RESEARCH INTO THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

Final Report

To the Water Research Commission

by

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EXECUTIVE SUMMARY

1 BACKGROUND TO THE PROJECT

Two major problems threatening water users in South Africa are :-

(i) the availability of adequate quantities of water, and

(ii) the deterioration of the quality of water resources due to increasing concentration of total dissolved solids (TDS).

In attempting to deal with these two problems of quantity and quality, increasing use has been made of water conservation and recycling technology. These measures have however, resulted in an increased production of inorganic brines and concentrates. For the purpose of this report, a quantitative definition of a brine has been avoided, and brine has been defined as any stream of high total dissolved solids concentration which cannot be treated adequately by conventional means.

Treatment and/or responsible disposal is however essential for these streams as unless these are adequately treated, they will eventually enter the aquatic environment, threatening the quality of both surface and groundwaters.

The basis of this research project was to provide a framework of information which would enable brine producers to assess the best treatment options for their brine and be aware of the latest technology available to them.

The options available for controlling brine disposal into the aqueous environment include :-

(i) engineering out the source of brine,

(ii) converting the brine into a saleable product,

(iii) indirect or diffuse discharge to the environment,

(iv) deactivation or conversion to an inert substance,

(v) immobilisation or passive storage,

(vi) disposal into designated brine sink impoundments or discharge by pipeline into the sea.

The above options have been listed in terms of increasing environmental impact.

Where brine production cannot be prevented it would be advantageous to develop techniques for the on-site disposal of brines. The Water Research Commission contracted with the Pollution Research Group, University of Natal (Project No. 201) to investigate the treatment of inorganic brines and concentrates by physical, chemical, physio-chemical and electrical techniques.

A number of point sources of brine were identified and some specific problematic streams were characterised.

Priority sources of brine include :-

(i) effluent streams generated at some AECI plants,

(ii) acid mine drainage,

(iii) cooling tower blow-down water,

(iv) saline wastes generated at SASOL 2 and 3.

(v) bottle washing effluents.

This final report of the project, summarises work undertaken on selected brine and concentrate streams.

2 PROJECT AIMS

The aims of this project were to:

(i) identify point sources of brine and to characterise those with a particulatly problematic chemistry,

(ii) identify options for controlling brine disposal into the aqueous environment,

(iii) develop techniques for on-site disposal of brines in situations were brine production was unavoidable.

3 PROJECT OBJECTIVES

The aims of the project were to be realised by initially undertaking a series of site visits to identify and characterise problematical brine streams. At each site, the brine-producing process or processes would be examined and where possible measures to reduce brine volumes would be suggested. Where appropiate, new treatment methods would be explored or novel application of existing technology treatment options would be recommended.

4 SUMMARY OF RESULTS

4.1 Identification of Brine Sources

Various organisations including Sentrachem, AECI, Sasol, Iscor, the Chamber of Mines, Eskom, the Department of Water Affairs and the Department of Agriculture and Water Supply were contacted With their aid, a number of point sources of brine have been identified. They include :-

(i) regeneration liquors from anion, cation and mixed bed ion-exchange reactors,

(ii) concentrates from electrodialysis units,

(iii) concentrates from reverse osmosis units,

(iv) cooling tower blow-down streams,

(v) concentrates from evaporator units,

(vi) saline mine concentrates,

(vii) leachates from ash disposal sites,

(viii) concentrates from industrial manufacturing processes.

Priority sources of brine include :-

(i) effluent streams generated at some AECI plants,

(ii) acid mine drainage,

(iii) cooling tower blow-down water,in particular that arising from power station cooling towers,

(iv) saline wastes generated at SASOL 2 and 3.

(v) bottle washing effluents.

Site visits were made to a number of organisations to gain first hand experience and appreciation of the processes leading to the generation of particular brines and concentrates. These are described and investigations summarised. Where results are of a confidential nature, this has been noted.

4.2 AECI

The AECI plants at Zommerveld and Modderfontein manufacture mining explosives. An effluent is produced which contains approximately 3 g/ℓ of ammonium nitrate, the discharge of which is problematical because of the high TDS (8,5 g/ℓ) and nitrogen content.

At Zomerveld, a comprehensive water and effluent survey was conducted, and recommendations were made to enable the rescheduling and recycling of various process streams. Suggestiions were given to minimise contamination of the final effluent by oils, suspended solids and dissolved salts, particularly ammonium nitrate.

At Modderfontein, a series of investigations were carried out in conjunction with the Environmental Services Department at AECI Chemicals and Explosives Ltd. Particular attention was paid to ion-exchange regeneration wastes as these streams contain heavy salt loads. Opportunities for the purification and recovery of sodium hydroxide from caustic regeneration waste by electrochemical means were noted. In addition the precipitation potential of selected effluent streams was examined. This information was required to ascetrain what treatment options might be appropiate and to determine to what degree streams could be concentrated before precipitation would commence.

The treatment and disposal of nitrogenous effluents was examined. A pilot plant study was undertaken to evaluate the treatment of such streams in an electrochemical membrane process. The products of such a process are gas streams, (ammonia, hydrogen and oxygen), an aqueous stream of relatively good quality water, and a stream capable of being concentrated to dryness. Results indicated that process could be tailored to produce a concentrate stream of either calcium nitrate or ammonium nitrate, both of which have resale or reuse potential.

4.3 ESKOM

Site visits were made to Lethabo and Matimba Power Stations. Lethabo is a wet-cooled power station wheras Matimba is a dry-cooled station. Each type of ststion presents different problems. For their wet-cooled stations, Eskom have adopted a zero liquid discharge philosophy and have implemented a number of water recovery measures at their newer power stations. These include either reverse osmosis or electrodialysis reversal for the treatment of cooling water blow-down, further brine concentration and condensate recovery in evaporators, sludge thickening and sludge dewatering to recover water from clarifier underflow. The brines produced by these various measures are disposed of in the ash system which acts as a salt sink, thus no brine concentrate leaves the power station.

At Lethabo Power station, the various water and effluent reticulation systems were examined and insight was gained into the water management strategies employed on a power station. As a major water user Eskom have identified the increasing salinity of Vaal River water as an issue of concern and investigations by ESKOM are constantly in progress to develop techniques for reducing the salt load of their various water circuits. A sulphate removal process, developed at the University of Natal under contract to the Water Research Commission, (WRC Project No. 203, *The Chemical Removal of Sulphates*) was of particular interest to them. The process which could be based at a power station such as Lethabo, could be operated on a regional scale. The process involves precipitation of the sulphates as barium sulphate, using barium carbonate. The barium sulphate is reduced to barium sulphide using coal in a rotary kiln. The barium sulphide is then leached and converted to insoluble barium carbonate by contacting the solution with carbon dioxide. The barium carbonate is recycled at 95 % recovery and the sulphide is liberated as hydrogen sulphide gas. The conversion of this gas to sulphur and/or subsequently to sulphur tri- or dioxide gas is conventional technology.

It was envisaged that the sulphate rich wastes at Lethabo could be desulphonated and recycled. In addition, the acid mine waters from the surrounding mines could be treated at Lethabo. It was estimated that the total sulphate loading of the mine waters would be approximately 50 to 70 tons/day as sulphate. The sulphate loading of Lethabo wastes is a function of the raw water concentration and, assuming a sulphate level of 20 mg/ℓ, and a water consumption 150 Mℓ/day, was estimated to be 3 ton/day as sulphate.

It was envisaged that the sulphur produced by the process from the combined mine waters and cooling tower blow-down streams, approximately 24 tons/day as sulphate, could be converted to sulphur trioxide for use in the Lethabo boiler stacks to increase the conductivity of the waste flue gas in the electrostatic precipitators. Each boiler requires approximately 6 tons/day of sulphur as sulphur trioxide.

The results obtained from Water Research Commission Project No. 203 (*The Chemical Removal of Sulphates)* were evaluated by a firm of industrial contractors and a firm of consulting engineers. Assistance was provided to these investigations under this project. The relevant reports have been submitted directly to the Water Research Commission.

At Matimba Power station, problems were being experienced with iron contamination of the boiler feed water and its effect on the ion exchange resins. Suggestions were made to improve the system and to solve the problem.

4.4 SASOL

A visit was made to the SASOL 2 and SASOL 3 plants at Secunda. The Sasol plants have a large number of organic and inorganic wastes, as well as the conventional boiler and cooling water blow-down streams.

Saline waters are segregated and handled separately from other wastes. The three major sources of inorganic wastes are :-

(i) regenerant streams from boiler feed water pretreatment,

(ii) boiler blow-down,

(iii) process water ion-exchange regenerants.

The saline effluents are treated in one of three vapour compression evaporators operating in a seeded slurry mode. The condensate is reused in processing. Some of the concentrate is used for ash quenching and ash transport; the remainder is discharged to solar evaporation dams. Some problems, mainly operational, are being experienced.

The cooling tower blow-down and organic wastes are treated biologically and then settled, clarified and filtered through sand, carbon and ion-exchange columns before reuse.

Recommendations were made regarding the operation of the treatment units and the water and effluent handling system in general.

4.5 ISCOR

A visit was made to Iscor Iron and Steel Works at Newcastle. The works produces a range of iron and steel alloys and by-products such as ammonium sulphate, sulphuric acid, tar and oil.

Waste liquid effluents from the plant are divided into four stream :-

(i) recoverable water,
(ii) irrigation effluent,
(iii) evaporation effluent,
(iv) storm water.

An evaporator has been installed to concentrate the evaporation effluent which is of such poor quality that neither discharge nor irrigation is allowed.

Oil is a general contaminant around the plant and efforts should be made to improve the performance of the oil removal systems that are in place and to install additional ones.

Recommendations were made to improve the performance of the demineralisation plant, and to reduce the load of regeneration chemicals used. Suggestions were given as to how chemicals could be extracted from certain waste streams, purified and reused.

4.6 Acid Mine Water and Sulphuric Acid-containing Wastewater

Sulphuric acid, because of its relative low cost and availibility, is used widely in industry where acidic or anhydrous conditions are required. In addition , the weathering of sulphide bearing rocks and the extraction and beneficiation of sulphide containing ores, leads to the production of acid mine water. The treatment of these wastes by conventional technologies such as, lime softening, electrodialysis and seeded slurry evaporation is limited by the precipitation of calcium sulphate.

A process was developed to neutralise sulphuric acid and remove sulphates from an effluent stream, without the addition of further chemicals to the system.

The electromembrane process is similar to that developed for the denitrification of ammonium nitrate solutions except that :-

(i) sulphate ions migrate across the membrane instead of nitrate ions,
(ii) only hydrogen gas is evolved from the cathode,
(iii) calcium sulphate is formed in the anolyte, precipitates, and is separated by filtration.

Laboratory trials were undertaken on acidic ion exchange regenerant wastes and on acidic mine drainage waters. A provisional South African patent has been assigned to the Water Research Commission for this process. Applications for international patents have also been lodged.

4.7 NATIONAL BEVERAGE SERVICES

Following a meeting with National Beverages Services, a proposal has been prepared for the pilot plant evaluation of an electrochemical system for the recovery of sodium hydroxide from bottle washing effluents. The trials will be financed jointly the Water Research Commission and the National Beverage Services and will be conducted at the Peninsular Beverage Company Ltd, Parowvallei.

4.8 TEXTILE DYE EFFLUENT

A closed-loop recycle system using a charged ultrafiltration membrane to decolourise reactive dye effluents from a textile yarn and fabric dyeing process was developed by a research student. The concentration of sodium chloride in a reactive dyebath ranges from 50 to 100 g/ℓ.

The value of the electrolyte, sodium chloride, in the permeate ranges from R10 to R20 per kℓ. A pilot plant has been designed for installation at Ninian and Lester's Pinetown factory. This plant will handle the concentrated dye effluent from one machine. The plant should be operational by the end of 1989.

5 REALISATION OF PROJECT OBJECTIVES

Point sources of brine production have been identified. Insight has been gained on the processes from which these brines originate and on the nature and characteristics of brine streams whose chemistry is particularly problematical in seeking a treatment method. At most sites visited various water and chemical saving measures were recommended and received favourably by the companies concerned. The extent to which these recommendations have been acted upon has been dependant on changing factory requirements and economic constraints.

Options for controlling brine disposal into the aqueous system have been identified. These options have formed the basis of the evolving Pollution Research Group philosophy on waste minimisation and pollution prevention. In this regard, the project has played an important development and capacity building role. The direct benefits of this are difficult to quantify at this stage but sufficient people have interacted in this project to ensure that there is a pool of young researchers with an awareness of the difficulties involved in the treatment and disposal of brines and that future new industrial developments should take effluent production and treatment options into account at the planning and development stage of a new venture.

Where the prevention of brine production proved unavoidable, new techniques have been developed for on-site disposal. Arising from the development of these techniques, two patent applications have been made. They are entitled :-

(i) The Removal of Ammonium Salts from an Aqueous Medium Containing the Salt. S.A. Application No. 88/8898.

(ii) The Removal of Sulphuric Acid from an Aqueous Medium Containing the Acid. S.A. Application No. 88/5487.

