# APPENDIX 4

## AMMONIUM NITRATE REMOVAL BY ELECTROLYSIS

## PRELIMINARY LABORATORY RESULTS

WRC Project No. 201 : Brines and Concentrates

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## SUMMARY

An electrochemical process has been proposed which will enable the desalting of ammonium nitrate waste streams with the formation of reusable products.

Preliminary laboratory tests have indicated that, under the conditions employed, 80 to 100% current efficiency could be achieved for the desalting of a 6 g/l ammonium nitrate solution to yield :-

(i) a depleted, slightly alkaline solution containing insignificant traces of ammonia or nitrate for reuse as low quality water.

(ii) a solution of soluble calcium nitrate which may be further processed by evaporation and drying.

(iii) a stream of ammonia and hydrogen gases and a stream of oxygen gas.

## 1. INTRODUCTION

This report describes initial laboratory results for the removal of ammonium nitrate from solution by the application of electrochemical techniques.

## 2. PROCESS DESCRIPTION

The proposed treatment system is illustrated in Figure 1.

The reaction is carried out in an electrochemical stack containing a series of individual cells each consisting of an anode and a cathode compartment separated by anion exchange membrane.

The ammonium nitrate stream is passed through the cathode compartments in either a series or a parallel flow arrangement. A saturated lime solution (or any other sparingly soluble hydroxide solution) is used as the anolyte.

The application of an electric potential across the electrodes of each cell results in :-

(i) the anodic oxidation of water :

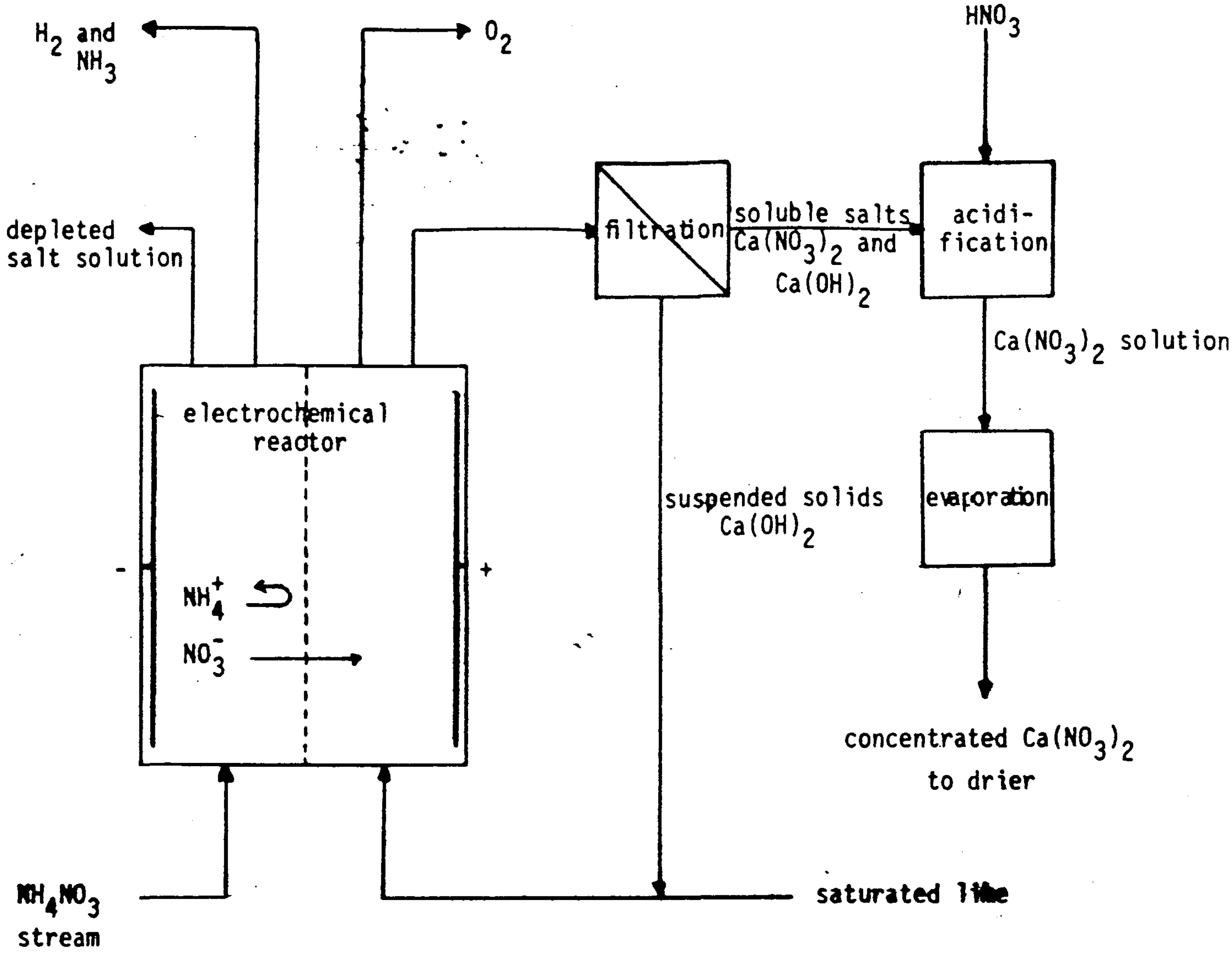
$$H_2O - 2e \longrightarrow 2H^+ + \frac{1}{2}O_2 \qquad Eo = 0{,}99V$$

