WATER RESEARCH COMMISSION PROJECT NO. 201

THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

APPENDIX 5

Report on Visit to AECI, Modderfontein 30th November 1987

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CONFIDENTIAL:

REPORT ON VISIT TO AECI, MODDERFONTEIN

30th November 1987

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SUMMARY

This report summarises the discussions held between various representatives of AECI Explosive and Chemicals, Modderfontein and members of the Pollution Research Group on the 30 November 1987.

The scope of the discussions included an analysis of the various options available for the treatment and upgrading of various effluent streams. The options included possible process modifications. A strategy was developed to reduce the contribution of effluents loadings from the following processes to the final factory discharge load:

- (i) kiering, in particular the sodium ion contribution,
- (ii) explosives and fertiliser production, in particular the ammonium nitrate contribution,
- (iii) demineralisation unit regeneration, in particular the sodium and sulphate ion contributions.

Finally, preliminary recommendations were made concerning the denitrification of effluents discharged by Manganese Metal Co (Pty) Ltd, a client of AECI Explosive and Chemicals.

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Appendix 1 : Effluent treatment : SA Patent No. 87/4406.

Appendix 2 : The removal of ammonium salts from an aqueous medium

containing the salt : SA Provisional Patent No. 87/8990.

Appendix 3 : The removal of sulphuric acid from an aqueous medium

containing the acid : SA Provisional Patent No. 87/5749.

Appendix 4 : Ammonium nitrate removal by electrolysis : Preliminary

laboratory results.

1. INTRODUCTION

All the effluents produced at AECI Explosives and Chemicals Ltd, Modderfontein are segregated into two discharge streams:

- (i) the weak stream, flowing at a rate of 1 000 to 1 200 m³/h, and
- (ii) the strong stream, flowing at a rate of 20 to 30 m³/h.

The weak effluent is discharged under permit to the Jukskei River and the strong effluent is disposed by land spray techniques.

The Environmental Services Department at AECI have been involved in a concerted effort to minimise effluent production, both in terms of TDS loading and volume. The Pollution Research Group, of the Chemical Engineering Department at the University of Natal have been appointed consultants to AECI. In particular, the disposal of the following streams are being considered:

(i) the regeneration liquors from the ion exchange units operating at No. 4 Ammonia and No. 11 Nitric Acid plants. The 'spent' regeneration liquor from No. 4 Ammonia Plant is discharged at a rate of 160 to 200 m³/h and is the only strong effluent entering the weak effluent system. The 'spent' regeneration liquor from No. 11 Nitric Acid plant is discharged at a rate of 10 to 15 m³/h into the strong effluent system.

The combined daily chemical consumption in these two ion exchange systems is estimated as 5 to 6 tons of 98% sulphuric acid and 3 to 4 tons of 100% sodium hydroxide. The contribution of these regeneration liquors to the sodium and sulphate ion concentrations in both the final strong and weak effluent streams is significantly high.

(ii) the 'spent' kier liquor and the effluent from the subsequent washing of kiered cotton in the Detenator Department. The 'spent' kier liquor is discharged to the strong effluent system and contributes to an estimated 15 to 20% of the final sodium ion loading in the final effluent. The kier washings are discharged to the weak effluent system.

(iii) the ammonium nitrate effluent streams which arise from the manufacturing process of various explosives and fertilisers.

The discussions held at AECI Explosives and Chemicals Ltd, Modderfontein on the 30th November 1987 incorporated four areas of concern:

- (i) the production and disposal of kiering liquors in the Detonator Department,
- (ii) the denitrification of the ammonium nitrate streams contributing to the strong effluent.
- (iii) the treatment of the sulphuric acid and sodium hydroxide based ion exchange regeneration liquors from the demineralisation units on No. 4 Ammonia and No. 11 Nitric Acid.
- (iv) the treatment of an ammonium sulphate stream from Manganese Metal Co (Pty) Ltd.

2. **KIERING**: Detenator Department

AECI Representatives: Allan Lubbe (Section Manager, Nitrocotton), Peter Chennels and Sam Mokoane, C.J. Breyer-Menke, Ellen Schramm, Leon Baben (Environmental Services Department)

2.1 The Kiering Process

Low grade cotton is kiered using atmospheric boil-off methods in the manufacture of fuse for explosives production.