Application for international patents have also been lodged.

One of the most satisfactory and important aspects of this project is the relationship built up between the Pollution Research Group and the companies visited. This relationship has extended from management levels to operational levels. The different attitudes and perceptions of the same problem has enabled the Pollution Research Group to gain realistic appreciation of many problems and so produce recommendations and suggestions that have practical as well as academic merit.

Arising from this project, 2 papers and 6 conference proceedings have been published.

6 CONCLUSIONS

The treatment and disposal of brines and concentrates will continue to be a problem in South African industry. The magnitude of the problem is related to the scale of water use. Major water users are aware of their responsibility in protecting the scarce water resources of the country and have implemented or seek to implement brine-production reducing measures or responsible disposal measures. Industry has been made aware that new techniques are being developed which are tailored to South African conditions and that local expertise is available for such development. Through funding of such projects the status of the Water Research Commision is enhanced in the eyes of industry.

7 RECOMMENDATIONS

Recommendations arising from this project are :

(i) contacts made with industry should be maintained and strengthened so that future research can be market driven and thus of a practical importance.

(ii) commonly-occurring problems identified during the course of this project, for example, the general problem of unwanted precipitation, should form the basis for future research proposals.

(iii) clean technologies, waste minimisation and pollution prevention should be the first consideration in solving industrial effluent problems.

ACKNOWLEDGEMENTS

The work in this report was funded by the Water Research Commission, for a project entitled: *The Treatment of Inorganic Brines and Concentrates*

The financing of the project by the Water Research Commission and the contribution by the members of the Steering Committee are gratefully acknowledged.

During the course of the project, many people at the various plants and factories visited, freely gave of their time and expertise. Thanks are extended to them.

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Copies of Appendices to this Final Report may be obtained from the Water Research Commission, P.O.Box 824, Pretoria, 0001, Republic of South Africa.

1 INTRODUCTION

Two major problems threatening water users in South Africa are :-

(i) the availability of adequate quantities of water, and

(ii) the deterioration of the quality of water resources due to increasing concentration of total dissolved solids (TDS).

In attempting to deal with these two problems of quantity and quality, increasing use has been made of water conservation and recycling technology. These measures have however, resulted in an increased production of inorganic brines and concentrates. Unless these are adequately treated, they will eventually enter the aquatic environment. The options available for controlling brine disposal into the aqueous environment include :-

(i) engineering out the source of brine,

(ii) converting the brine into a saleable product,

(iii) indirect or diffuse discharge to the environment,

(iv) deactivation or conversion to an inert substance,

(v) immobilisation or passive storage,

(vi) disposal into designated brine sink impoundments or discharge by pipeline into the sea.

The above options have been listed in terms of increasing environmental impact.

Where brine production cannot be prevented it would be advantageous to develop techniques for the on-site disposal of brines. In 1987 the Water Research Commission contracted with the Pollution Research Group, University of Natal (Project No. 201) to investigate the treatment of inorganic brines and concentrates by physical, chemical, physio-chemical and electrical techniques.

A number of point sources of brine were identified and some specific problematic streams were characterised.

Priority sources of brine include :-

(i) effluent streams generated at some AECI plants,

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(iii) cooling tower blow-down water,

(iv) saline wastes generated at SASOL 2 and 3.

(v) bottle washing effluents.

This final report of the project, summarises work undertaken on selected brine and concentrate streams. A quantitative definition of a brine has been avoided, and brine has been defined as any stream of high total dissolved solids concentration which cannot be treated adequately by conventional means.

It is the policy of the Pollution Research Group to prevent or minimise pollution by in-house modifications to existing processes. Where pollution problems cannot be totally engineered out of a process, only then should an effluent treatment approach be adopted. Where this is considered necessary, the aim should be to recover and recycle water, process chemicals and heat energy within the production process. The segregation of effluent streams is central to this approach as it allows high pollution load streams to be preferentially treated without dilution by less contaminated streams. The site visits detailed in this report and the recommendations given are based within the framework of this philosophy.

Arising from this project, 2 papers and 6 conference proceedings have been published. Two patent applications have been made. They are entitled :-

(i) The Removal of Ammonium Salts from an Aqueous Medium Containing the Salt. S.A. Application No. 88/8898.

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2 IDENTIFICATION OF BRINE SOURCES

The Pollution Research Group contacted various organisations including Sentrachem, AECI, SASOL, ISCOR, the Chamber of Mines, ESKOM, the Department of Water Affairs and the Department of Agriculture and Water Supply. With their aid, a number of point sources of brine have been identified. The include :-

(i) regeneration liquors from anion, cation and mixed bed ion-exchange reactors,

(ii) concentrates from electrodialysis units,

(iii) concentrates from reverse osmosis units,

(iv) cooling tower blow-down streams,

(v) concentrates from evaporator units,

(vi) saline mine concentrates,

(vii) leachates from ash disposal sites,

(viii) concentrates from industrial manufacturing processes.

Site visits were made to a number of organisations to gain first hand experience and appreciation of the processes leading to the generation of particular brines and concentrates. These are described and investigations summarised. Where results are of a confidential nature, this has been noted.

3 SITE VISITS

3.1 AECI

The AECI plants at Zommerveld and Modderfontein manufacture mining explosives. An effluent is produced which contains approximately 3 g/ℓ of ammonium nitrate, the discharge of which is problematical because of the high TDS (8,5 g/ℓ) and nitrogen content.

3.1.1 Zommerveld

A comprehensive water and effluent survey was conducted at the Zommerveld complex (**Appendix 1**). Intake water to the site comes from a borehole and consumption was estimated at 8 kℓ/h. The various production and water consuming processes, together with effluents arising and existing treatment facilities are shown in Figure 1.

Water is consumed :-

(i) for domestic uses, for example showers, toilets, drinking

(ii) at the tank farm where all spillages during transfers from tankers and tanks are washed away with water and where water is used to flush all hoses (daily) and pipes (after each transfer) conveying the explosive base, ANS, and the oxidising solution, to prevent solidification of the chemicals.

(iii) in the production houses where water is used to wash the floor, to clean the extruding, cutting and clipping machines and to cool the explosive cartridges

Each area of water use produces effluent with different characteristics. The effluents arising from the tank farm are generally oil free and consist of a fairly concentrated stream of ammomium nitrate which may contain some sodium nitrate or other process chemicals. A single combined effluent stream is discharged form the production houses. This stream is contaminated by dissolved ammonium and sodium nitrate, suspended solids, mainly waste product and by detergents and spindle oil. The waste domestic water is insignificant in volume and has minimum contamination.

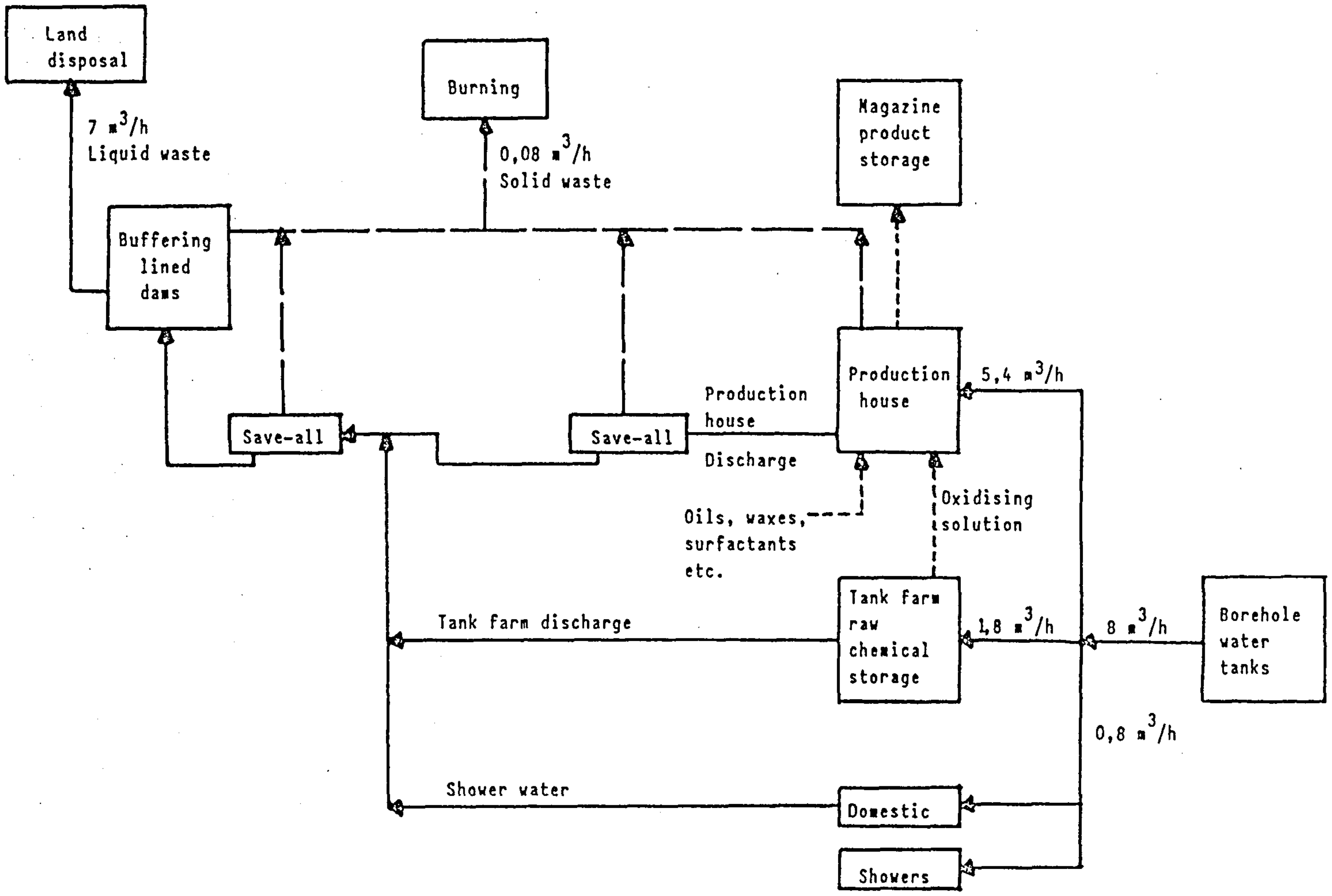


Figure 1 : Schematic diagram of Zomerveld Plant

These wastewater streams are conveyed to two lined buffering dams. Save-alls, situated outside each production house and prior to dam entry, remove solids from the wastewater streams. From the dams the effluent is pumped to a disposal site for discharge onto the ground at a rate of 7 kℓ/h.

Recommendations were made to enabled the rescheduling and recycling of various process streams and the minimisation of final effluent contamination by oils, suspended solids and dissolved salts, particularly ammonium nitrate. A schematic diagram of the proposed water and chemical reticulation scheme is shown in Figure 2.

Implementation of the recommendations made would:

(i) significantly reduce product, water and chemical usage.

(ii) enable effective and efficient monitoring of the water and chemical reticulation systems within the plant.

(iii) enable the recycle and reuse of large proportions of water, raw chemicals and oils.

(iv) enable the production of a small volume, high concentration effluent containing minimum suspended matter which could be treated, concentrated or discharged.

3.1.2 Modderfontein

The AECI plant at Modderfontein manufactures both chemicals and a wide range of nitroglycerine-based and ammonium nitrate-based explosives, together with accessories such as detonators and fuses.

The factory consumes approximately 30Mℓ/day of water supplied by the Rand Water Board. In addition, 1,2 Mℓ/day of sewage effluent is provided by the Modderfontein and Johannesburg sewage works. A recycle system within the factory enables a further reuse of approximately 8,4 Mℓ/day of weak effluent.

All the effluents produced at the factory are segregated into two discharge streams, known as the weak effluent and the strong effluent. The effluent system at the factory is depicted in Figure 3.

The weak effluent is discharged under permit into the Jukskei River at a rate of 1 000 kℓ/h. Approximately 35 to 54 tons of TDS are discharged daily into the Jukskei river in the form of weak effluent. The chemical loads contained in weak effluent discharge for the winter of 1986 and the summer of 1986 and 1987 are given in Table 1. Up to 60 % of the volume of weak effluent comprises water from the power station. Ion exchange regeneration chemicals from No 4 Ammonia plant make up 25 % of the volume of weak effluent, but have a TDS loading some 5 to 10 times higher than the final weak effluent.