The oxygen gas is evolved and the hydrogen ions neutralise the lime solution, lowering its pH.

(ii) the cathodic reduction of water :

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \qquad Eo = -0{,}84V$$

The hydrogen gas is evolved. The hydrogen ions increase the pH of the catholyte, shifting the ammonium-ammonia equilibrium (Figure 2) toward the formation of ammonia.



Cathode Reaction

$2H_2O + 2e \longrightarrow 2OH^- + H_2$ Eo = -0,84V

Anode Reaction

$H_2O - 2e \longrightarrow 2H^+ + \frac{1}{2}O_2$ Eo = 0,99V

FIGURE 1 : Proposed Treatment of Ammonium Nitrate Stream Using Electrochemical Techniques

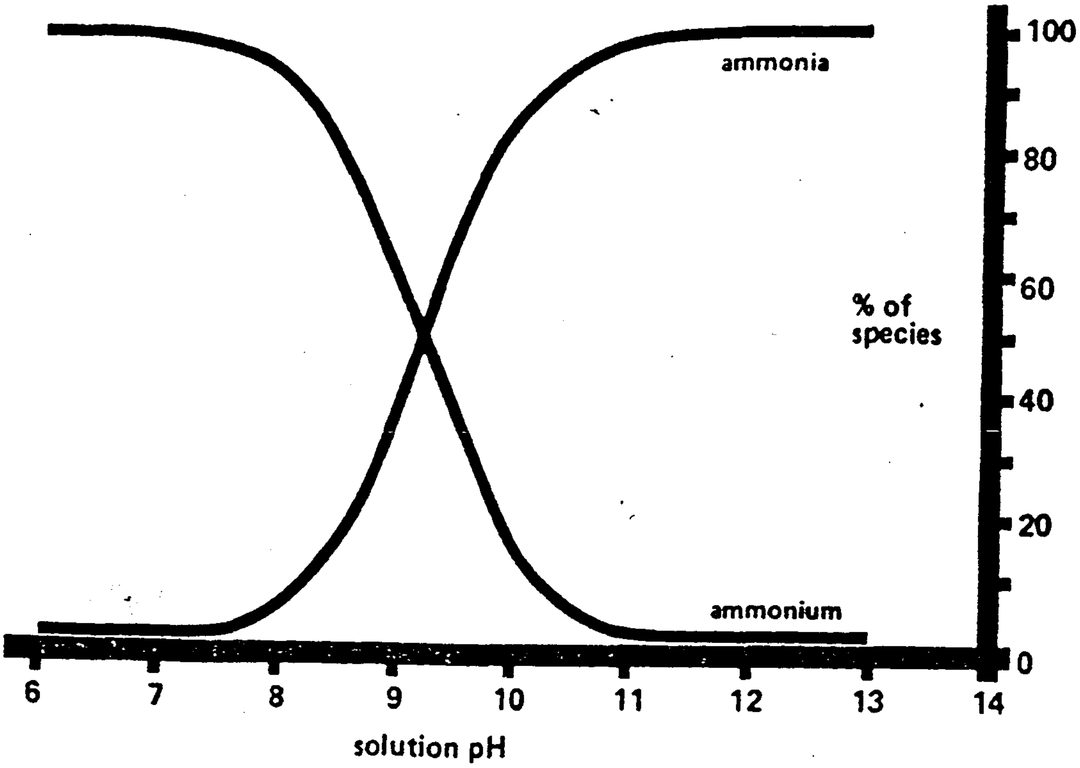


FIGURE 2 : Fraction of Ammonia and Ammonium Ions as a Function of pH. (Ref. Orion instruction manual for ammonia electrode model 95-10, Orion Research Incorporate - 1972)

The ammonia is soluble in cold water and exists as ammonium hydroxide. The process is conducted at elevated temperatures where ammonium hydroxide rapidly dissociates releasing ammonia gas from solution. Alternately air may be used to sparge the ammonia from the catholyte.

(iii) nitrate ions migrate through the anion exchange membrane from the catholyte toward the positively charged anode.

The products of the process are :

(i) a depleted catholyte stream containing insignificant quantities of either ammonium or nitrate.

(ii) an anolyte stream containing soluble nitrate and hydroxide salts of calcium perhaps together with undissolved lime. The pH at which this stream is produced may be tailored to the desired level by controlling lime addition. The undissolved lime is filtered out and returned to the catholyte compartment of the electrochemical unit. The stream containing the dissolved salts is neutralised with nitric acid if necessary to convert any soluble hydroxide salt to nitrate salt which are concentrated and dried to produce calcium nitrate powder.