The raw cotton contains approximately 12% m/m of contaminants. Figure 1 is a schematic of the kier boiling process.

Kiering is conducted in one of four tanks each of a 3 000 to 4 000 l capacity. Approximately 750 kg of raw cotton is manually packed into each tank. A 3% sodium hydroxide solution is made up in a 4 000 to 5 000 1 storage vessel and heated to 80°C before being pumped through the kiering tanks where it percolates through the cotton. Detergent is added to the system by addition to the kiering tanks. The kiering solution is recirculated in the system for 3 hours during which time the cotton impurities are extracted and saponified with a consumption of 0,2 to 0,3% m/v of sodium hydroxide. The 'exhausted' kier liquor (2,7 to 2,8% NaOH) is drained from the system and discharged with other strong effluents into Dam VI.

The cotton is then washed by overflow rinse for 2 hours using cold water. These washings are discharged into the weak effluent system.

The Detonator Department processes 14 tons of cotton per month. The kiering process is operated on a single shift per day basis and each kier boil-off operation takes place over two days. The specific chemical usage during kiering is 1 kg of 100% NaOH per 7,5 kg raw cotton. It is estimated that approximately 100 kg of 100% NaOH is discharged from the kiering section each day.

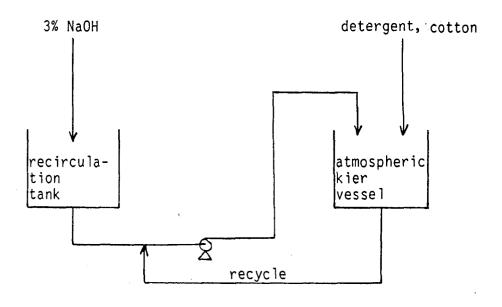


Figure 1 : Schematic of Kier Boil-Off Equipment

2.2 Recommendations

The following recommendations were made in order to minimise the effluent volume and the contribution by the kiering effluents to the final factory effluent sodium concentration.

- (i) The cost implications of commission kiering should be investigated. If the cotton can be kiered outside the factory at reasonable rates, the sodium hydroxide problem in the Detonator Department would be alleviated. If commission kiering is not cost effective, then process modifications and possible effluent treatment must be addressed.
- (ii) Process variables during kiering include temperature, pressure, sodium hydroxide concentration and contact time. In order that the sodium hydroxide concentration be minimised it is recommended that the factory investigate operation at elevated pressures.
- (iii) The feasibility of reusing the kiering liquor together with make-up caustic should be investigated in detail. Preliminary tests in this regard have been conducted by AECI, but investigations were discontinued due to the production of a poor quality cotton. It is recommended that these tests be continued since the reuse of kiering liquors is common practice in the textile industry. If the quality of the raw cotton is the major factor preventing the reuse of kier liquor, the advantages of processing a less contaminated cotton fibre with kier liquor reuse should be weighed up against the processing of low quality fibre with no kier liquor reuse.
- (iv) The rinse water, in particular the initial washings, should be used for making up the subsequent batch of sodium hydroxide.

- (v) In order to minimise water consumption, batchfill and drop rinsing, as opposed to overflow rinsing should be investigated. In practice, for the same degree of washing efficiency batchfill and drop rinsing consumes less than half the water that overflow rinsing consumes.
- (vi) The possibility exists for the application of a process developed by the Pollution Research Group and patented by the Water Research Commission (Appendix 1), which will enable the recovery of pure sodium hydroxide from the 'spent' kier liquor. Such a plant would be small, recovering 2 to 3 tons 100% NaOH/month. Consideration should be given to combining the kier effluent with other sodium containing effluents prior to recovery.
- (vii) The suitability of the concentration and quality of spent caustic regeneration chemicals for reuse in kiering should be investigated.

3. DENITRIFICATION OF AMMONIUM NITRATE EFFLUENTS

AECI Representatives : C.J. Breyer-Menke, L. Baben, E. Schramm

3.1 Introduction

All nitrogenous effluents produced at the factory are discharged to the strong effluent system for spray disposal. The three principle nitrogenous arisings are:

- (i) from the fertiliser prilling section; the flow and concentration of this effluent are variable.
- (ii) from the nitration process in the manufacture of nitroglycerine for explosives.
- (iii) the contaminated condensate from the ammonium nitrate plant which is discharged as an effluent when the nitric acid plant is not operating.