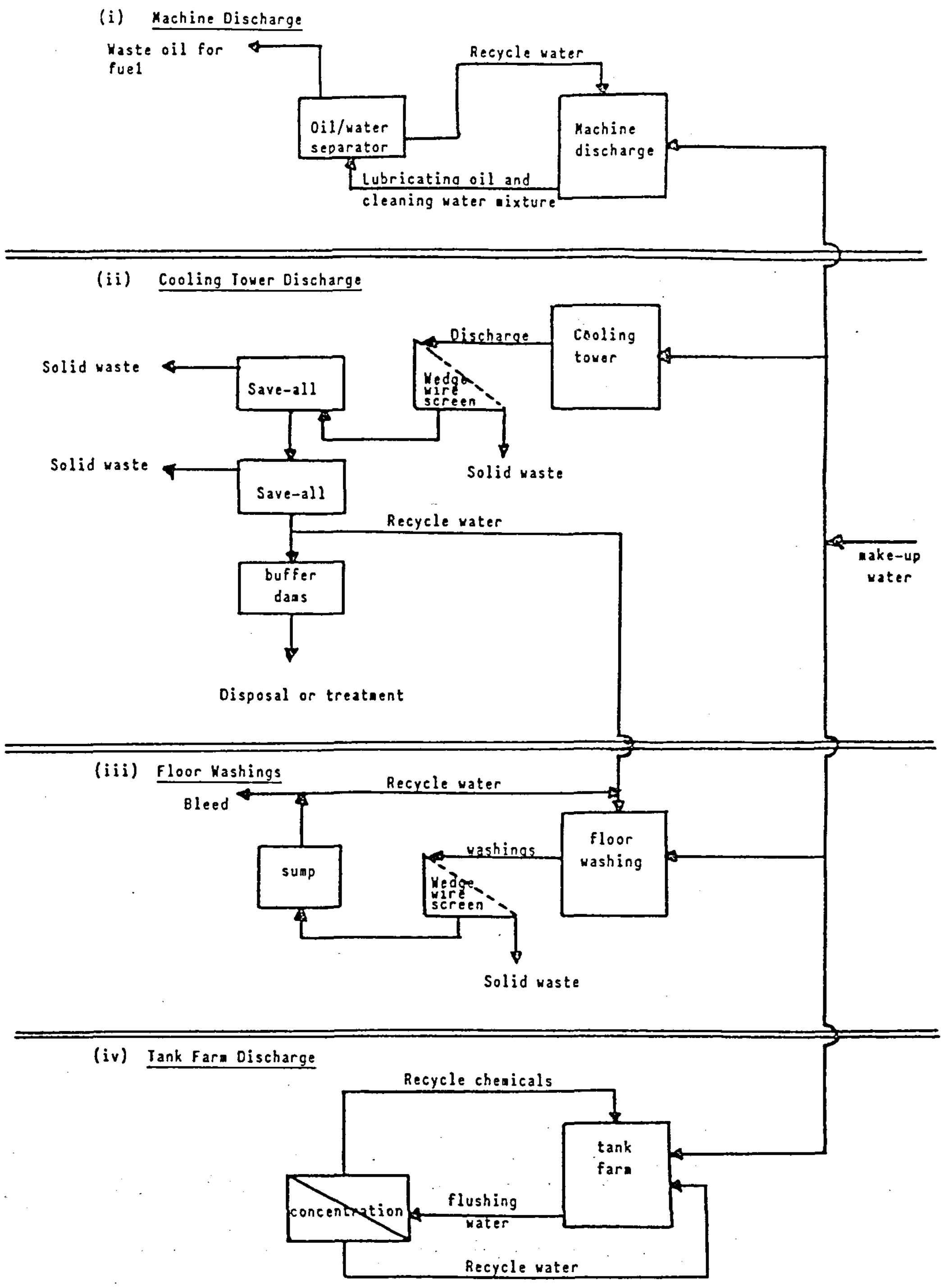
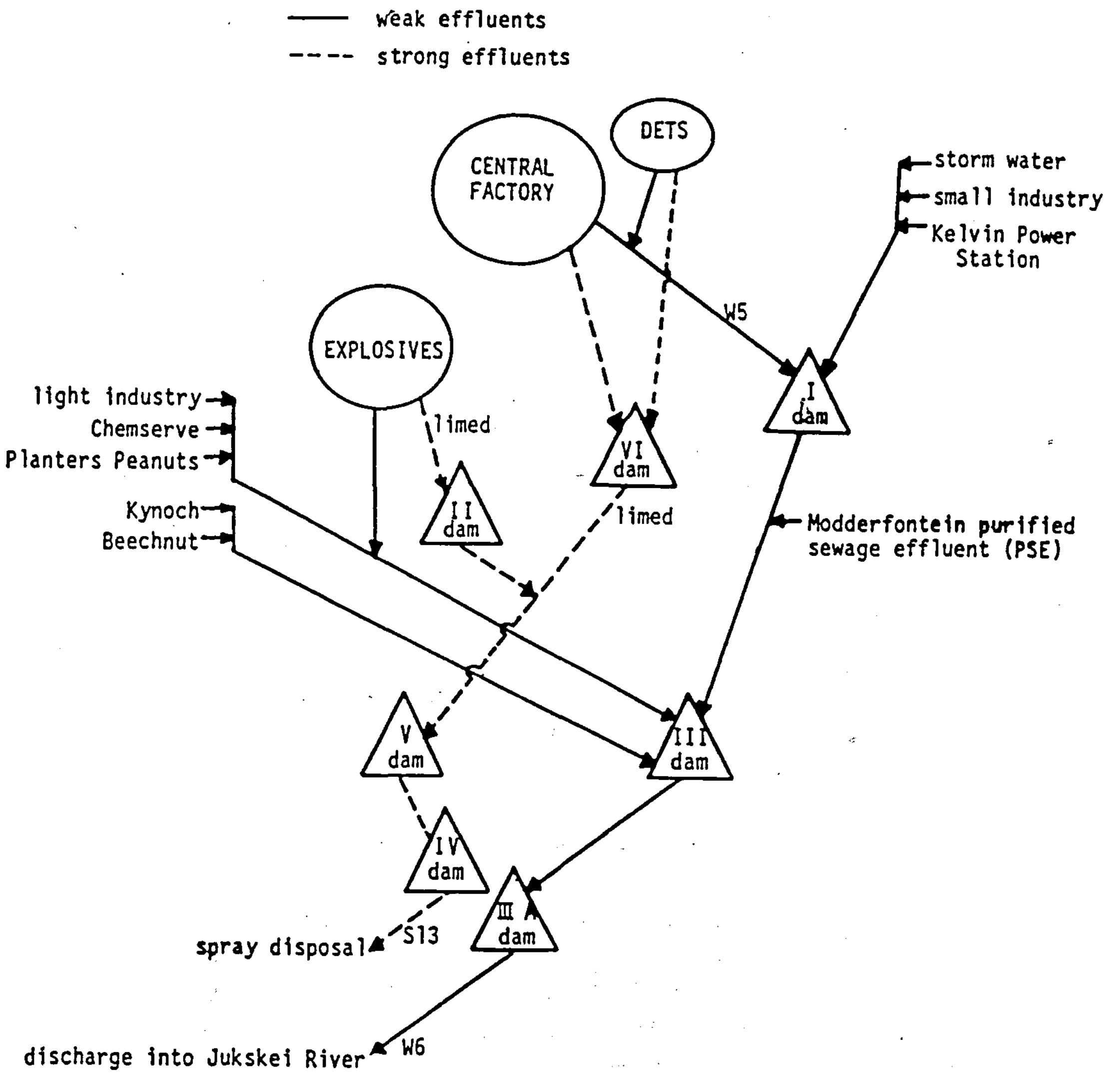


Figure 2 : Schematic diagram of proposed water and chemical reticulation



Notes : (i) Dam VI is limed.

(ii) Dam IIIA is a bypass dam

(iii) Some of the Modderfontein PSE is used in the central factory as raw water and there is a 30% recycle of weak effluent from Dam III back to the factory.

Figure 3 : The effluent system at AECI, Modderfontein

TABLE 1 : Annual average chemical loading in weak effluent;(a) from the central factory (b) final effluent discharge

	Discharge from central factory		Final weak effluent discharge	
Determinand	Winter 1986	Summer 1986-1987	Winter 1986	Summer 1986-1987
TDS	1 445	2 238	681	1 052
NH_4	46	64	26	53
NO_3	69	113	29	60
Na	197	293	83	156
Cl	163	196	37	60
SO_4	530	734	291	411

Strong effluent, which is nitrogenous in character, is produced at a rate of 20 kℓ/h, is sprayed onto 2 500 hectares of leased or owned land. The main contributor to the volume of strong effluent produced is the demineralised water from No 11 nitric acid plant (10 kℓ/h). Various ammomium nitrate discharges make up the remaining volume of strong effluent.

A series of investigations, were carried out in conjunction with the Environmental Services Department at AECI Chemicals and Explosives Ltd. (**Appendices 2 to 5**). The purpose of these investigations was to examine areas of concern. Three effluents were identified which make significant contributions to the pollution load from the factory. These are :

(i) ion-exchange regenerant wastes. The combined daily chemical consumption in the two ion exchange systems (No 4 Ammomium plant and No 11 Nitric acid plant) is estimated to be 5 to 6 tons of 98 % sulphuric acid and 3 to 4 tons of 100 sodium hydroxide. The contribution of the regeneration liquors to the sodium and sulphate ion concentrations in both the final weak and strong effluent streams is significantly high.

(ii) keiring effluents. The spent keir liquor contributes an estimated 15 to 20 % of the sodium ion concentration of the strong effluent.

(iii) ammomium nitrate effluents from explosives and fertiliser production

Ion-exchange regenerant wastes

Measures taken at the factory to minimise chemical consumption during resin regeneration and to reduce effluent loadings include the following :-

(i) an additional set of columns has been installed at the beginning of the existing demineralisation unit and spent regeneration liquors are used for the regeneration of this new set. After commissioning of this set, it is estimated that chemical consumption will be reduced by 50 %. The overall water recovery of the demineralisation unit will also be improved.

(ii) the reuse of selected rinse streams.

(iii) consideration of the implementation of shorter regeneration times.

(iv) consideration of the feasibility of using reverse osmosis as a pretreatment to ion-exchange. It has been estimated that this would result in a 98 % savings in regeneration chemicals and a 50 % reduction in selected dissolved salts in the effluent stream discharged to the Jukskei River.

(v) consideration of the feasibility of using multistage distillation prior to ion-exchange.

(vi) consideration of the feasibility of using reverse osmosis as a barrier between ion-exchange and steam generation, allowing for considerable reduction in the frequency of ion-exchange regeneration, while at the same time ensuring minimal reverse osmosis membrane fouling.

(vii) increasing the efficiency of the degasser, situated prior to the anion exchange columns, to minimise carbonate carry-over into the resin, thus delaying anion break-through.

(viii) consideration of the use of various process condensates in place of Rand Water Board water as the feed to the demineralisation unit.

(ix) consideration of the need for cross-flow microfiltration as a pretreatment to prevent sludge build-up in the demineralisation unit.

(x) consideration of the removal of precipitated salts from the waste regeneration liquors prior to dilution and resolution

(xi) consideration of the separation of the strong sulphuric acid washes, followed by liming and filtration, to remove calcium sulphate, to yield an effluent with a TDS loading below that of the strong wash.

(xii) consideration of the reuse of caustic regenerant waste as a process chemical in the cotton kiering section of the fusing factory.

(xiii) consideration of the purification and recovery of sodium hydroxide from caustic regenerant waste by electrochemical means (**Appendix 6**).

Kiering

In order to minimise the effluent loading and the volume of caustic kiering effluents it was recommended that :-

(i) commission kiering be investigated,

(ii) the existing batch atmospheric kiering process be replaced by a more modern process which enables the more efficient use of chemicals,

(iii) the feasibility of reusing the spent caustic be investigated,

(iv) the reuse of initial rinse water for subsequent chemical batch make-up be investigated,

(v) overflow rinsing be placed with batch fill and drop rinsing,

(vi) the recovery of sodium hydroxide be investigated.

Denitrification

In order to overcome ultimate disposal problems associated with treating the nitrogenous effluent, a process was developed for the removal of ammonium nitrate from industrial wastes. A provisional patent for this process has been assigned to the Water Research Commission (**Appendix** 7).

The process involves an electrochemical membrane unit (Figure 4), in which the ammonium nitrate solution forms the catholyte and a saturated hydroxide solution forms the anolyte.

Under the influence of an electric potential :-

(i) the ammonium nitrate is split and the nitrate ions migrate through the anion selective membrane into the saturated calcium hydroxide solution where a soluble salt, 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 released 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 calcium 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 for recycle or discharge.

(ii) a stream of oxygen gas.

(iii) a depleted effluent suitable for reuse as relatively good quality water.

(iv) a concentrated calcium nitrate stream for resale as a solution or as a solid after evaporation and spray drying.