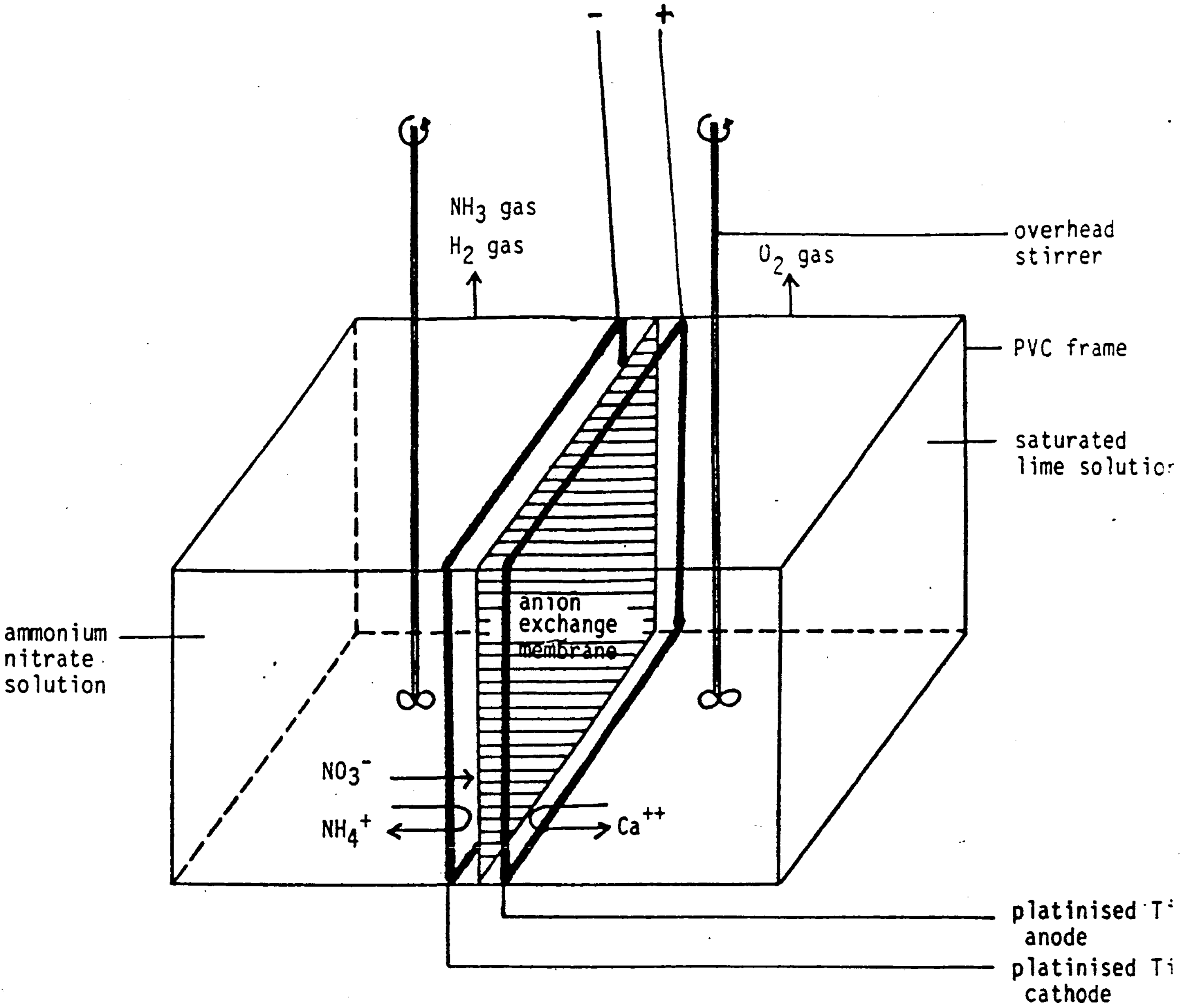
(iii) two separate gas streams, one containing oxygen and the other containing a mixture of hydrogen and ammonia gases.

The process enables the splitting of waste ammonium nitrate streams into the component acid and base fractions which may be reused in the production of saleable commodities.

## 3. LABORATORY PROCEDURE

### 3.1 Apparatus Description

The trial was conducted in a small laboratory cell (Figure 3). The cell was constructed from PVC, the electrodes were platinised titanium mesh and the anion membrane was type 103 QZL 336 supplied by Ionics. The exposed membrane area was 0,0081 $m^2$.



anode reaction : $2H_2O - 4e \longrightarrow O_2 + 4H^+$

cathode reaction : $4H_2O + 4e \longrightarrow 4OH^- + 2H_2$

FIGURE 3 : Apparatus for Electrolysis Trials

The membrane specifications are given in Appendix 1.

The electrodes were inserted 23 mm apart on either side of the membrane. The required conditions of current were maintained across the electrodes by means of a regulated DC power supply capable of delivering a maximum of 3A and 60V.

Two overhead stirrers, inserted into the compartments, maintained electrolyte turbulance at the membrane surface.

## 3.2 Method

The anolyte compartment was charged with 800 ml of a saturated lime solution containing 3 g/l $Ca(OH)_2$. The catholyte compartment was charged with 800 ml of an ammonium nitrate solution containing 6 g/l $NH_4NO_3$. A current of 0,5A (62 $A/m^2$) was applied across the electrodes for a period of 3,75 h. Cell voltages, temperatures and electrolyte compositions were monitored.