3.2 <u>Denitrification Process</u>

In order to overcome ultimate disposal problems associated with treating the nitrogenous effluent it would be advantageous to use the effluent to make a saleable product. Two potential products, calcium nitrate and lead nitrate, have been identified.

The proposed process for the removal of ammonium nitrate from these effluents (Appendix 2) involves an electrochemical membrane unit to form a sabeable product, calcium nitrate. The ammonium nitrate solution forms the catholyte. A saturated hydroxide solution, say lime, forms the anolyte. Under the influence of an electric potential:

(i) the ammonium nitrate salt is split and the nitrate ions migrate through the membrane into the saturated hydroxide solution where a soluble salt, say calcium nitrate, is formed.

- (ii) the ammonium nitrate solution is made alkaline by the reduction of water at the catholyte to form hydroxide ions and hydrogen gas. Ammonia gas is release from the alkaline solution by air sparging or by heating.
- (iii) the pH of the anolyte or lime solution is lowered by the oxidation of water at the anode to form hydrogen ions and oxygen gas. The lime is thus neutralised. Careful control of the rate of lime addition will enable the amount of Ca present in the hydroxide form and the amount of Ca present in the nitrate form to be tailored to a predetermined ratio.

The products of such a process would be:

- (i) a stream of ammonia and hydrogen gases which could be either discharged or recycled to the ammonia production plant.
- (ii) a stream of oxygen gas.
- (iii) a depleted effluent containing no ammonium nitrate which is suitable for reuse as relatively good quality water in the factory.
- (iv) a reasonably concentrated catholyte stream of say calcium nitrate which could be marketed either as a solution or as a powder after further concentration and drying.

3.3 <u>Economic Predictions</u>

Based on preliminary laboratory results, and assuming:

- (i) an effluent flow of 30 m³/h,
- (ii) an effluent concentration of 5 g/1 NH₄NO₃,
- (iii) an electrical power cost of RO,05/kWh and
- (iv) a current efficiency for the transport of nitrate ions across the membrane of 80%,

the annual operating costs for the complete denitrification of the effluent are predicted to be in the order of R150 000.

AECI have a potential market for the calcium nitrate and the construction of a 10 ton/day plant has been proposed. Based on the above effluent loadings a plant treating the effluent by the described process would produce approximately 5 ton/day of calcium nitrate.

3.4 Advantages of Denitrification

Obviously further development and optimisation of the denitrification process is required. The potential advantages of a successful solution are:

- (i) the complete denitrification of the nitrogenous strong effluent streams alleviating the need for spray disposal of these effluents.
- (ii) the production of reusable and saleable by-products in the form of ammonia and hydrogen gases and say calcium nitrate or the nitrate of any other cation chosen as the anolyte.
- (iii) the release of land, for development or sale (which is presently being used for spray disposal).

4. TREATMENT OF DEMINERALISATION UNIT REGENERATION LIQUORS

4.1 Introduction

The total flow of ion exchange regeneration liquors from the factory is estimated at 170 to 210 m $^3/h$. Approximately 95% of this flow originates at the No. 4 Ammonia plant. The remaining 5% originates at the No. 11 Nitric Acid plant. The two main problems facing AECI with regard to the disposal of these effluents are :

- (i) volume : the effluent from the No. 4 Ammonia plant, although strong, is discharged with the weak effluent since the flow is too large for spray disposal.
- (ii) concentration: this effluent forms a major contribution to the sodium and sulphate levels in the weak and strong effluents.

4.2 <u>Proposed Demineralisation Unit Expansion</u>

AECI are in the process of installing a R1,8 million expansion to their demineralisation unit on the No. 4 Ammonia plant. This expansion involves the addition of two cation/anion exchange trains (to be operated and regenerated alternatively) in front of the existing plant. It is envisaged that the new plant will treat 50% of the incoming water which will then be blended with untreated water as the feed to the existing plant. Regeneration of the new plant will be achieved using waste regeneration liquor from the existing plant.