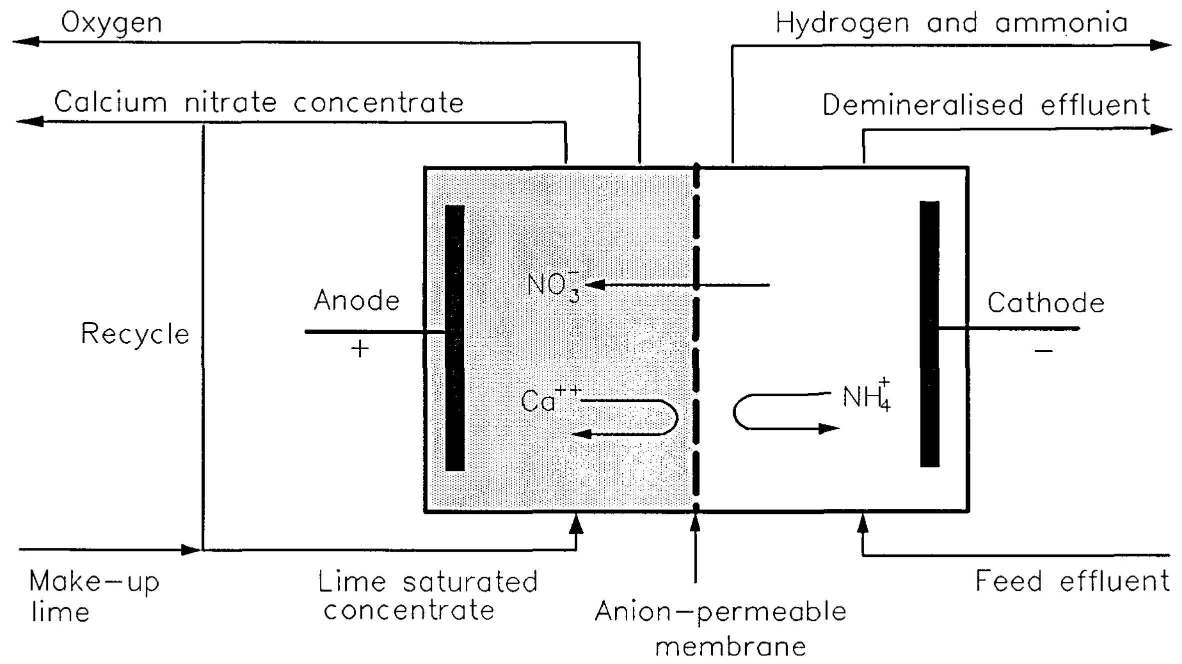


Figure 4 : Schematic diagram of electromembrane unit for denitrification

Appendix 8 summarise the results of initial laboratory investigations. Current efficiencies of 80 to 100 % could be achieved for the desalting of ammonium nitrate streams (5 to 10 g/ℓ).

Following the successful laboratory scale studies, a pilot plant scale study was undertaken at Modderfontein. This study was financed by AECI who felt that as well as providing a treatment for ammonium nitrate effluent, the process had economic benefits to them as a method for calcium nitrate production. Calcium nitrate is used by deciduous fruit producers.

The results from the pilot plant study (**Appendix 9**) indicated that removal efficiencies of 98 % could be achieved at a 96 % removal of ammonium nitrate. The specific power consumption varied from 1,5 to 3,5 kWh/kg ammonium nitrate removed (depending on the current density and feed concentration). The fouling and rupturing of the ion exchange membrane by calcium carbonate was a serious problem, which must be overcome if the process is to be viable.

Subsequent to the initiation of this investigation, the overall concept of the treatment of ammonium nitrate effluent was reviewed because the requirement for the manufacture of calcium nitrate fell away.

Suggestions were made to modify the electrochemical process to produce pure concentrated ammonium nitrate, which could be used in the manufacture of explosives. The proposed treatment process would consist of effluent cleaning stage followed by concentration. Initially testing showed that flocculation was a successful cleaning technique. Alternatively cross-flow microfiltration could be undertaken on the raw effluent, removing the need for further chemical addition to the effluent. Multi-effect evaporation was suggested as a suitable concentration stage, as factory personnel are familiar with this technology and steam is readily available.

Other Areas of Investigation

Tests were conducted (**Appendix 4**) in which selected effluent streams were evaporated. Precipitates appeared at intervals throughout the evaporation procedure and were identified. This enabled information to be obtained regarding the precipitation potential of effluent constituents, which, on concentration of the effluent, might interfere with the performance of treatment techniques such as reverse osmosis, evaporation, electrodialysis etc. In addition, the degree of concentration which could be achieved without the precipitation of insoluble constituents was determined.

It was recommended that minimum use be made of liquid carriers for washing down.

Contaminated condensates produced at the factory were dumped and discharged if a use for them cannot be found. In the case where these condensates contain ammonium nitrate, a concentration process involving electrodialysis and reverse osmosis has been proposed to enable reuse and recycling of these streams.

3.2 ESKOM

3.2.1 Lethabo Power Station

Site visits were made to the Lethabo Power Station and the various water and effluent reticulation systems were examined. Details of the water and effluent circuits operating at Lethabo are given in **Appendix 10**.

Lethabo Power Station is a zero-discharge plant and the technologies which Eskom have employed to enable water recovery from effluent include :-

(i) reverse osmosis for cooling water blow-down,
(ii) electrodialysis (in place of reverse osmosis at selected power stations),
(iii) evaporation for additional brine concentration,
(iv) sludge thickening to enable water recovery from clarifier sludges,
(v) sludge dewatering.

In addition to water recovery from effluent, Eskom have implemented various cascading systems in which product water from one process is cascaded for use as low quality water in another process. Finally, the ash system is designed to function as a salt sink for TDS disposal.

The largest consumer of water at the station is the cooling water circuit which is operated at approximately twenty cycles of concentration. The frequency of blowdown is determined by the sulphate level in the recycled stream, and is maintained below 1 300 mg/ℓ. Thus a significant impact on water and effluent pollution loading would be to decrease blowdown by operating at higher cycles of concentration. The quality of the cooling water is maintained by:

(i) sidestream clarification which treats 90 Mℓ/day of cooling water in one of three clarifiers

(ii) pH control using sulphuric acid to maintain the scaling index,

(iii) operating the concentration cycle as close to the maximum as possible; this is achieved by good control.

Increased cycles of concentration would be possible if:

(i) non-concrete or improved concrete materials of construction were used for the packing in the cooling towers, such that higher levels of sulphate could be attained.

(ii) a method of sulphate removal and control were available

Investigations by Eskom are constantly in progress to develop techniques for increasing the number of cooling cycles to maximise water reuse before cooling tower blow-down. Eskom is presently investigating the feasibility of implementing a sulphate removal process (**Appendix 11**) which has been developed at the University of Natal under contract to the Water Research Commission. The process involves precipitation of the sulphates as barium sulphate, using barium carbonate. The barium sulphate is reduced to barium sulphide using coal in a rotary kiln. The barium sulphide is then leached and converted to insoluble barium carbonate by contacting the solution with carbon dioxide. The barium carbonate is recycled at 95 % recovery and the sulphide is liberated as hydrogen sulphide gas. The conversion of this gas to sulphur and/or subsequently to sulphur tri- or dioxide gas is conventional technology.

It is envisaged that the sulphate rich wastes at Lethabo could be desulphonated and recycled. In addition, the acid mine waters from the surrounding mines could be treated at Lethabo. It is estimated that the total sulphate loading of the mine waters would be approximately 50 to 70 tons/day as sulphate. The sulphate loading of Lethabo wastes is a function of the raw water concentration and, assuming a sulphate level of 20 mg/ℓ, and a water consumption 150 Mℓ/day, is 3 ton/day as sulphate.

It is envisaged that the sulphur produced by the process from the combined mine waters and cooling tower blow-down streams, approximately 24 tons/day as sulphate, could be converted to sulphur trioxide for use in the Lethabo boiler stacks to increase the conductivity of the waste flue gas in the electrostatic precipitators. Each boiler requires approximately 6 tons/day of sulphur as sulphur trioxide.

3.2.2 Matimba Power Station

To reduce the use of water for power generation, Eskom is in the process of moving towards dry-cooling processes in future power stations where this is economically feasible. Dry cooling reduces the water use per unit of electricity generated to about 22 % of that of the latest wet-cooled stations. A visit was made to Matimba Power Station, a dry-cooled station, where problems of iron contamination of the boiler feed and its effect on the ion exchange resins were being experienced. The station operates on a closed boiler water circuit. The turbine exhaust is directly cooled in an array of air coolers. The anion exchange resin bed served to remove particulate, colloidal and dissolved iron from the boiler feed water.

Suggestions were made to improve the system and to solve the problem.

3.3 SASOL

A visit was made to SASOL 2 and SASOL 3 at Secunda (**Appendix 12**). The factories take in coal, water from the Grootdraai Dam, and air, from which a series of products including fuel, chemicals, fertilisers, explosives and wastes are manufactured. Generally Sasol 3 is a mirror image of Sasol 2 but there are common facilities such as the ash water dams.

The SASOL plants have a large number of organic and inorganic waste streams. Saline effluents arise from :

(i) ion exchange regeneration liquors from the utility circuit

(ii) ion exchange regeneration liquors from the process recovery plant (Unit 52)

(iii) cooling tower blowdown

(iv) boiler blowdown

(v) concentrate from the evaporation plant (Unit 66)

At the time of the visit problems were being experienced in Unit 66. Unit 66 comprised three falling film vapour compression evaporators which operate in a seeded slurry mode. A schematic diagram of the layout of Unit 66 is shown in Figure 5. The objectives of Unit 66 are to reduce the volume of brine stream requiring disposal and to produce a distillate of sufficient quality to be recycled as boiler feedwater. The concentrate from the evaporative process reports to the ash dams. Some is used for ash quenching and ash transport.

At the time of the visit only two trains were operational. The third train was being refurbished following corrosion of the titanium tubes.

Effluents reporting to Unit 66 enter the storage tanks. Tank 1 holds boiler blowdown and anion exchange regeneration liquors. The solution in Tank 1 consists mainly of sodium ions, together with hydroxyl, chloride, carbonate and sulphate ions. The pH of the solution is between 12 and 13.

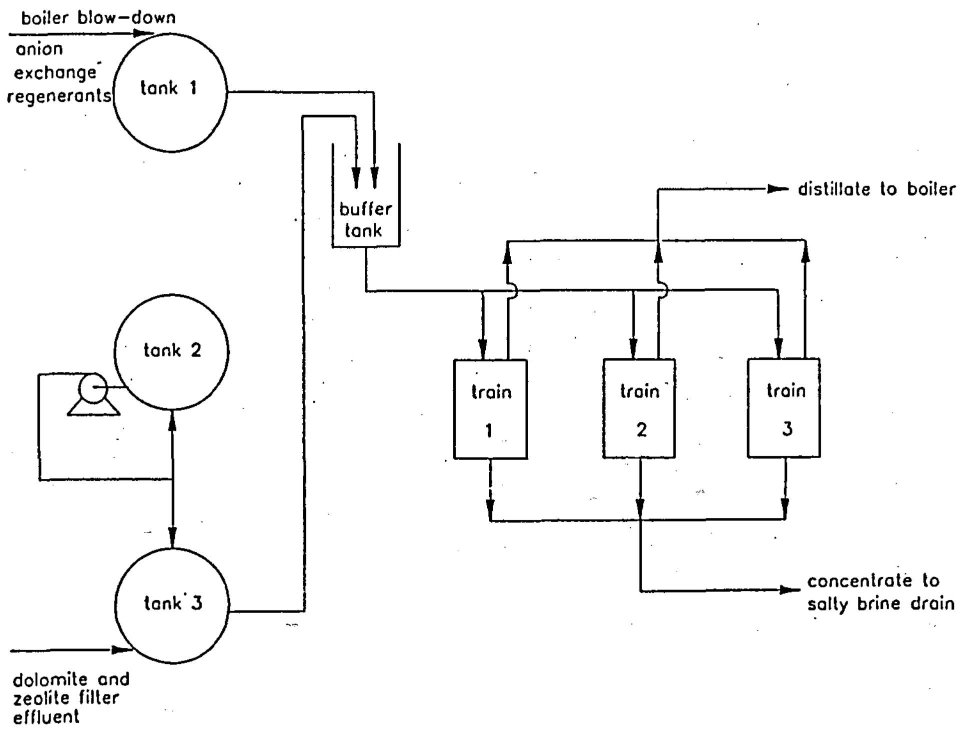


Figure 5 : Layout of Unit 66 at Sasol 2

Tank 2 and Tank 3 are interconnected and solutions are circulated continuously between them to obtain good mixing and equalisation of composition. The effluents in these tanks are rich in sodium chloride and calcium carbonate and have a pH value of approximately 7,8.

The contents of the storage tanks are combined in the buffer tank and the pH adjusted to 5,5 with sulphuric acid. Scale formation is inhibited by the use of calcium sulphate seed crystals. The concentration of circulating suspended solids is controlled by the use of hydrocyclones.

Between 14 and 20 cycles of concentration are achieved in Unit 66. The limiting factor in water recovery is the formation of the double salt, $CaSO_4.Na_2SO_4$, glauberite. The formation of this salt is dependant on the chemical composition of the circulating brine rather than on solids concentration.

Liquid concentrate from the evaporators is discharged to the salty brine dams. Some is used for ash quenching and ash transport.

Operational problems associated with the evaporators are:

(i) breakage of pH probes. Probes robust enough to withstand conditions in the system are difficult to obtain. In addition, probes must be mechanically scrapped every 8 to 24 hours to remove crystal deposits.

(ii) rapid and unexpected changes in feed water to the evaporators.