Appendix 2 summarises the analytical procedures employed.

## 4. RESULTS

The analytical and physical results are presented in Table 1.

Table 2 gives the current efficiencies for the splitting of ammonium nitrate to yield ammonia gas and calcium nitrate.

TABLE 1 : Ammonium Nitrate Removal by Electrolysis - Results

| Time (h-min) | Faradays x10$^{-3}$ | Electrolyte | Cell potential (V) | Temp (°C) | Electrolyte volume (ml) | pH | Analysis | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Cond (mS/cm) | $NH_4$ (mg/l) | $NO_3$ (mg/l) | Ca$^b$ (mg/l) |
| 0 | 0 | Anolyte | 4,0 | 23 | 800 | 12,3 | 6,1 | - | 0 | 630 |
| | | Catholyte | | | 800 | 5,2 | 9,2 | 1 300 | 3 150 | 0 |
| 0-35 | 10,9 | Anolyte | 4,1 | 24 | 800 | 12,3 | 6,4 | - | 369 | - |
| | | Catholyte | | | 800 | 9,0 | 7,6 | 1 100 | 2 835 | - |
| 1-15 | 23,3 | Anolyte | 4,4 | 24 | 790 | 12,1 | 5,9 | - | 981 | 790 |
| | | Catholyte | | | 790 | 9,4 | 5,7 | 950 | 1 890 | - |
| 2-00 | 37,3 | Anolyte | 6,0 | 25 | 780 | 9,4 | 3,6 | - | 1 785 | - |
| | | Catholyte | | | 780 | 9,8 | 4,7 | 700 | 1 350 | - |
| 2-55 | 54,4 | Anolyte | 9,2 | 25 | 770 | 3,9$^a$ | 6,0 | - | 2 625 | 1 030 |
| | | Catholyte | | | 770 | 10,2 | 1,3 | 0 | 468 | - |
| 3-45 | 70,0 | Anolyte | 18,0 | 25 | 760 | 12,3 | 9,1 | - | 2 948 | 1 535 |
| | | Catholyte | | | 760 | 11,0 | 0,3 | 0 | 20 | 13 |

a After collecting this sample 2 g of lime was added to the anolyte.

b Analysis on filtered samples.

TABLE 2 : Ammonium Nitrate Removal by Electrolysis - Current Efficiencies

| Faradays x10$^{-3}$ | Electrolyte | Nitrate | | | Ammonium | | |
|---|---|---|---|---|---|---|---|
| | | moles x10$^{-3}$ | mole change x10$^{-3}$ | current efficiency % | moles x10$^{-3}$ | mole change x10$^{-3}$ | current efficiency % |
| 0 | Anolyte | 0 | - | - | - | - | - |
| | Catholyte | 60,0 | - | - | 57,6 | - | - |
| 10,9 | Anolyte | 7,2 | 7,2 | 66 | 48,8 | - | - |
| | Catholyte | 54,4 | 5,6 | 51 | - | 9,2 | 84 |
| 23,3 | Anolyte | 18,2 | 18,2 | 78 | 41,9 | - | - |
| | Catholyte | 35,6 | 24,4 | 100 | - | 15,7 | 67 |
| 37,3 | Anolyte | 33,5 | 33,5 | 90 | 30,4 | - | - |
| | Catholyte | 25,0 | 35,0 | 94 | - | 27,2 | 73 |
| 54,4 | Anolyte | 48,5 | 48,5 | 89 | 0 | - | - |
| | Catholyte | 8,5 | 51,5 | 95 | - | 57,6 | 100 |
| 70,0 | Anolyte | 53,2 | 53,2 | 76 | 0 | - | - |
| | Catholyte | - 3,8 | 56,2 | 80 | - | - | - |

# 5. DISCUSSION AND CONCLUSIONS

## 5.1 Performance of Process

The process enabled virtually the complete desalting of a 6 g/l $NH_4NO_3$ solution to yield :

(i) a depleted catholyte, slightly alkaline and very low in inorganics (conductivity = 0,3 mS/cm).

