
Feed													
temp	OC	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	
Q	m3/hr	28	28	28	28	28	28	28	28	28	28	28	308
C	mS/cm	6	6	8.5	7	5.5	6	6.5	6	6.5	6.5	5	
Conc	g/l	3.9	3.9	5.525	4.55	3.575	3.9	4.225	3.9	4.225	4.225	3.25	
AN	Kg	54.6	54.6	77.35	63.7	50.05	54.6	59.15	54.6	59.15	59.15	45.5	632.45
Dilute product													
C	mS/cm	1.7	2	1.4	1.7	1.65	1.4	1.65	1.7	1.4	1.3	1	1.5
Conc	g/l	1.105	1.3	0.91	1.105	1.0725	0.91	1.0725	1.105	0.91	0.845	0.65	

Batch Product Results

Initial Gauge reading 85076550

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	Gallon	Gallon	m3/h	mS/cm	g/l	Kg
1	85077430	880	3.331	29.7	19.305	64.30789
2	85078210	780	2.953	27.8	18.07	53.3537
3	85078940	730	2.763	28.3	18.395	50.83168
4	85079670	730	2.763	27.5	17.875	49.39474
5	85080410	740	2.801	27.3	17.745	49.70722
6	85081170	760	2.877	34.2	22.23	63.95358
7	85081950	780	2.953	26.6	17.29	51.05066
8	85082270	320	1.211	24.8	16.12	19.52661
Total		5720	21.652			402.1261

Notes: The concentrate product was pumped batchwise

EDR Trial 19/02/2002

Conductivity conversion factor 0.65

Continuous Results

Time		10:00	10:30	11:00	11:30	12:00	12:30	13:00	13:30	Totals
Stack Vol	1	356	356	356	356	356	356	356	356	
	2	357	357	357	357	357	357	357	357	
	3	332	332	332	332	332	332	332	332	
Inlet										
temp	OC	34.3	34.3	34.3	34.3	34.3	34.3	34.3	34.3	
Q	m3/hr	8.4	11.5	11.5	10.9	10.4	11.8	12.2	11.5	88.2
C	mS/cm	13.4	13.3	13.3	11.6	10.7	10.6	10.3	10.2	
Conc	g/l	8.71	8.645	8.645	7.54	6.955	6.89	6.695	6.63	
AN	Kg	36.582	49.70875	49.70875	41.093	36.166	40.651	40.8395	38.1225	332.8715
Feed										
temp	OC	36.1	36.1	36.1	36.1	36.1	36.1	36.1	36.1	
Q	m3/hr	29	29	29	29	29	29	29	29	
C	mS/cm	7.5	6	6.5	7	5.5	6	6.5	5.5	
Conc	g/l	4.875	3.9	4.225	4.55	3.575	3.9	4.225	3.575	
AN	Kg	70.6875	56.55	61.2625	65.975	51.8375	56.55	61.2625	51.8375	
Dilute product										
C	mS/cm	0.95	1.15	0.85	1.2	1.4	1.25	1.1	1.3	
Conc	g/l	0.6175	0.7475	0.5525	0.78	0.91	0.8125	0.715	0.845	

Batch Product Results

Initial Gauge reading 85082270

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	Gallon	Gallon	m3/h	mS/cm	g/l	Kg
1	85083010	740	2.801	29.4	19.11	53.53086
2	85083760	750	2.839	32.6	21.19	60.15947
3	85084460	700	2.650	32.4	21.06	55.80437
4	85085180	720	2.725	31.6	20.54	55.98152
5	85085900	720	2.725	30.3	19.695	53.67849
6	85086140	240	0.908	30.5	19.825	18.01093
Total		3870	14.649			297.1656

Notes: The concentrate product was pumped batchwis

EDR Trial 01/03/2002

Conductivity conversion factor 0.65

Continuous Results

Time		10:00	10:30	11:00	11:30	12:00	12:30	13:00	13:30	14:00	14:30	Totals
Stack Voltage	1	320	320	356	356	356	356	356	356	356	356	
	2	321	321	357	357	357	357	357	357	357	357	
	3	315	315	332	332	332	332	332	332	332	332	
Inlet												
temp	OC	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	
Q	m3/hr	8.7	9.8	9.2	5.3	9.2	8.4	9	8.4	9	8	42.5
C	mS/cm	8.9	9.1	9.6	6.9	12.12	16.4	13.23	11.7	11.8	11.2	
Conc	g/l	5.785	5.915	6.24	4.485	7.878	10.66	8.5995	7.605	7.67	7.28	
AN	Kg	25.16475	28.9835	28.704	11.88525	36.2388	44.772	38.69775	31.941	34.515	29.12	310.0221
Feed												
temp	OC	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	31.8	
Q	m3/hr	29	29	29	29	29	29	29	29	29	29	290
C	mS/cm	5	4.5	4	5	5	5.5	6.5	5.5	5.8	5.5	
Conc	g/l	3.25	2.925	2.6	3.25	3.25	3.575	4.225	3.575	3.77	3.575	
AN	Kg	47.125	42.4125	37.7	47.125	47.125	51.8375	61.2625	51.8375	54.665	51.8375	492.9275
Dilute product												
C	mS/cm	1.2	1.2	1.1	1.1	1.2	1.5	1.3	1	1.1	1	1.5
Conc	g/l	0.78	0.78	0.715	0.715	0.78	0.975	0.845	0.65	0.715	0.65	

Batch Product Results

Initial Gauge reading 85092780

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	Gallon	Gallon	m3/h	mS/cm	g/l	Kg
1	85093520	740	2.801	19	12.35	34.59477
2	85094280	760	2.877	20	13	37.39975
3	85095020	740	2.801	22	14.3	40.0571
4	85095760	740	2.801	24.4	15.86	44.42697
5	85097280	1520	5.754	24	15.6	89.7594
6	85098050	770	2.915	25.5	16.575	48.31211
Total		5270	19.949			294.5501