(iii) formation of the double salt, glauberite

(iv) dilution of the concentrate prior to discharge to the salty dams. This situation arises because of the length of the pipeline (4km) conveying concentrate to the dams. In order to prevent pipe blockages, the flow velocity in the pipe must be sufficient to maintain transport of the solids. This also limits the degree of water recovery that can be achieved.

The following recommendations and suggestions to improve the situation at Unit 66 were made:

(i) maintain the sodium sulphate concentration in the feed to a minimum to control the formation of the double salt. A major contributor to the sodium sulphate load of the feed is the use of sulphuric acid for pH adjustment. A electrochemical membrane process such as that illustrated in Figure 7 (Section 4), would neutralise the effluent without addition of further salts to the system. The neutralise effluent stream would be depleted in sodium allowing higher water recoveries to be obtained.

(ii) reduce the solids loading to the evaporators by recovering and recycling sodium chloride regeneration liquors from the zeolite filters, rather than have them report to the evaporators. A possible treatment and direct reuse system is shown in Figure 6.

The process recovery plant upgrades all process effluent streams including the stripped gas liquor, reaction water, the API liquor and cooling tower blowdown. These effluents are treated biologically and then settled, clarified and filtered through sand, carbon and ion-exchange columns before reuse as process cooling water.

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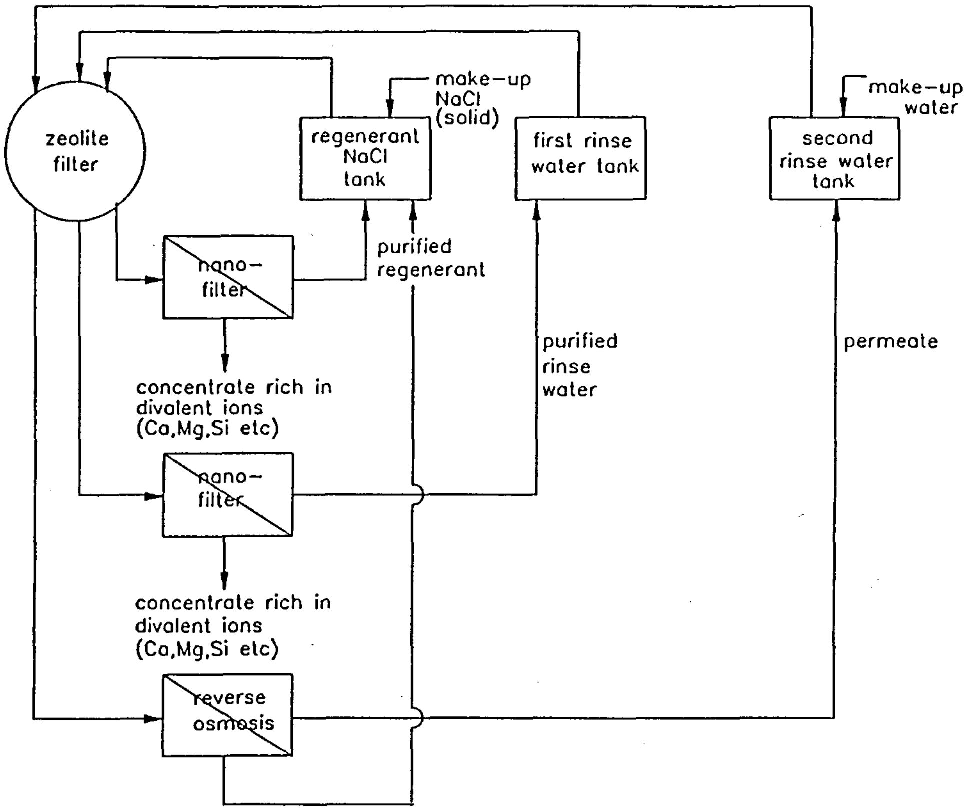

Figure 6 : Possible treatment system for direct reuse of sodium chloride regeneration liquors

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The works withdraw water from the Chelmsford Dam which is situated on the Ingagane River. The volume abstracted is only a small proportion (2,1 %) of the total process water circulating in the works (42 000 kℓ/h)

The intake water is flocculated using alum and the pH is adjusted with lime to provide water for domestic purposes. This water is processed further in one of three softeners which are regenerated using sodium chloride (750 kg/d). The softened water may be used directly as process water in the coke ovens and furnaces, or is used to make high quality boiler feed water in the demineralisation plant. Ion exchange regeneration liquors are concentrated in a seeded slurry evaporator prior to transport to solar evaporation dams by tanker. Condensate from the evaporator is recycled to the demineralisation plant. Evaporator scaling is controlled by the addition of a phosphate-acrylate scale prevention modifier. Ideally the concentration of this modifier should be 30 mg/ℓ, but may be as high as 300 mg/ℓ. Water flushes and acid washes are also used to control scaling of the evaporator tubes.

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(iv) storm water not contaminated with industrial chemicals can be discharged to the environment in terms of the General Standard. The storm water is often out of specification with respect to pH, fluoride, oil and suspended solids.

Recommendations were made to improve several areas of the plant. These are detailed in **Appendix 13** and include:

(i) improvement of existing oil removal measures and the addition of new ones

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(v) segregation of streams and/or removal of potential pollutants at source.

4 ACID-CONTAINING WASTEWATER AND MINE DRAINAGE WATER

A process has been developed to remove sulphuric acid from industrial effluents and waste waters. The process is illustrated schematically in Figure 7.

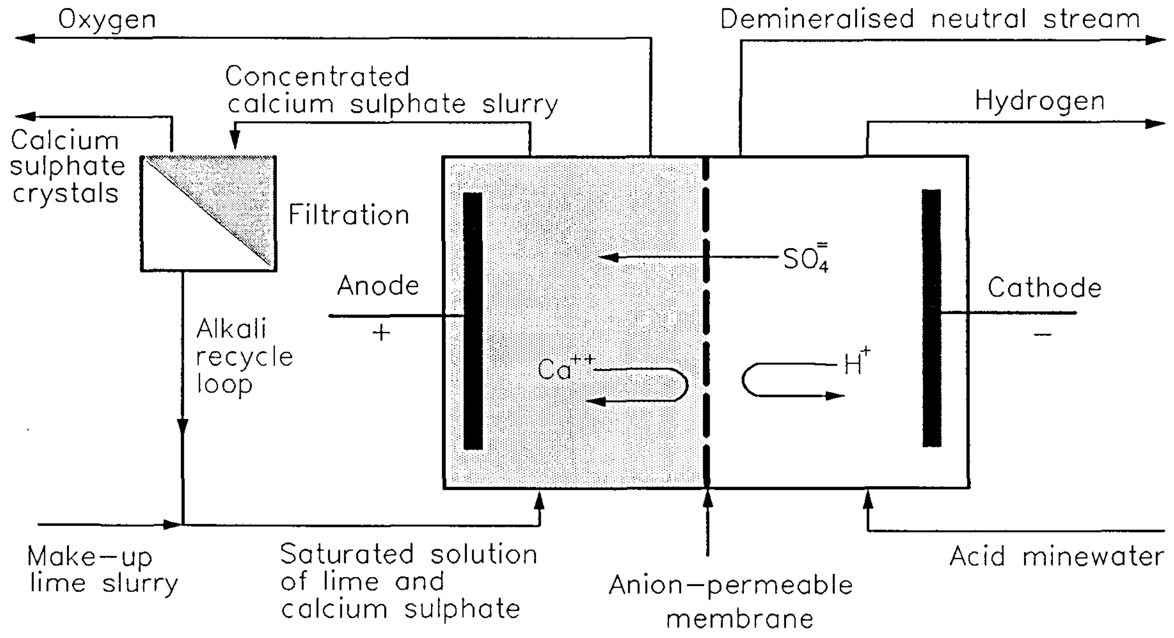

Figure 7 : Schematic diagram of electromembrane process for the removal of sulphuric acid from acid mine water and acid-containing effluents

The process and equipment are similar to those described for the denitrification of ammonium nitrate solutions (Section 3.1.2 and Appendix 7) except that :-

(i) sulphate ions migrate across the membrane instead of nitrate ions,

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A provisional South African patent has been assigned to the Water Research Commission for this process. **Appendix 14** contains the patent specifications and **Appendix 15** presents the results of laboratory trials on acidic ion exchange regenerant wastes and on acidic mine drainage waters. Applications for international patents have also been lodged.

5 NATIONAL BEVERAGE SERVICES

A proposal has been prepared (**Appendix 16**) for the pilot plant evaluation of an electrochemical system for the recovery of sodium hydroxide from bottle washing effluents. A schematic diagram of the bottle washing and proposed water recovery units is shown in Figure 8 and details are given in **Appendix 17**. The trials will be financed jointly the Water Research Commission and the National Beverage Services and will be conducted at the Peninsular Beverage Company Ltd, Parowvallei.

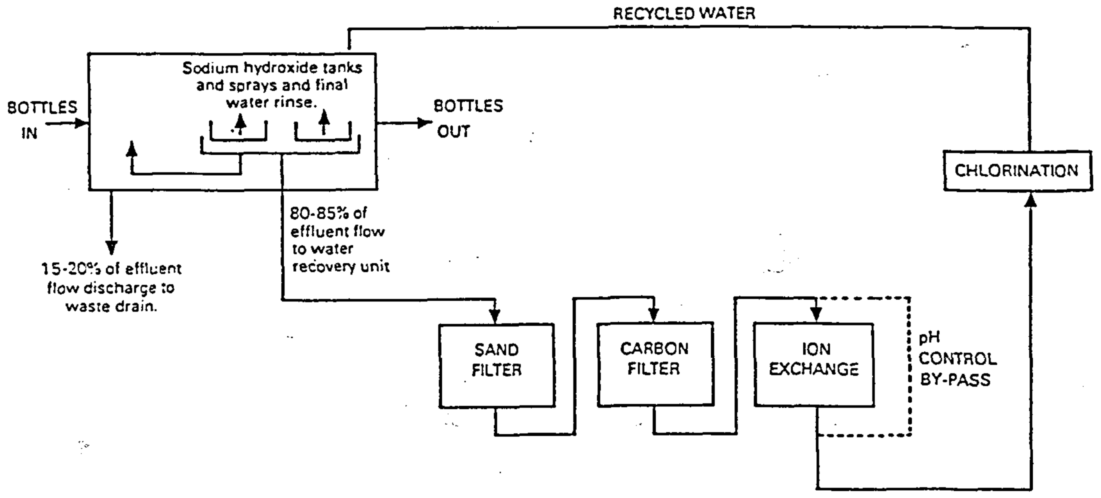

Figure 8 : Bottle washing and proposed water recovery units

6 RECOVERY OF SODIUM CHLORIDE FROM DYE EFFLUENT USING CHARGED ULTRAFILTRATION

A closed-loop recycle system using a charged ultrafiltration membrane to decolourise reactive dye effluents from a textile yarn and fabric dyeing process was developed by a research student. The concentration of sodium chloride in a reactive dyebath ranges from 50 to 100 g/ℓ.

The value of the electrolyte, sodium chloride, in the permeate ranges from R10 to R20 per kℓ. A pilot plant has been designed for installation at Ninian and Lester's Pinetown factory. This plant will handle the concentrated dye effluent from one machine. The plant should be operational by the end of 1989.

7 REALISATION OF PROJECT OBJECTIVES AND CONCLUSIONS

Point sources of brine production have been identified. Insight has been gained on the processes from which these brines originate and on the nature and characteristics of brine streams whose chemistry is particularly problematical in seeking a treatment method. At most sites visited various water and chemical saving measures were recommended and received favourably by the companies concerned. The extent to which these recommendations have been acted upon has been dependant on changing factory requirements and economic constraints.

Options for controlling brine disposal into the aqueous system have been identified. These options have formed the basis of the evolving Pollution Research Group philosophy on waste minimisation and pollution prevention. In this regard, the project has played an important development and capacity building role. The direct benefits of this are difficult to quantify at this stage but sufficient people have interacted in this project to ensure that there is a pool of young researchers with an awareness of the difficulties involved in the treatment and disposal of brines and that future new industrial developments should take effluent production and treatment options into account at the planning and development stage of a new venture.

Where the prevention of brine production proved unavoidable, new techniques have been developed for on-site disposal. Arising from the development of these techniques, two patent applications have been made.

One of the most satisfactory and important aspects of this project is the relationship built up between the Pollution Research Group and the companies visited. This relationship has extended from management levels to operational levels. The different attitudes and perceptions of the same problem has enabled the Pollution Research Group to gain realistic appreciation of many problems and so produce recommendations and suggestions that have practical as well as academic merit.

The treatment and disposal of brines and concentrates will continue to be a problem in South African industry. The magnitude of the problem is related to the scale of water use. Major water users are aware of their responsibility in protecting the scarce water resources of the country and have implemented or seek to implement brine-production reducing measures or responsible disposal measures. Industry has been made aware that new techniques are being developed which are tailored to South African conditions and that local expertise is available for such development. Through funding of such projects the status of the Water Research Commision is enhanced in the eyes of industry.

8 RECOMMENDATIONS

Recommendations arising from this project are :

(i) contacts made with industry should be maintained and strengthened so that future research can be market driven and thus of a practical importance.