It is estimated that such an expansion will result in a 40% savings in regeneration chemicals. At present the daily consumption of regeneration chemicals is:

- 4,2 tons of 98% sulphuric acid at a cost of R150/ton
- 2.7 tons of 100% sodium hydroxide at a cost of R825/ton.

Assuming a feed water conductivity of 500 mS/cm it is estimated that the installation of the new plant will reduce the frequency of regeneration from 7 to 1 cycles per day for the cation units and from 5 to 2 cycles per day for the anion units.

To date no prefiltration of the raw feed water to the ion exchange units has been conducted, resulting in a considerable consumption of water (40% of the total throughput of the units) for backwashing. Since vigorous backwashing is required, attrition of the beads occurs and there is a significant loss of beads in the backwash product. In addition the colloidal nature of impurities in the backwash water is a disadvantage, since these impurities are absorbed onto the beads, decreasing the efficiency of the bed and increasing the regeneration chemical requirement.

The new ion exchange trains are to function as prefilters to the existing plant and have been designed for economic backwash. The contractors did not feel that prefiltration was warranted due to the usually low concentration of suspended solids in the feed water. However, the new plant will remove, at best, one half of the suspended solids from the feed water to the existing plant.

4.3 Improvements to the Existing Plant

Previously the degasser on the No. 4 Ammonia demineralisation plant had not been functioning to specification. A new distributor is presently on order. It is projected that the improvements to the degasser will increase the efficiencies of the unit from 60 to 90%, which will have considerable implications on regeneration chemical requirements resulting in significant savings.

4.4 Treatment of Waste Regeneration Liquors

The proposed expansion to the existing No. 4 Ammonia demineralisation unit should result in considerable reductions in

the mass flow of chemicals to the effluent systems. After optimisation of the demineralisation process to minimise both water and chemical consumptions the development of an effluent treatment strategy is required.

The Pollution Research Group have developed electrochemical membrane processes for sulphuric acid removal and for the recovery of sodium hydroxide from industrial effluents. The implementation of either of these processes is dependent on the effective separation of:

- (i) the anion, cation and mixed bed regeneration liquors,
- (ii) the strong and weak anion regeneration liquors,
- (iii) the strong and weak cation regeneration liquors,
- (iv) the strong and weak mixed bed regeneration liquors.

4.4.1 Sulphuric Acid Removal

The provisional patent specifications for the removal of sulphuric acid from industrial effluents and waste waters is attached (Appendix 3). The process and equipment are similar to those described for the denitrification of ammonium nitrate streams (Section 3.2), except that:

- (i) sulphate ions migrate across the membrane instead of nitrate ions,
- (ii) only hydrogen gas is evolved from the catholyte as opposed to a mixed gas stream,
- (iii) calcium sulphate is formed in the analyte, the formation of which is allowed to exceed its solubility limit, enabling continual separation of the calcium sulphate by precipitation and filtration.

Although only preliminary laboratory trials have been conducted, estimated operating costs are similar to those predicted for ammonium nitrate removal (Section 3.3)

A further possibility for consideration is that the sulphuric acid removal and denitrification processes be combined in the same electrochemical reactor to produce:

- (i) hydrogen, ammonia and oxygen gases,
- (ii) a depleted effluent stream containing minimal amounts of sulphate, ammonium or nitrate ions which will be suitable for reuse as low quality water,
- (iii) a mixed calcium salt stream containing soluble calcium sulphate and soluble calcium nitrate. Since the solubility of the sulphate is much lower than that of the nitrate, this soluble salt will be predominantly nitrate.

The possible combination of the two processes will depend on the degree of purity required for the production of the calcium nitrate by-product.

4.4.2 Sodium Hydroxide Recovery

The patent specifications for the recovery of sodium hydroxide from industrial effluents is attached (Appendix 1). The process involves four stages:

- (i) the neutralisation of the effluent with carbon dioxide gas to produce a sodium bicarbonate stream.
- (ii) the cross-flow microfiltration of the neutralised effluent to remove suspended and colloidal matter.
- (iii) the nanofiltration of the filtered effluent to separate the sodium bicarbonate salt from the other contaminants, in particular calcium, magnesium and any other cation which forms an insoluble hydroxide.
- (iv) the electrochemical recovery of the sodium, as sodium hydroxide in an electromembrane cell. Carbon dioxide is also generated in this process and is recycled to the neutralisation process.