Notes: The concentrate product was pumped batchwise

EDR Trial 04/03/2002

Conductivity conversion factor 0.65 BMU 4 m3/hr

Continuous Results

Time		10:00	10:30	11:00	11:30	12:00	12:30	13:00	13:30	14:00	14:30	15:00	Totals
Stack Voltage	1	347	347	347	347	347	347	347	347	347	347	347	
	2	348	348	348	348	348	348	348	348	348	348	348	
	3	323	323	323	323	323	323	323	323	323	323	323	
Inlet													
temp	0C	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	
Q	m3/hr	10.1	10.9	8.1	8.2	7.8	7.9	7.8	9.2	8.4	8.4	8.9	47.85
C	mS/cm	12.3	11.9	11.1	10.9	10.6	11.2	11.1	10.8	10.8	11.2	11.1	
Conc	g/l	7.995	7.735	7.215	7.085	6.89	7.28	7.215	7.02	7.02	7.28	7.215	
AN	Kg	40.37475	42.15575	29.22075	29.0485	26.871	28.756	28.1385	32.292	29.484	30.576	32.10675	349.024
Feed													
temp	0C	32.4	32.4	32.4	32.4	32.4	32.4	32.4	32.4	32.4	32.4	32.4	
Q	m3/hr	29	29	29	29	29	29	29	29	29	29	29	319
C	mS/cm	5.5	8	5.5	5	5.5	7	6.5	5.5	5.5	5	5	
Conc	g/l	3.575	5.2	3.575	3.25	3.575	4.55	4.225	3.575	3.575	3.25	3.25	
AN	Kg	51.8375	75.4	51.8375	47.125	51.8375	65.975	61.2625	51.8375	51.8375	47.125	47.125	603.2
Dilute product													
C	mS/cm	1.7	1.5	1.4	1.6	1.2	0.85	0.9	1.2	1.5	1.4	1.3	1.5
Conc	g/l	1.105	0.975	0.91	1.04	0.78	0.5525	0.585	0.78	0.975	0.91	0.845	

Batch Product Results

Initial Gauge reading 85098050

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	Gallon	Gallon	m3/h	mS/cm	g/l	Kg
1	85098720	670	2.536	27	17.55	44.51063
2	85099380	660	2.498	29	18.85	47.09416
3	85100010	630	2.385	29.1	18.915	45.10853
4	85100690	680	2.574	29.2	18.98	48.85589
5	85101360	670	2.536	29.5	19.175	48.63198
6	85102020	660	2.498	28.9	18.785	46.93177
7	85102680	660	2.498	30.5	19.825	49.53007
Total		3970	15.028			330.663

Notes: The concentrate product was pumped batchwise

EDR Trial 05/03/2002

Conductivity conversion factor

0.65

brine Make up

4 m3/hr

Continuous Results

Time		10:00	10:30	11:00	11:30	12:00	12:30	13:00	13:30	14:00	14:30	15:00	15:30	Totals
Stack Voltage	1	375	375	356	356	356	356	356	356	356	356	356	356	
	2	378	378	357	357	357	357	357	357	357	357	357	357	
	3	352	352	332	332	332	332	332	332	332	332	332	332	
Inlet														
temp	OC	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	30.1	
Q	m3/hr	10.5	10.4	10.7	10.4	10.6	10.7	9.2	9.6	9.8	9.8	9.8	9.8	60.65
C	mS/cm	10.2	12.7	15.5	15.2	13.8	13.4	12.8	12.7	12.9	12.8	12.8	13	
Conc	g/l	6.63	8.255	10.075	9.88	8.97	8.71	8.32	8.255	8.385	8.32	8.32	8.45	
AN	Kg	34.8075	42.926	53.90125	51.376	47.541	46.5985	38.272	39.624	41.0865	40.768	40.768	41.405	519.0738
Feed														
temp	OC	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2	
Q	m3/hr	29	29	29	29	29	29	29	29	29	29	29	29	348
C	mS/cm	6.5	8.5	8.5	8.5	7.5	7.5	7	6.5	7.5	7	7	8	
Conc	g/l	4.225	5.525	5.525	5.525	4.875	4.875	4.55	4.225	4.875	4.55	4.55	5.2	
AN	Kg	61.2625	80.1125	80.1125	80.1125	70.6875	70.6875	65.975	61.2625	70.6875	65.975	65.975	75.4	848.25
Dilute product														
C	mS/cm	1.3	1.2	1.9	1.7	1.8	1.4	1.4	1.3	1.4	1.4	1.3	1.4	1.5
Conc	g/l	0.845	0.78	1.235	1.105	1.17	0.91	0.91	0.845	0.91	0.91	0.845	0.91	

Batch Product Results

Initial Gauge reading

85102680

Run	Gauge reading	Quantity	Quantity	Conductivity	Conc	AN
	<i>Gallon</i>	<i>Gallon</i>	<i>m3/h</i>	<i>mS/cm</i>	<i>g/l</i>	<i>Kg</i>
1	85103350	670	2.536	28.5	18.525	46.98344
2	85104080	730	2.763	40	26	71.84689
3	85104830	750	2.839	41.2	26.78	76.02976
4	85105500	670	2.536	39.1	25.415	64.45798
5	85106140	640	2.423	38.9	25.285	61.25686
6	85106810	670	2.536	38.4	24.96	63.304
7	85107460	650	2.461	38.4	24.96	61.41433
8	85108120	660	2.498	39.6	25.74	64.30789
Total		5440	20.593			509.6011

Notes: The concentrate product was pumped batchwise