(ii) commonly-occurring problems identified during the course of this project, for example, the general problem of unwanted precipitation, should form the basis for future research proposals.

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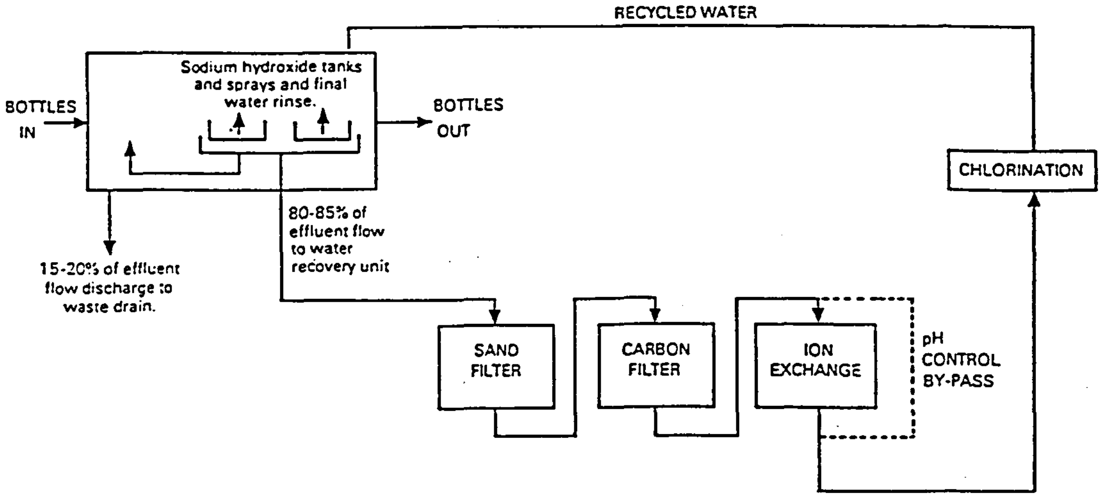

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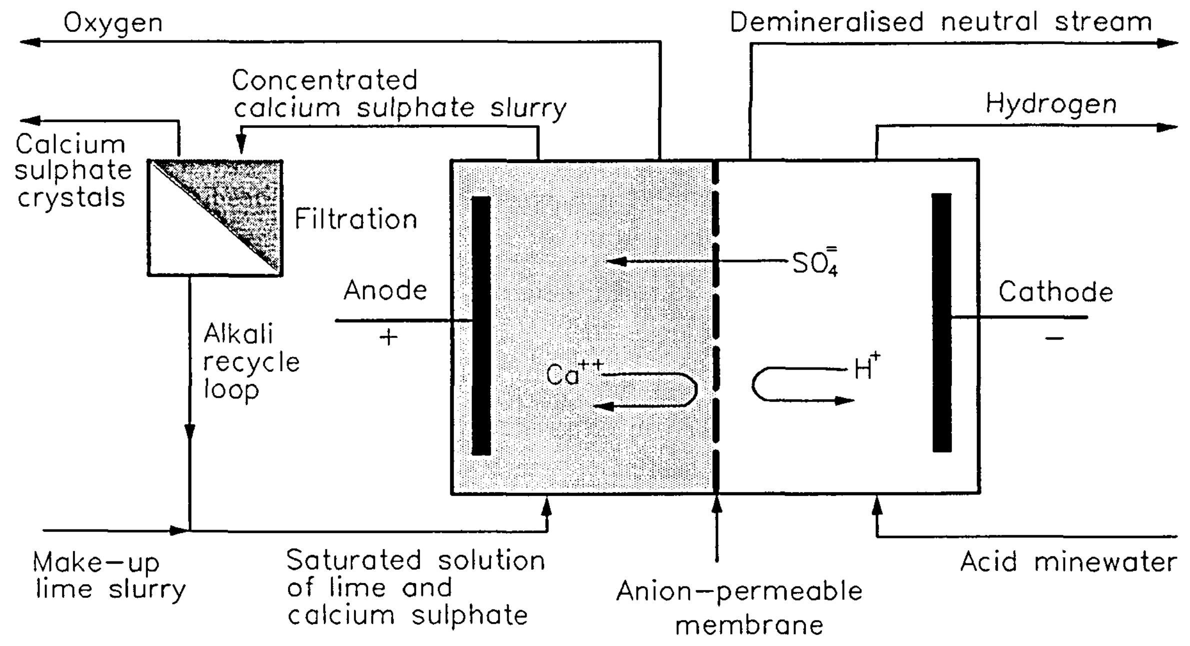

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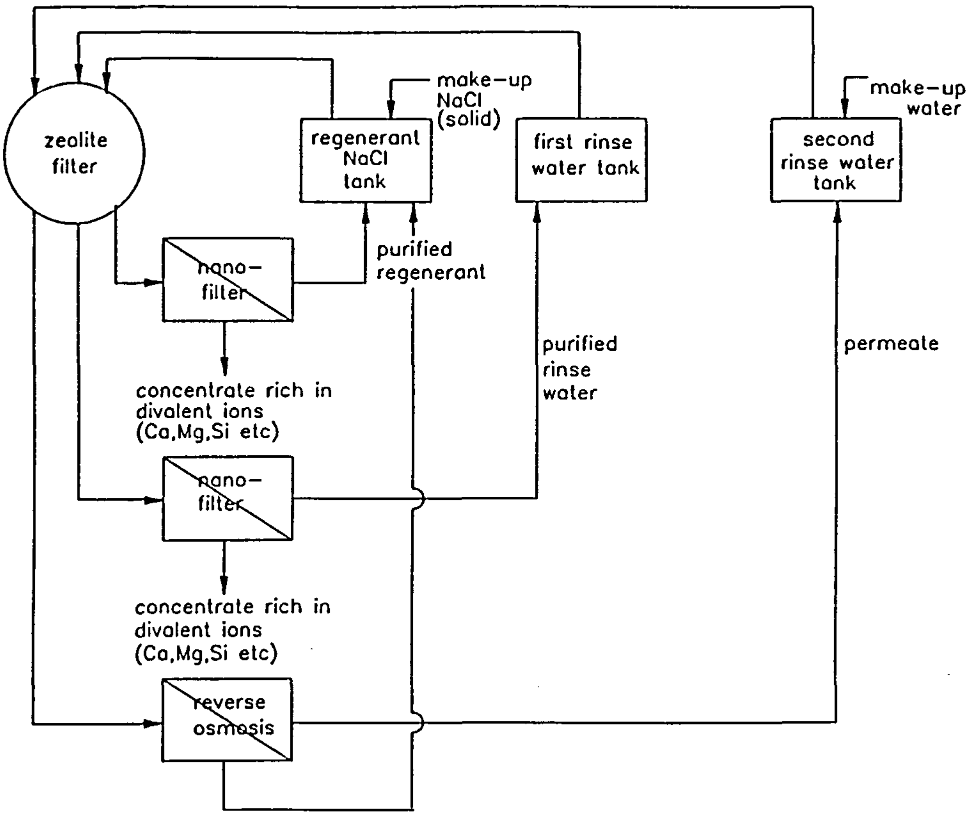

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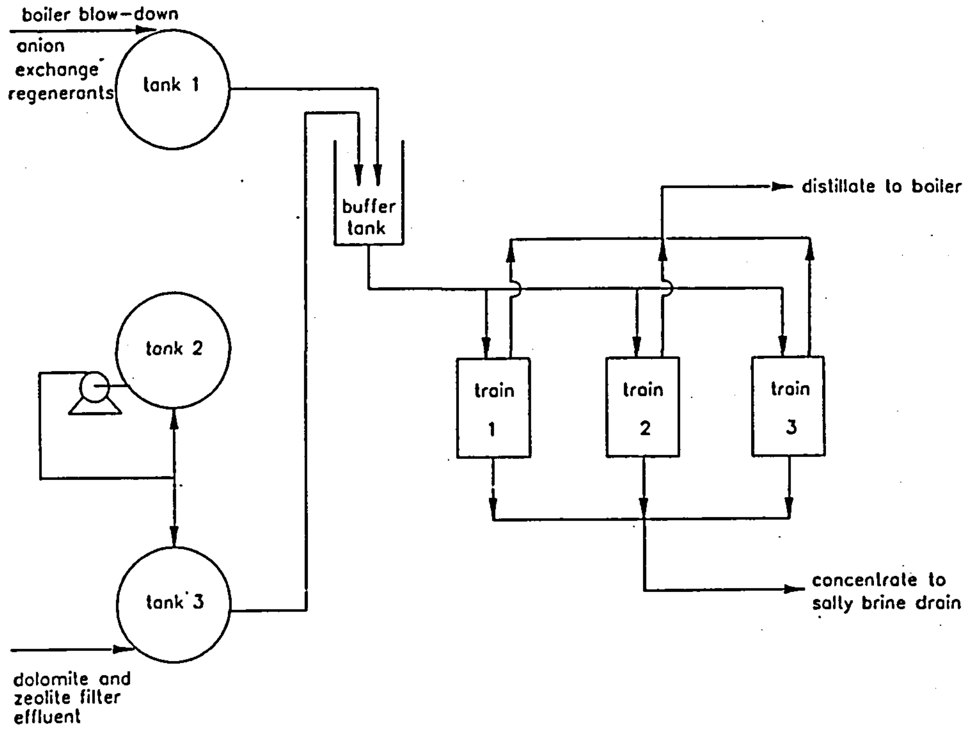

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Suggestions were made to improve the system and to solve the problem.

3.3 SASOL

A visit was made to SASOL 2 and SASOL 3 at Secunda (**Appendix 12**). The factories take in coal, water from the Grootdraai Dam, and air, from which a series of products including fuel, chemicals, fertilisers, explosives and wastes are manufactured. Generally Sasol 3 is a mirror image of Sasol 2 but there are common facilities such as the ash water dams.

The SASOL plants have a large number of organic and inorganic waste streams. Saline effluents arise from :

(i) ion exchange regeneration liquors from the utility circuit

(ii) ion exchange regeneration liquors from the process recovery plant (Unit 52),

(iii) cooling tower blowdown

(iv) boiler blowdown

(v) concentrate from the evaporation plant (Unit 66)

At the time of the visit problems were being experienced in Unit 66. Unit 66 comprised three falling film vapour compression evaporators which operate in a seeded slurry mode. A schematic diagram of the layout of Unit 66 is shown in Figure 5. The objectives of Unit 66 are to reduce the volume of brine stream requiring disposal and to produce a distillate of sufficient quality to be recycled as boiler feedwater. The concentrate from the evaporative process reports to the ash dams. Some is used for ash quenching and ash transport.

At the time of the visit only two trains were operational. The third train was being refurbished following corrosion of the titanium tubes.

Effluents reporting to Unit 66 enter the storage tanks. Tank 1 holds boiler blowdown and anion exchange regeneration liquors. The solution in Tank 1 consists mainly of sodium ions, together with hydroxyl, chloride, carbonate and sulphate ions. The pH of the solution is between 12 and 13.

below 1 300 mg/ℓ. Thus a significant impact on water and effluent pollution loading would be to decrease blowdown by operating at higher cycles of concentration. The quality of the cooling water is maintained by:

(i) sidestream clarification which treats 90 Mℓ/day of cooling water in one of three clarifiers

(ii) pH control using sulphuric acid to maintain the scaling index,

(iii) operating the concentration cycle as close to the maximum as possible; this is achieved by good control.

Increased cycles of concentration would be possible if:

(i) non-concrete or improved concrete materials of construction were used for the packing in the cooling towers, such that higher levels of sulphate could be attained.

(ii) a method of sulphate removal and control were available

Investigations by Eskom are constantly in progress to develop techniques for increasing the number of cooling cycles to maximise water reuse before cooling tower blow-down. Eskom is presently investigating the feasibility of implementing a sulphate removal process (**Appendix 11**) which has been developed at the University of Natal under contract to the Water Research Commission. The process involves precipitation of the sulphates as barium sulphate, using barium carbonate. The barium sulphate is reduced to barium sulphide using coal in a rotary kiln. The barium sulphide is then leached and converted to insoluble barium carbonate by contacting the solution with carbon dioxide. The barium carbonate is recycled at 95 % recovery and the sulphide is liberated as hydrogen sulphide gas. The conversion of this gas to sulphur and/or subsequently to sulphur tri- or dioxide gas is conventional technology.

It is envisaged that the sulphate rich wastes at Lethabo could be desulphonated and recycled. In addition, the acid mine waters from the surrounding mines could be treated at Lethabo. It is estimated that the total sulphate loading of the mine waters would be approximately 50 to 70 tons/day as sulphate. The sulphate loading of Lethabo wastes is a function of the raw water concentration and, assuming a sulphate level of 20 mg/ℓ, and a water consumption 150 Mℓ/day, is 3 ton/day as sulphate.

It is envisaged that the sulphur produced by the process from the combined mine waters and cooling tower blow-down streams, approximately 24 tons/day as sulphate, could be converted to sulphur trioxide for use in the Lethabo boiler stacks to increase the conductivity of the waste flue gas in the electrostatic precipitators. Each boiler requires approximately 6 tons/day of sulphur as sulphur trioxide.

