WATER RESEARCH COMMISSION PROJECT NO. 201

THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

APPENDIX 7

The Removal of Ammonium Salts from an Aqueous Medium Containing the Salt

Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

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STEERING COMMITTEE 1988

APPENDIX 1

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November 1987

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The Executive Director
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Our Ref.: JP/W 331

Your Ref.:

Date: 30 November 1987

Dear Sir,,

SOUTH AFRICAN PATENT APPLICATION BY: WATER RESEARCH COMMISSION ENTITLED: THE REMOVAL OF AMMONIUM SALTS FROM AN AQUEOUS MEDIUM CONTAINING THE SALT

In accordance with instructions received from Mr. Chris Buckley, we have prepared and filed the above patent application. A copy of the specification as filed is attached. The filing particulars will follow.

Also attached is a Patents Form P.3 for signature where indicated and return to us.

Yours faithfully,
SPOOR AND FISHER

per: ANTHONY R.L. HOOPER

Encl:
PAA

SPOOR AND FISHER FORM P.6

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

PROVISIONAL SPECIFICATION

(Section 30 (1) – Regulation 27)

OFFICIAL APPLICATION NO.			LODGING DATE	
21	01		22	30 NOVEMBER 1987

FULL NAME(S) OF APPLICANT(S)

71	WATER RESEARCH COMMISSION

FULL NAME(S) OF INVENTOR(S)

72	CHRISTOPHER ANDREW BUCKLEY and ALISON ELIZABETH SIMPSON

TITLE OF INVENTION

54	THE REMOVAL OF AMMONIUM SALTS FROM AN AQUEOUS MEDIUM CONTAINING THE SALT

BACKGROUND OF THE INVENTION

This invention relates to the removal of ammonium salts, particularly ammonium nitrate, from a process or effluent stream.

Ammonium salts are manufactured and used extensively in industries including those of textile finishing, pharmaceuticals, ceramics, photography, electroplating, polymers and plastics, fertilisers and explosives.

Effluents discharged from these industries often contain high concentrations of the ammonium salts and discharge into the natural waterways or sewers is prohibited.

In South Africa saline effluents are particularly problematic in that the increasing salinity of the rivers and water reticulation systems inhibits recycle or reuse of water. In addition, the particular nature of nitrogen containing streams and the consequences associated with their indiscriminate discharge, have resulted in the imposition of stringent nitrogen disposal standards.

Methods of overcoming the disposal problems of ammonium salt containing effluents include:

(i) algae or biological treatment resulting in the conversion of ammonium ions to nitrogen gas.

(ii) pH adjustment by addition of an alkaline substance resulting in the release of ammonia gas and the formation of a salt from the alkaline cation and ammonium anion.

(iii) spray disposal onto land.

Disadvantages of these processes include the large surface area required [in particular for (i) and (iii)], the further addition of chemicals [as in (ii)] and the formation of a final stream still containing the anion originally associated with the ammonium ion. In some cases the disposal of the anion associated with the ammonium ion may also be prohibited in terms of the discharge regulations, as for example is the disposal of the nitrate anion.

SUMMARY OF THE INVENTION

According to the present invention a process for ammonium salt removal from an aqueous medium containing the salt includes the steps of:

(i) providing a membrane cell in which two compartments are separated from each other by an anion selective membrane;

(ii) passing the ammonium salt rich aqueous medium into one compartment of the membrane cell;

(iii) passing an alkali solution through the other compartment of the membrane cell, the alkali solution containing cations which will form a soluble salt with the anion of the ammonium salt; and

(iv) passing an electrical direct current through the cell such that the ammonium salt compartment is at a negative potential relative to the alkali compartment.

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

(i) the anodic oxidation of water:

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

The oxygen gas is evolved and the hydrogen ions neutralise the alkali 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 hydroxide ions increase the pH of the catholyte, shifting the ammonium-ammonia equilibrium toward the formation of ammonia.

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

(iii) anions from the ammonium salt migrate through the anion exchange membrane from the catholyte toward the positively charged anode. These anions will carry with them water molecules.

DESCRIPTION OF THE DRAWING

The drawing illustrates a flow diagram of an embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The ammonium salt medium will preferably be continuously passed through one compartment of the membrane cell in the form of a stream. The ammonium salt is removed from this stream without any undesirable build-up of either cations or anions.

The cations of the alkali solution are preferably alkaline earth metal cations or other cations which form only slightly soluble metal hydroxides, particularly calcium and lead. The alkali solution may be a carbonate or a hydroxide solution. The most preferred alkali solution would be a saturated hydroxide solution. particularly calcium or lead.

Generally, turbulence will be maintained in the compartments to minimise precipitation build-up on the membrane in the anode compartment and to minimise ion depletion at the membrane surface in the cathode compartment.

The invention may be used to remove ammonium salts from effluents or process streams. It has the advantage over prior art methods that:

(i) there is no undesirable build-up of additional ions in the effluent.

(ii) nitrogen removal may be achieved in relatively small plants, reducing the space requirements for treatment/disposal.

(iii) a pure concentrated solution containing the salt of the ammonium anion and alkaline cation is formed.

(iv) a gas stream consisting of ammonia gas and hydrogen which could be recycled back to an ammonia synthesising plant.