(ii) an anolyte containing suspended lime and soluble calcium nitrate and calcium hydroxide. Control of lime addition will enable the pH of this electrolyte to be controlled and hence the ratio of calcium nitrate to calcium hydroxide.

(iii) a hydrogen and ammonia gas stream and an oxygen gas stream. Since the present trials were conducted at ambient temperatures, little ammonia gas was evolved. It is however, envisaged that the process be carried out at elevated temperatures to accelerate the release of dissolved ammonia ($NH_4OH$).

## 5.2 Current Efficiencies

Only two electrode processes are likely to occur :

(i) the oxidation of water at the anode to release oxygen gas and hydrogen ions.

(ii) the reduction of water at the cathode to release hydrogen gas and hydroxide ions.

It is likely that both these reactions will proceed at 100% efficiency. The current efficiency at which ammonium hydroxide is formed in the catholyte and at which nitrates are transported to the anolyte average 80 to 100% (Table 2). Factors decreasing these currents efficiencies include :

(i) the transport of $OH^-$ ions across the anion exchange membrane in place of $NO_3^-$ ions, particularly at low nitrate concentrations.

(ii) the back-migration of small amounts of calcium ions from the anolyte to the catholyte, which occurred due to incomplete selectivity of the anion exchange membrane. These calcium ions become associated with evolved hydroxide ions, thus reducing the amount of hydroxide available for ammonium hydroxide formation.

## 5.3 Operating Parameters

The initial test proved that the technology achieves the objective of denitrification of an ammonium nitrate stream. However, the operating parameters, in particular the current densities, power consumptions and electrolyte temperatures, need to be investigated to determine the economic feasibility of the process.

As an example, however, preliminary predictions have been made concerning plant size for the desalting of an effluent stream of the characteristics shown are given in Table 3. Predicted membrane area for the removal of 2,4 tons/day of $NH_4NO_3$ at 80% current efficiency and at ambient temperature varies from 5 $m^2$ for operation at a current density of approximately 8 400 $A/m^2$ to 40 $m^2$ for operation at a current density of approximately 1 050 $A/m^2$.

## TABLE 3 : Full-Scale Plant - Required Membrane Area

**Assumptions :**

Effluent flow : 20 $m^3/h$
Effluent concentration : 5 g/l $NH_4NO_3$
Effluent mass flow : 100 kg/h $NH_4NO_3$
Current efficiency : 80%
Electricity required for 100% removal : 1 563 F/h

| Current Density $A/m^2$ | Membrane Area $m^2$ |
|---|---|
| 8 376 | 5 |
| 4 188 | 10 |
| 2 792 | 15 |
| 2 094 | 20 |
| 1 047 | 40 |

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APPENDIX 1

# ANION-TRANSFER MEMBRANES

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Printed in USA

## CUSTOM MADE

## PROPERTIES AND CHARACTERISTICS

Ionics makes varieties of both tight and loose membranes to fit many applications on a custom basis. Further, membranes are prepared on highly resistant backings for use in media which is very acidic or is mildly oxidizing. Finally, Ionics has recently developed membranes which have very large diameter pores which are most useful in the treatment of fouling waters.