3.2.2 Matimba Power Station

To reduce the use of water for power generation, Eskom is in the process of moving towards dry-cooling processes in future power stations where this is economically effluent, removing the need for further chemical addition to the effluent. Multi-effect evaporation was suggested as a suitable concentration stage, as factory personnel are familiar with this technology and steam is readily available.

Other Areas of Investigation

Tests were conducted (**Appendix 4**) in which selected effluent streams were evaporated. Precipitates appeared at intervals throughout the evaporation procedure and were identified. This enabled information to be obtained regarding the precipitation potential of effluent constituents, which, on concentration of the effluent, might interfere with the performance of treatment techniques such as reverse osmosis, evaporation, electrodialysis etc. In addition, the degree of concentration which could be achieved without the precipitation of insoluble constituents was determined.

It was recommended that minimum use be made of liquid carriers for washing down.

Contaminated condensates produced at the factory were dumped and discharged if a use for them cannot be found. In the case where these condensates contain ammonium nitrate, a concentration process involving electrodialysis and reverse osmosis has been proposed to enable reuse and recycling of these streams.

3.2 ESKOM

3.2.1 Lethabo Power Station

Site visits were made to the Lethabo Power Station and the various water and effluent reticulation systems were examined. Details of the water and effluent circuits operating at Lethabo are given in **Appendix 10**.

Lethabo Power Station is a zero-discharge plant and the technologies which Eskom have employed to enable water recovery from effluent include :-

(i) reverse osmosis for cooling water blow-down,

(ii) electrodialysis (in place of reverse osmosis at selected power stations),

(iii) evaporation for additional brine concentration,

(iv) sludge thickening to enable water recovery from clarifier sludges,

(v) sludge dewatering.

In addition to water recovery from effluent, Eskom have implemented various cascading systems in which product water from one process is cascaded for use as low quality water in another process. Finally, the ash system is designed to function as a salt sink for TDS disposal.

The largest consumer of water at the station is the cooling water circuit which is operated at approximately twenty cycles of concentration. The frequency of blowdown is determined by the sulphate level in the recycled stream, and is maintained

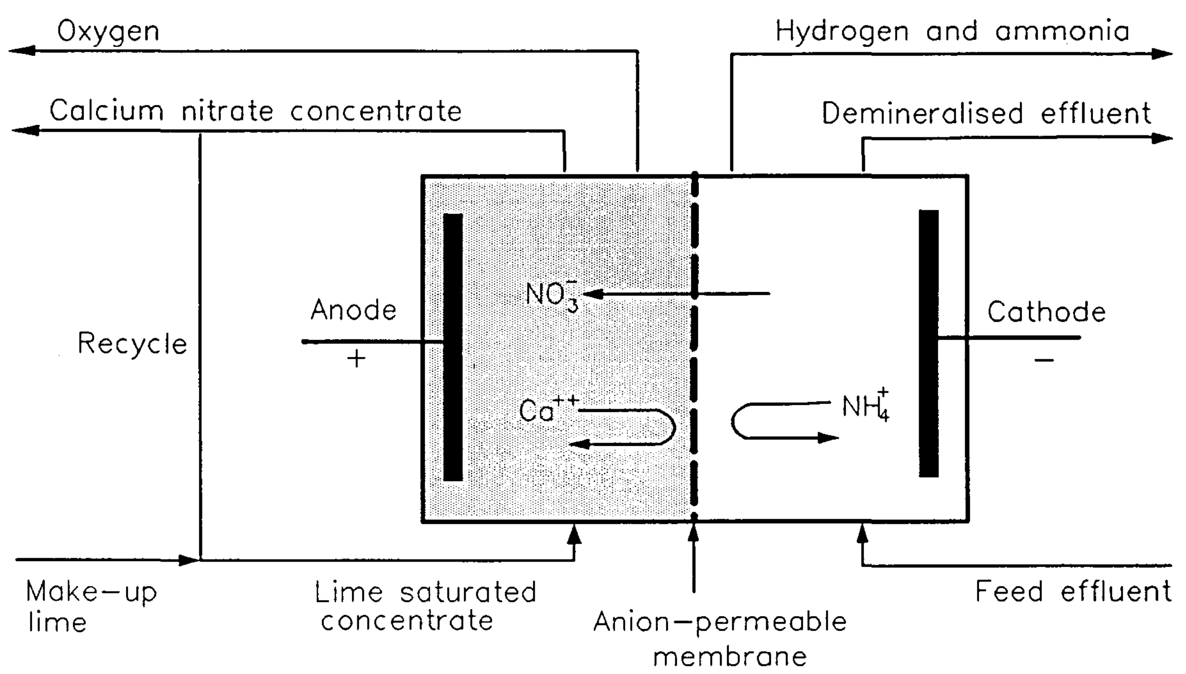


Figure 4 : Schematic diagram of electromembrane unit for denitrification

Appendix 8 summarise the results of initial laboratory investigations. Current efficiencies of 80 to 100 % could be achieved for the desalting of ammonium nitrate streams (5 to 10 g/ℓ).

Following the successful laboratory scale studies, a pilot plant scale study was undertaken at Modderfontein. This study was financed by AECI who felt that as well as providing a treatment for ammonium nitrate effluent, the process had economic benefits to them as a method for calcium nitrate production. Calcium nitrate is used by deciduous fruit producers.

The results from the pilot plant study (**Appendix 9**) indicated that removal efficiencies of 98 % could be achieved at a 96 % removal of ammonium nitrate. The specific power consumption varied from 1,5 to 3,5 kWh/kg ammonium nitrate removed (depending on the current density and feed concentration). The fouling and rupturing of the ion exchange membrane by calcium carbonate was a serious problem, which must be overcome if the process is to be viable.

Subsequent to the initiation of this investigation, the overall concept of the treatment of ammonium nitrate effluent was reviewed because the requirement for the manufacture of calcium nitrate fell away.

Suggestions were made to modify the electrochemical process to produce pure concentrated ammonium nitrate, which could be used in the manufacture of explosives. The proposed treatment process would consist of effluent cleaning stage followed by concentration. Initially testing showed that flocculation was a successful cleaning technique. Alternatively cross-flow microfiltration could be undertaken on the raw

(ii) the existing batch atmospheric kiering process be replaced by a more modern process which enables the more efficient use of chemicals,

(iii) the feasibility of reusing the spent caustic be investigated,

(iv) the reuse of initial rinse water for subsequent chemical batch make-up be investigated,

(v) overflow rinsing be placed with batch fill and drop rinsing,

(vi) the recovery of sodium hydroxide be investigated.

Denitrification

In order to overcome ultimate disposal problems associated with treating the nitrogenous effluent, a process was developed for the removal of ammonium nitrate from industrial wastes. A provisional patent for this process has been assigned to the Water Research Commission (**Appendix 7**).

The process involves an electrochemical membrane unit (Figure 4), in which the ammonium nitrate solution forms the catholyte and a saturated hydroxide solution forms the anolyte.

Under the influence of an electric potential :-

(i) the ammonium nitrate is split and the nitrate ions migrate through the anion selective membrane into the saturated calcium hydroxide solution where a soluble salt, 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 released 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 calcium 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 for recycle or discharge.

(ii) a stream of oxygen gas.

(iii) a depleted effluent suitable for reuse as relatively good quality water.

(iv) a concentrated calcium nitrate stream for resale as a solution or as a solid after evaporation and spray drying.

(i) an additional set of columns has been installed at the beginning of the existing demineralisation unit and spent regeneration liquors are used for the regeneration of this new set. After commissioning of this set, it is estimated that chemical consumption will be reduced by 50 %. The overall water recovery of the demineralisation unit will also be improved.

(ii) the reuse of selected rinse streams.

(iii) consideration of the implementation of shorter regeneration times.

(iv) consideration of the feasibility of using reverse osmosis as a pretreatment to ion-exchange. It has been estimated that this would result in a 98 % savings in regeneration chemicals and a 50 % reduction in selected dissolved salts in the effluent stream discharged to the Jukskei River.

(v) consideration of the feasibility of using multistage distillation prior to ion-exchange.

(vi) consideration of the feasibility of using reverse osmosis as a barrier between ion-exchange and steam generation, allowing for considerable reduction in the frequency of ion-exchange regeneration, while at the same time ensuring minimal reverse osmosis membrane fouling.

(vii) increasing the efficiency of the degasser, situated prior to the anion exchange columns, to minimise carbonate carry-over into the resin, thus delaying anion break-through.

(viii) consideration of the use of various process condensates in place of Rand Water Board water as the feed to the demineralisation unit.

(ix) consideration of the need for cross-flow microfiltration as a pretreatment to prevent sludge build-up in the demineralisation unit.

(x) consideration of the removal of precipitated salts from the waste regeneration liquors prior to dilution and resolution

(xi) consideration of the separation of the strong sulphuric acid washes, followed by liming and filtration, to remove calcium sulphate, to yield an effluent with a TDS loading below that of the strong wash.

(xii) consideration of the reuse of caustic regenerant waste as a process chemical in the cotton kiering section of the fusing factory.

(xiii) consideration of the purification and recovery of sodium hydroxide from caustic regenerant waste by electrochemical means (**Appendix 6**).

Kiering

In order to minimise the effluent loading and the volume of caustic kiering effluents it was recommended that :-

(i) commission kiering be investigated,

TABLE 1 : Annual average chemical loading in weak effluent;(a) from the central factory (b) final effluent discharge

	Discharge from central factory		Final weak effluent discharge	
Determinand	Winter 1986	Summer 1986-1987	Winter 1986	Summer 1986-1987
TDS	1 445	2 238	681	1 052
NH_4	46	64	26	53
NO_3	69	113	29	60
Na	197	293	83	156
Cl	163	196	37	60
SO_4	530	734	291	411

Strong effluent, which is nitrogenous in character, is produced at a rate of 20 kℓ/h, is sprayed onto 2 500 hectares of leased or owned land. The main contributor to the volume of strong effluent produced is the demineralised water from No 11 nitric acid plant (10 kℓ/h). Various ammomium nitrate discharges make up the remaining volume of strong effluent.

A series of investigations, were carried out in conjunction with the Environmental Services Department at AECI Chemicals and Explosives Ltd. (**Appendices 2 to 5**). The purpose of these investigations was to examine areas of concern. Three effluents were identified which make significant contributions to the pollution load from the factory. These are :

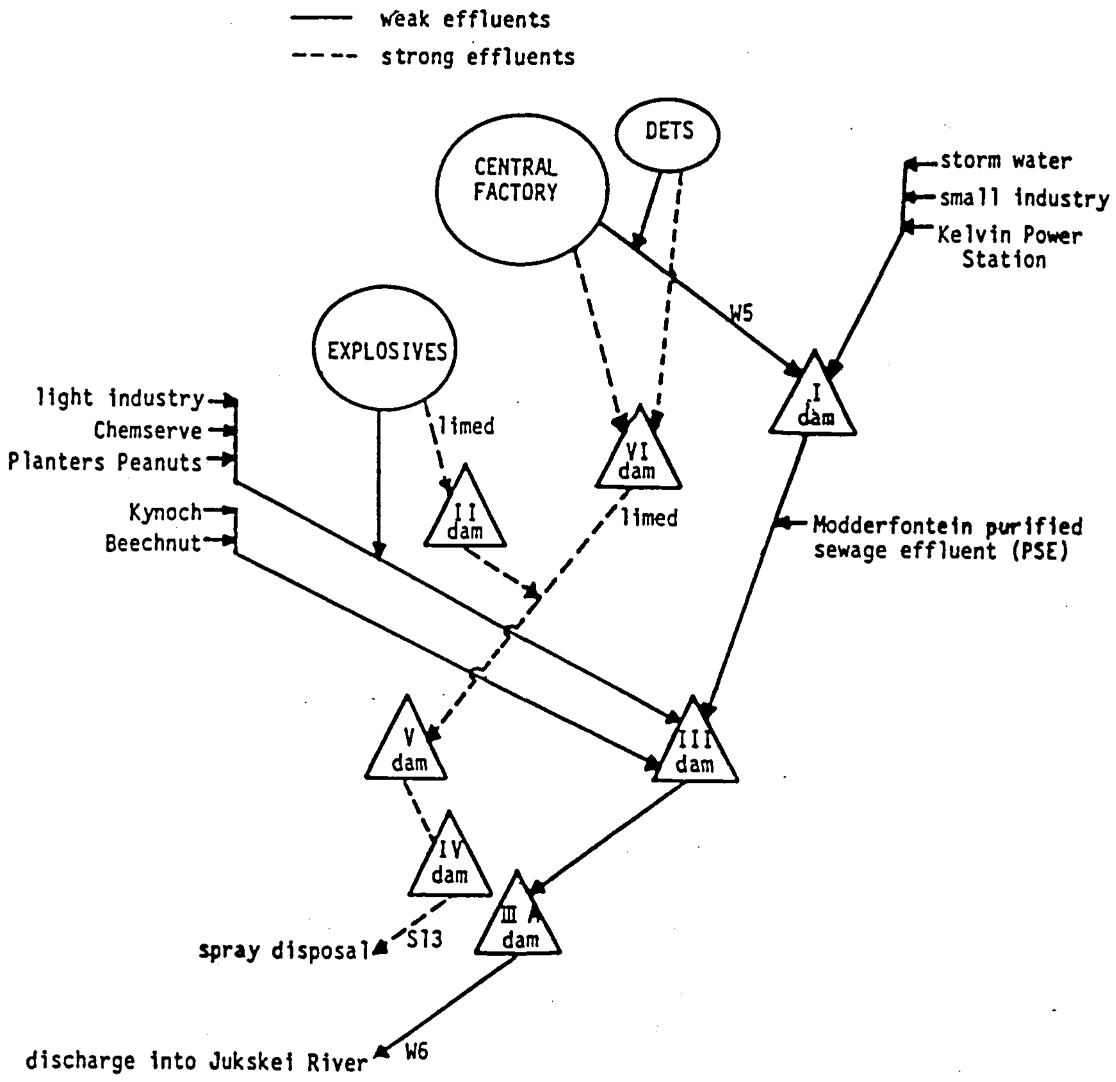
(i) ion-exchange regenerant wastes. The combined daily chemical consumption in the two ion exchange systems (No 4 Ammomium plant and No 11 Nitric acid plant) is estimated to be 5 to 6 tons of 98 % sulphuric acid and 3 to 4 tons of 100 sodium hydroxide. The contribution of the regeneration liquors to the sodium and sulphate ion concentrations in both the final weak and strong effluent streams is significantly high.