The products are:

- (i) a pure sodium hydroxide solution of any desired concentration between 3 and 35%.
- (ii) a desalinated effluent stream suitable for reuse as wash water.
- (iii) hydrogen and oxygen gases.
- (iv) two concentrate streams (5% of the initial effluent volume) from the cross-flow microfiltration and nanofiltration stages.

Pilot plant results obtained by the Pollution Research Group during the testing of this process against textile scour effluent (20 g/l NaOH) indicated that sodium hydroxide may be recovered at an electrical power cost of approximately R200/ton of 100% NaOH.

5. MANGANESE METAL CO (PTY) LTD

5.1 Introduction

An in-house technical survey conducted by Manganese Metals investigated the possibility of the application of a dozen or so established technologies for the treatment of their effluent. Using feedback obtained from commercial suppliers of waste water treatment plants the preferred methods of effluent treatment were ranked as follows:

- (i) lime precipitation followed by air stripping,
- (ii) electrodialysis and reverse osmosis,
- (iii) evaporation,
- (iv) biological denitrification,
- (v) ion exchange.

As a client of AECI, Manganese Metal Co (Pty) Ltd have approached the Environmental Services Department for further advice concerning the transfer of technology with regard to the disposal of their effluents. In particular AECI were requested to give feedback on spray disposal and biological reduction options.

5.2 Factory Process

Manganese metal is produced by the process laid out in Figure 2. The metal ore is dried, milled and reduced before being leached with sulphuric acid. The heavy metal contaminants are removed by precipitation as sulphides before the manganese metal is plated out using an electrolytic process. Ammonium sulphate is added during the electrolytic process as a buffer to increase the conductivity of the solution.

5.3 <u>Effluent Production</u>

Three effluent streams are produced:

- (i) 'spent' ammonium sulphate process solution and ammonium sulphate washings from the final rinsing of the product.
- (ii) from rinsing the plates which is essential for the removal of adhered manganese.
- (iii) washings produced during the cleaning of the diaphragms in the electrolytic cell.

The effluent is produced at a rate of 500 to 1 000 m³/day and is discharged to a settling dam. The overflow from this dam enters the river. Table 1 characterises the factory effluent and compares its composition to the standard requirements for discharge. The principle species requiring immediate attention are the manganese and ammonium sulphate components of the effluent.

5.4 <u>Effluent Treatment Options</u>

The treatment options selected in Section 5.1 have the following disadvantages:

- (i) lime precipitation followed by air stripping results in the addition of additional TDS, and usually SS, into the system to produce a stream which is still contaminated, although by a different chemical species.
- (ii) any treatment process involving a concentration step (electrodialysis, reverse osmosis or evaporation) will be prone to fouling or scaling since a precipitation step has occurred in the factory process and further concentration will cause additional heavy metal sulphide precipitation.