We list below a variety of membranes that we would be capable of preparing on a custom order basis:

| Membrane Designation | Thickness (cm) | Area Spec. Resist. Ohm-cm$^2$ in 0.01 N NaCl | Current Efficiency 0.1 N NaCl | Water Transport (1/Faraday) | Remarks |
|---|---|---|---|---|---|
| AR 103 UZL 386 | 0.060 | 25 | 0.99 | 0.085 | Very tigh |
| AR 103 MZL 386 | 0.060 | 20 | 0.78 | 0.190 | Very open |
| AR 204 SXZ1 385 | 0.060 | 12 | 0.87 | 0.120 | Foulant Resistan |
| AR 103 PZP 400 | 0.060 | 18 | 0.80 | 0.150 | Polypropy Backed |
| AR 103 QZP 400 | 0.060 | 14 | 0.92 | 0.117 | Polypropy Backed |
| AR 103 UZP 400 | 0.060 | 25 | (0.99) | (0.085) | Tight, Po pylene B |

*Values in parenthesis are estimated

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# ANION-TRANSFER MEMBRANES

Bulletin No. AR 103.0-E

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TYPE AR 103

## GENERAL INFORMATION

Ionics' AR 103 membranes are anion-selective membranes comprising cross-linked copolymers of vinyl monomers and containing quaternary ammonium anion exchange groups. The membranes are homogeneous films, cast in sheet form on reinforcing synthetic fabrics.

Ionics' anion-transfer membranes have a combination of properties and characteristics which is unique. This includes:

- Low electrical resistance
- High permselectivity (ability to exclude cations)
- High burst strength
- Rugged reinforced construction
- Except in hydroxide ion form, excellent long-term stability at temperatures up to 65°C and in solutions having pH's < 9. May be used for brief periods at temperatures up to 95°C
- Long-term resistance to aqueous acid solutions
- Very high dimensional stability in solutions of different compositions
- Ability to withstand harsh chemical and physical treatments to remove surfac and interior deposits. (Ionics membranes may be sandpapered, steel wooled c wire-brushed, contacted with 5-10% acids or salts and stabilized chlorine dioxide when the cleaning requirements warrant same.)
- Extensive use in more than 1000 electrodialysis installations. Ionics membranes have been produced for more than 25 years.
- All membranes produced at Ionics are required to pass rigorous quality contr examinations.

Ionics can custom make membranes for special applications, varying mechanical and electrochemical properties or using reinforcing fabrics which are resistant to oxidation, caustic or other corrosive media.

## REINFORCING FABRICS

**Modacrylic Polymer is the fabric most commonly used in Type AR 103.** Other fabrics can be furnished for applications where a modacrylic would exhibit insufficient chemical stability. Fabrics can be furnished in various thicknesses or weights. The lower the weight of the fabric, the lower in general will be the electrical resistance of the membrane. On the other hand, membranes with heavy weight fabrics may exhibit a longer life than membranes with lighter fabrics, especially in applications where erosion may become a factor.

## POROSITY

The formulation of AR 103 membranes can be varied to impart various average pore sizes or total pore volumes to the membrane. The smaller the average pore size of a membrane, the lower will be the transfer of non-electrolytes which accompany ion transfer, but the higher will be the electrical resistance of the membrane. The larger the total pore volume, the less efficient a membrane will be.

Ionics offers two different standard total pore volumes in production membranes. A variety of total pore volumes and average pore sizes can be made to custom order.

## CHEMICAL STABILITY

**At room temperature, the AR 103 anion membranes are stable to non-oxidizing solution** between pH 0 and 9 and exhibit fair stability to solutions outside of this range, e. 4-5 N HCl and $H_2SO_4$. They may be used at temperatures up to 65°C (except in the **hydroxide ion form) on a continuous operation in this pH range and for brief periods up to 95°C. At operating temperatures in the 65-95°C region slow losses in ion exchange capacity can be expected.**

Contact with oxidizing agents (chlorine, hypochlorites) and strong bases, e.g. 0.5 N sodium hydroxide should be avoided as should contact with low molecular weight organ **polyelectrolytes such as salts of humic acid, lignates, branched chain alkyl or aryl sulfonates, tannins, etc., the anions of which tend to be irreversibly absorbed on the surface of anion selective membranes if present at appreciable concentrations.**

## PHYSICAL STABILITY

If kept wet, physical stability is excellent. Membranes shrink upon drying and crac upon excessive drying.