An embodiment of the invention will now be described. The process used was as set out in the attached flow diagram.

Apparatus Description

The trial was conducted in a small laboratory cell. 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.

The electrodes were inserted 23mm 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 turbulence at the membrane surface.

Method

The anolyte compartment was charged with 800ml of a saturated lime solution containing 3 g/l $Ca(OH)_2$. The catholyte compartment was charged with 800ml 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 3,75h. Cell voltages, temperatures and electrolyte compositions were monitored.

RESULTS

The analytical and physical results are presented in Table 1.

TABLE 1

Ammonium Nitrate Removal by Electrolysis - Results

Time (h-min)	Faradays $\times 10^{-3}$	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 2g of lime was added to the anolyte

b Analysis on filtered samples

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

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	45,8	-	-
	Catholyte	54.4	5,6	51	-	-	-
	Anolyte	10,2	16,2	78	41,9	9,2	54
	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	-	-	-

DISCUSSION AND CONCLUSIONS

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).

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 current 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.

Operating Parameters

The initial test proved that the technology achieves the objective of denitrification of an ammonium nitrate stream.

As an example, 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	:	50%
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

DATED this 30th day of NOVEMBER 1987

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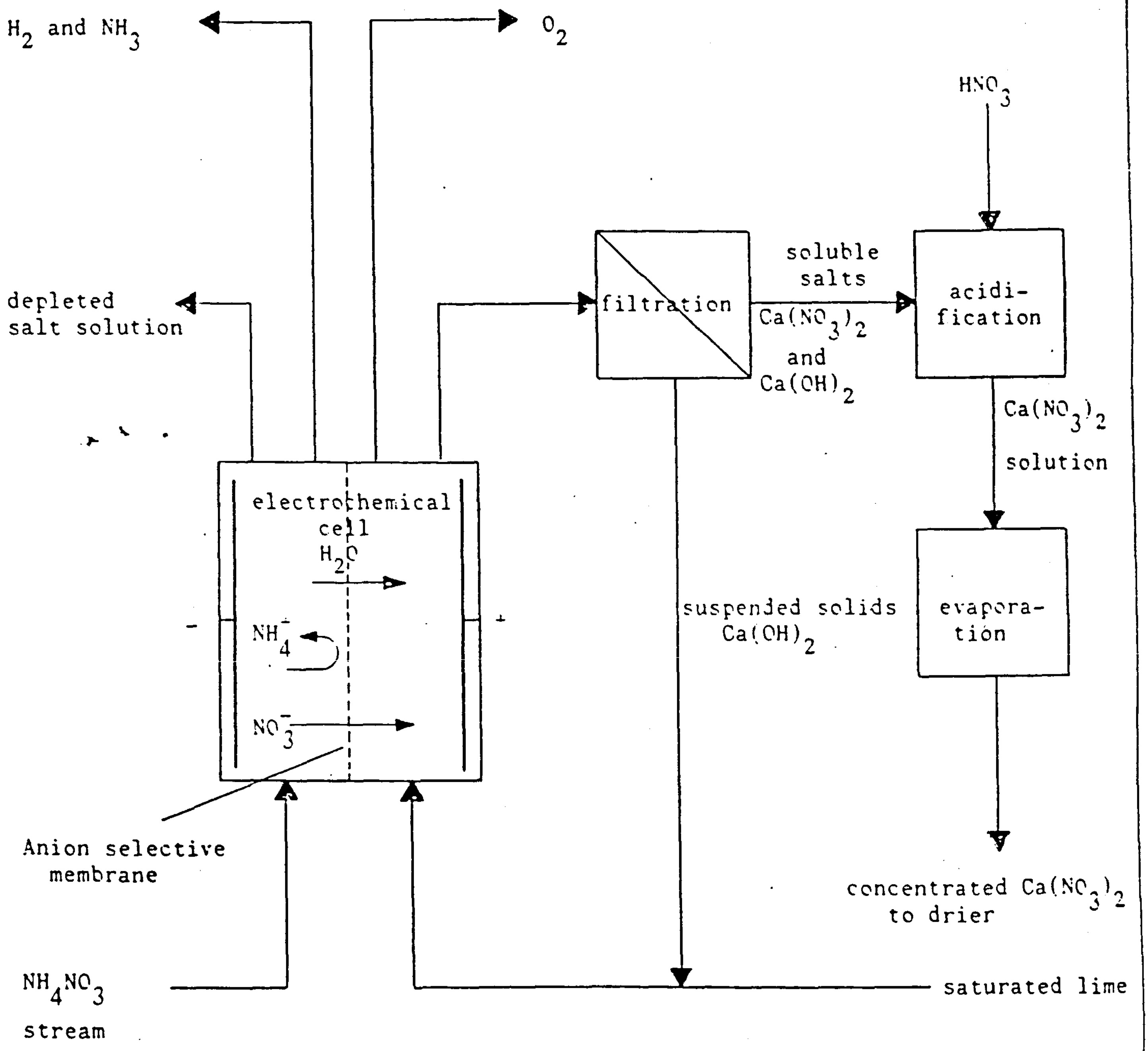
APPLICANT'S PATENT ATTORNEYS

WATER RESEARCH COMMISSION

PROVISIONAL SPECIFICATION

ONE SHEET



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