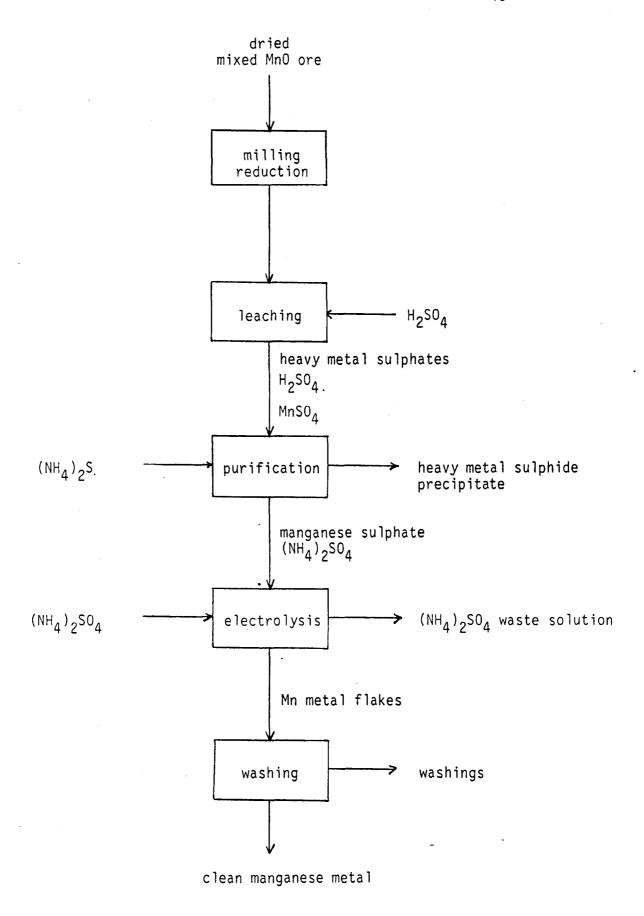


Figure 2 : Schematic of Manganese Production Process

<u>TABLE 1</u>: Range of Effluent Concentrations Compared to the General Standard for Effluent Discharge

Stream to be Treated		Treated Water
		Gov. Gazette General Standard No. 991 18 May 1984
Flow: m³/day	1 000	
рН:	3,5-8,0	5,5-9,5
Conductivity mS/m:	400-800	*
Alkalinity CaCO ₃	50-100	*
TDS g/1	5-10	*
Mn mg/l	200-1 000	0,4
Na mg/l	25-30	+90 above inlet H ₂ 0
Ca mg/1	200-225	*
Mg mg/l	150-250	*
SO ₄ mg/1	2 000-6 000	*
$(NH_4)_2SO_4$ mg/1	1 000-4 000	47
Suspended solids g/l		0,025

^{*} Denotes no specification or exemption from standards.

The General Standard applies to all quality requirements with the exemption of calcium, sulphate and boron.

(iii) although any treatment process involving a concentration step will produce reusable water, a concentrate will also be produced. The chemical loading in this concentrate will be equivalent to the chemical loading of the original effluent and its disposal will be equally difficult.

*

- (iv) the concentration of chemicals in the effluent is too high for denitrification by reduction using algae.
- (v) ion exchange methods have the disadvantage that regeneration chemicals are required. These are often costly and waste regeneration streams require disposal. Ion-exchange techniques transfer a TDS loading problem from one chemical species to another and often the total TDS in the final factory effluent is increased.
- (vi) land disposal by spray irrigation does not appear to be feasible due to both the type of vegetation in the surrounding area and also the lack of available land.

5.5 Effluent Treatment Strategy

Before an effluent treatment system is considered all possible in-house modifications to both the process and washing stages must be carried out to minimise effluent volumes and concentrations.

Thereafter the implementation of a treatment system should be considered, the most advantageous type being one which not only recovers reusable water but also recovers or produces useful chemicals which may be returned to the process or sold as by-products.

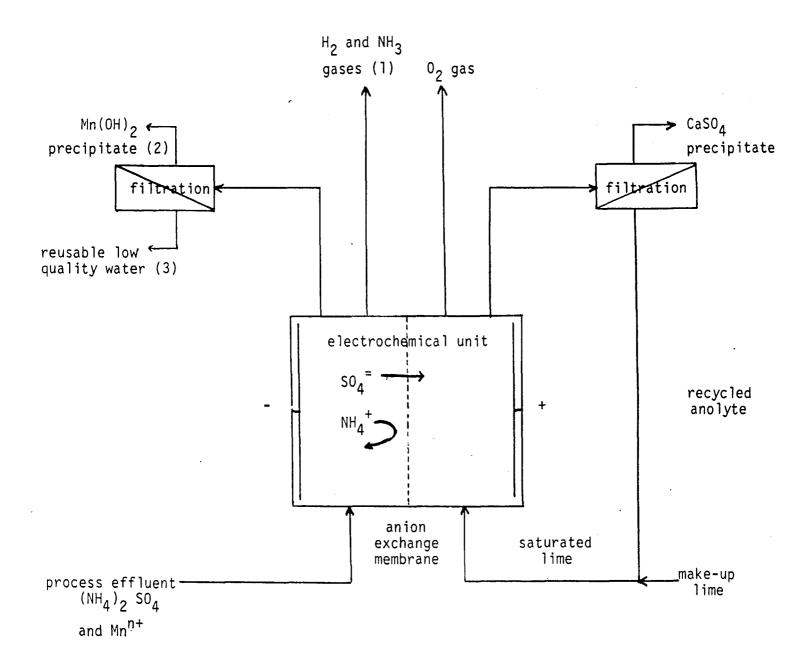
It is recommended that the process effluents be treated separately from the plate and diaphragm washings since the former stream contributes to a large fraction of the TDS in the effluent, in particular the ammonium sulphate and manganese concentrations.