Swelling of membranes in water as the temperature is increased is minimal for all types of Ionics membranes and rarely exceeds 5% in any dimension when heated from room temperature to 100°C.

## HANDLING/MOUNTING

Membranes can be mounted between gum rubber, neoprene, SBR, polyethylene, plasticize PVC, silicone and other soft, insulating elastomeric or thermoplastic materials.

Moderate pressure will seal a membrane against such materials satisfactorily for mos uses. Membrane sheets may be bent around curves of large radius but caution should be observed.

## NOTE

Anion membranes intended to be stored for long periods may sometimes contain small amounts of hydrochloric acid added during manufacture. Before use, such membranes should be flushed in water, preferably containing ions present in the solution to be processed.

## STORAGE

If long term (many months) storage of any AR 103 membrane is contemplated, the water of storage should be made up by first dissolving 1 gram of benzoic acid in 10 ml of ethyl alcohol and pouring this into each liter of storage water. This 0.1% solution will inhibit the growth of various micro-organisms during storage.

## PATENTS

Ionics, Incorporated, owns many U.S. and foreign patents pertaining to the manufactu and/or use of ion transfer membranes and the sale of these membranes shall not be construed as a license for their use in conflict with existing patents or patent applications owned by Ionics or others.

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Bulletin No. AR 103.3-D

# ANION-TRANSFER MEMBRANES

## TYPE 103-QZL-386

## PROPERTIES AND CHARACTERISTICS

Ionics' Modacrylic fiber backed anion transfer membrane AR-103-QZL-386 has smaller pore volume than AR-103-PZL-386. Therefore, it is suggested for use in electrodialysis or other separatory processes as a means of transporting anions while excluding cations in applications where a loss of solvent or non-ionized solute must be reduced below that obtainable with membrane AR-103-PZL-386.

| | |
|---|---|
| Reinforcing Fabric: | Modacrylic (copolymer of vinyl chloride and acrylonitrile) |
| Weight: | 4 oz/yd$^2$ (15.3 mg/cm$^2$) |
| Membrane Thickness: | 25 mils (0.63 mm) |
| Burst Strength (Mullen): | 140 psi (10.8 kg/cm$^2$) |
| Water Content: | 36 % of wet resin only |
| Capacity: | 2.1 meq/dry gram resin |

## VARIOUS ELECTROCHEMICAL PROPERTIES

| Concentration | 0.01 N NaCl | 0.1 N NaCl | 1.0 N NaCl | 3.0 N NaCl |
|---|---|---|---|---|
| Area Specific Resist. (ohm-cm$^2$) | 15 | 9 | 4 | 2 |
| Spec. Conductance (mho/cm) | $4.2 \times 10^{-3}$ | $7.0 \times 10^{-3}$ | $15.8 \times 10^{-3}$ | $31.8 \times 10^{-3}$ |
| Current Efficiency | 0.00 | 0.97 | 0.93 | -- |

## OTHER PROPERTIES

| | |
|---|---|
| Water Transport: | 0.117 liters per Faraday in 0.6 NaCl @ 16 ma/cm$^2$ |
| Sucrose Transport: | 6.0 grams per Faraday from 30% sucrose in 0.2 N KCl into 0.02 N KCl @ 16 ma/cm$^2$ |

NOTICE:
1. The property data are typical values only and no warranty as to such properties is given.
2. For patent and license clause, see Bulletin AR 103.0-D.

## APPENDIX 2

### Analytical Procedure

Ammonium : Ammonium ion concentration was determined using Nessler reagent. The colour complex absorbance was read at 420 nm. The samples were heated for one to two minutes prior to analysis to evolve the ammonia gas and enable the direct determination of $NH_4^+$.

Nitrate : Nitrates were determined from the absorbance of the acidified samples at 220 nm.

Calcium : Calcium was determined using atomic absorption spectrophotometry.