5.5.1 Process description

The proposed treatment stratergy is outlined in Figure 3. The treatment sequence is based on a process developed by the Pollution Research Group and patented by the Water Pollution Research Commission (Appendix 2) for the denitrification of solutions containing ammonium salts.

Essentially, the process involves:

- (i) passing the ammonium sulphate effluent into the cathode chamber of an electrochemical unit containing an anion exchange membrane.
- (ii) passing a saturated lime solution into the anode chamber of the same electrochemical unit.
- (iii) passing a direct electrical current across the electrodes such that :
 - water is oxidised at the anode producing oxygen gas and hydrogen ions, which neutralise the lime component in the anode compartment.
 - water is reduced at the cathode producing hydrogen gas and hydroxide ions, which increases the alkalinity of the catholyte enabling the release of ammonia gas from the solution and the precipitation of $Mn(OH)_2$ in the solution.
 - sulphate ions migrate through the anion exchange membrane from the catholyte to the anolyte.
- (iv) filtration of the neutralised calcium containing anolyte solution to separate the precipitated calcium sulphate salt.
- (v) recycling the filtrate from this stage to the anolyte chamber after addition of make-up lime.



Cathode reaction
$$2H_2O + 2e \rightarrow 2OH^2 + H_2$$

Anode reaction
$$H_2O - 2e \rightarrow \frac{1}{2}O_2 + 2H^+$$

- $\frac{\mathrm{Note}}{\mathrm{Note}}$: 1) the H $_2$ and NH $_3$ gases can be separated by absorption of the NH $_3$ gas into the leached process stream (Figure 2). The H $_2$ gas may then be used in a hydrogen electrode during the electrolytic production of manganese metal.
 - 2) the $Mn(OH)_2$ precipitate may be recycled to leaching.
 - 3) the treated effluent may be reused as process wash water.

Figure 3 : Proposed Effluent Treatment Sequence for the Purification of Process Streams at Manganese Metals Co (Pty) Ltd

- (vi) filtration of the alkaline denitrified anolyte solution to separate the precipitated manganese hydroxide.
- (vii) recycling the filtrate from this stage to the factory as low quality wash water and recycling the precipitated manganese hydroxide to the leaching stage of the production process.

5.5.2 Process optimisation

The rate of lime make-up is controlled to enable the anolyte to be produced at a predetermined pH such that calcium sulphate is the predominant precipitate. This will minimise wastage of lime and allow the production of purer calcium sulphate salts.

Maximum removal and recycle of manganese may be achieved if the pH of the catholyte is controlled by optimising the degree of electrolysis. Ammonia gas may be stripped from the alkaline catholyte by air sparging or by operating the process at elevated temperatures.

5.5.3 Process results

The process will enable:

- (i) the removal of ammonium, sulphate and manganese ions from the factory process stream.
- (ii) the manganese to be removed as manganese hydroxide and recycled to production.
- (iii) the sulphate to be removed as pure calcium sulphate salt for resale, for use or for solid waste disposal.
- (iv) the ammonium to be removed as ammonia gas for suggested recycling to the purification stage of the process to neutralise the sulphuric acid.

(v) the production of hydrogen gas which, after separation of the ammonia gas, may be used for a hydrogen electrode in the electrolytic manganese metal production process.

Preliminary results for the denitrification of an ammonium nitrate stream (Appendix 4) suggest that virtually all the ammonium salt can be removed from the effluent. The degree of manganese removal will depend on the varying solubility of manganese hydroxide with pH and temperature.

5.5.4 Additional Process Modifications

If all the ammonium, sulphate and manganese can be removed from the effluent with the recycle of ammonia gas to processing the implications would include the following:

- (i) faster leaching may be achieved by increasing the concentration of sulphuric acid in the leach stage. The excess sulphuric acid is then neutralised by the recycled ammonia gas to form ammonium sulphate.
- (ii) the purified manganese and ammonium sulphate solution produced after purification (Figure 2) will contain a greater concentration of ammonium sulphate, thus reducing the requirement for the addition of buffering chemicals.
- (iii) since any ammonium sulphate present during the electrolytic production of manganese is recoverable, electrolysis may be carried out at higher ionic strength, thus possibly increasing the efficiency and decreasing the electric potential of the electrolytic process.

5.5.5 Initial Effluent Treatment Plant Sizing

Before sizing or specifying an effluent treatment plant of the type described extensive pilot plant investigations will be required to optimise variables and to obtain reliable operational data including the dependency of the process on:

- (i) current density
- (ii) electrolyte temperatures
- (iii) electrolyte pH
- (iv) the degree of denitrification of the effluent.

Pilot plant investigations will also enable predictions to be made concerning specific power consumptions, typical current efficiencies and plant requirements.

A typical effluent sample (Table 2) shows that the mass flow rate of discharged contaminants is approximately 220 kg/h of ammonium sulphate and 20 kg/h of manganese.

<u>Table 2</u>: Typical Effluent Sample:

Manganese Metal Co (Pty) Ltd

Analysis		Result
pH Conductivity Suspended soli TDS		7,6 550 @ 20°C 0,086 5,14
Total alkalini		42
(NH ₄) ₂ SO ₄ SiO ₂	(g/l NH4 ⁺ (ppm)	2,19 15
Na Ca	(ppm) (ppm)	65
Mg Mn SO ₄ =	(ppm) (ppm) (g/1)	184 520 3,5
	(9/ • /	

Based on preliminary laboratory results (Appendix 4) and assuming that a current efficiency of 80% may be achieved for the transport of sulphate ions, initial plant sizing predictions may be made (Table 3).

The current density at which the process may be operated will determine the plant size. Maximum current densities may be achieved if the effluent is produced in as concentrated a form as possible.

TABLE 3: Initial Plant Size Projections

Assumptions

Effluent flow: 40 m³/h

Effluent concentration: $5,5 \text{ g/1 (NH}_4)_2 \text{ SO}_4$

 $0,5 \text{ g/1 Mn}^+$

Effluent mass flow: 220 kg/h (NH₄)2 SO₄

 20 kg/h Mn^+

Current efficiency: 80%

Electricity requirements: 2 100 F/h

Current density A/m ²	Membrane Area m²
5 628	10
2 814	20
1 407	40

The predicted membrane area of the removal of 220 kg/h of ammonium sulphate at 80% current efficiency and at ambient temperature varies from $10~\text{m}^2$ for operational current densities of approximately 5 600 A/m² to 40 m² for operational current densities of approximately 1 400 A/m².

In addition the following products will result:

- (i) 28 kg/h of NH_3 gas
- (ii) $114 \text{ kg/h of } \text{CaSO}_4$
- (iii) 1,7 kg/h of H_2 gas
- (iv) 1 000 m²/h of low quality water.

Depending on cell voltage, electrical power costs for the electrochemical unit would be approximately R120 000 to R150 000 per annum at R0,05/kWh.

6. FUTURE CO-OPERATION AECI AND THE POLLUTION RESEARCH GROUP

The application and further development of the denitrification and sulphuric acid removal options is to be discussed with AECI before a decision is made.

In order to assist with future investigations the Pollution Research Group is to be supplied with the following information from the management of the No. 4 Ammonia plant:

- (i) Complete analyses and volume flow data of the demineralisation regeneration liquors.
- (ii) Profiles of the various species in the spent regeneration liquors from the demineralisation plant during acceptance testing to enable a detailed characterisation of the effluent composition to be made as a function of the degree of regeneration.

AECI is also to investigate the relative saleability of various nitrate or ammonia salts other than calcium nitrate which could be produced in the ammonium nitrate denitrification process. In addition the purity which is required for calcium nitrate with respect to contamination by calcium sulphate is to be investigated since the possibility exists for the simultaneous denitrification and sulphuric acid removal if calcium nitrate purity requirements are not critical.

Further, the Detonator Department at AECI is to contact Romatex in connection with commission kiering of cotton required for the manufacture of fuse.

AECI is to approach Manganese Metal Company (Pty) Ltd. with regard to the envisaged effluent treatment options. Thereafter the Pollution Research Group would be happy to assist Manganese Metal Company (Pty) Ltd if the latter so desired.