(ii) keiring effluents. The spent keir liquor contributes an estimated 15 to 20 % of the sodium ion concentration of the strong effluent.

(iii) ammomium nitrate effluents from explosives and fertiliser production

Ion-exchange regenerant wastes

Measures taken at the factory to minimise chemical consumption during resin regeneration and to reduce effluent loadings include the following :-



Notes : (i) Dam VI is limed.

(ii) Dam IIIA is a bypass dam

(iii) Some of the Modderfontein PSE is used in the central factory as raw water and there is a 30% recycle of weak effluent from Dam III back to the factory.

Figure 3 : The effluent system at AECI, Modderfontein

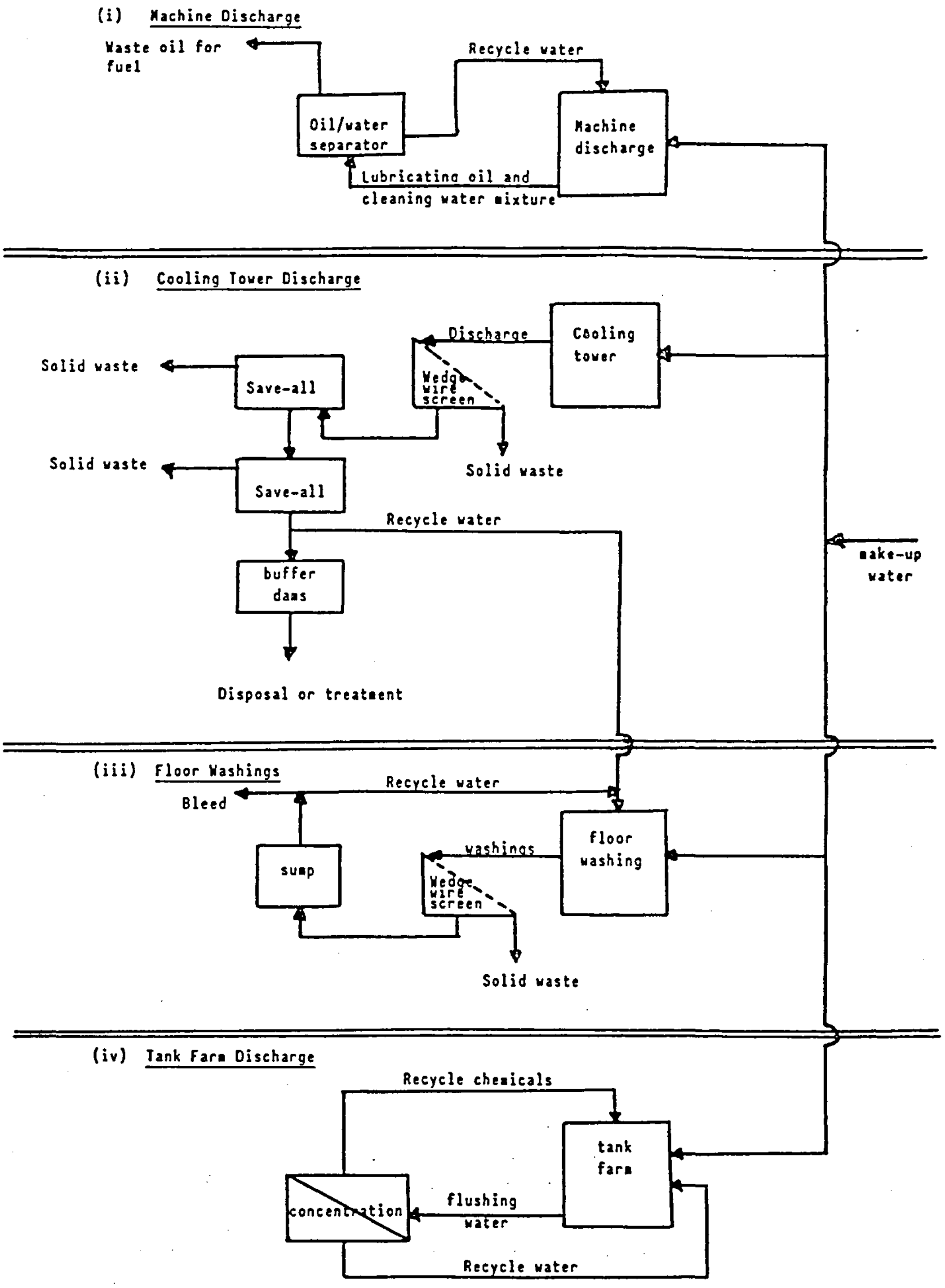


Figure 2 : Schematic diagram of proposed water and chemical reticulation

These wastewater streams are conveyed to two lined buffering dams. Save-alls, situated outside each production house and prior to dam entry, remove solids from the wastewater streams. From the dams the effluent is pumped to a disposal site for discharge onto the ground at a rate of 7 kℓ/h.

Recommendations were made to enabled the rescheduling and recycling of various process streams and the minimisation of final effluent contamination by oils, suspended solids and dissolved salts, particularly ammonium nitrate. A schematic diagram of the proposed water and chemical reticulation scheme is shown in Figure 2.

Implementation of the recommendations made would:

(i) significantly reduce product, water and chemical usage.

(ii) enable effective and efficient monitoring of the water and chemical reticulation systems within the plant.

(iii) enable the recycle and reuse of large proportions of water, raw chemicals and oils.

(iv) enable the production of a small volume, high concentration effluent containing minimum suspended matter which could be treated, concentrated or discharged.

3.1.2 Modderfontein

The AECI plant at Modderfontein manufactures both chemicals and a wide range of nitroglycerine-based and ammonium nitrate-based explosives, together with accessories such as detonators and fuses.

The factory consumes approximately 30Mℓ/day of water supplied by the Rand Water Board. In addition, 1,2 Mℓ/day of sewage effluent is provided by the Modderfontein and Johannesburg sewage works. A recycle system within the factory enables a further reuse of approximately 8,4 Mℓ/day of weak effluent.

All the effluents produced at the factory are segregated into two discharge streams, known as the weak effluent and the strong effluent. The effluent system at the factory is depicted in Figure 3.

The weak effluent is discharged under permit into the Jukskei River at a rate of 1 000 kℓ/h. Approximately 35 to 54 tons of TDS are discharged daily into the Jukskei river in the form of weak effluent. The chemical loads contained in weak effluent discharge for the winter of 1986 and the summer of 1986 and 1987 are given in Table 1. Up to 60 % of the volume of weak effluent comprises water from the power station. Ion exchange regeneration chemicals from No 4 Ammonia plant make up 25 % of the volume of weak effluent, but have a TDS loading some 5 to 10 times higher than the final weak effluent.

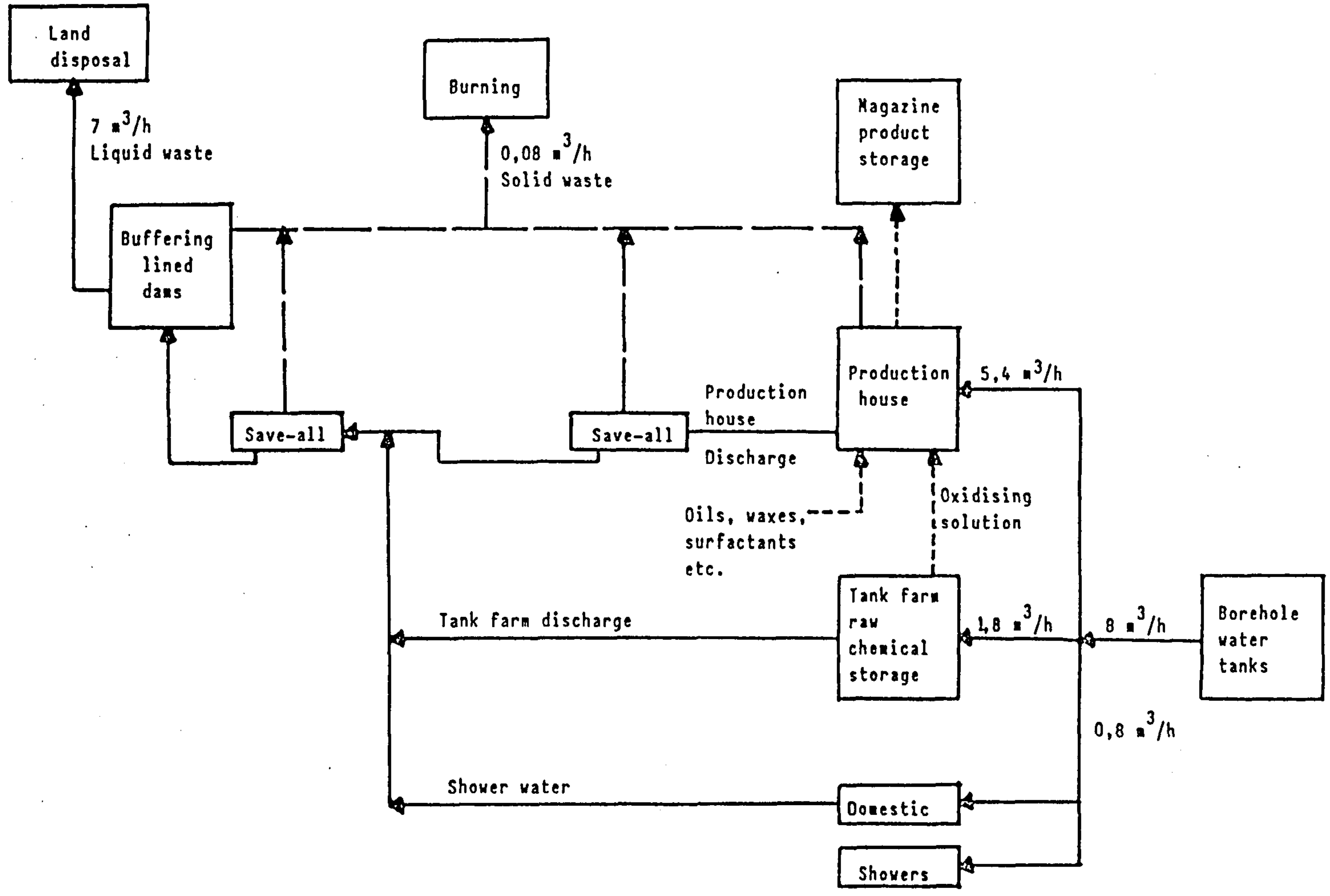


Figure 1 : Schematic diagram of Zomerveld Plant

(vii) leachates from ash disposal sites,

(viii) concentrates from industrial manufacturing processes.

Site visits were made to a number of organisations to gain first hand experience and appreciation of the processes leading to the generation of particular brines and concentrates. These are described and investigations summarised. Where results are of a confidential nature, this has been noted.

3 SITE VISITS

3.1 AECI

The AECI plants at Zommerveld and Modderfontein manufacture mining explosives. An effluent is produced which contains approximately 3 g/ℓ of ammonium nitrate, the discharge of which is problematical because of the high TDS (8,5 g/ℓ) and nitrogen content.

3.1.1 Zommerveld

A comprehensive water and effluent survey was conducted at the Zommerveld complex (**Appendix 1**). Intake water to the site comes from a borehole and consumption was estimated at 8 kℓ/h. The various production and water consuming processes, together with effluents arising and existing treatment facilities are shown in Figure 1.

Water is consumed :-

(i) for domestic uses, for example showers, toilets, drinking

(ii) at the tank farm where all spillages during transfers from tankers and tanks are washed away with water and where water is used to flush all hoses (daily) and pipes (after each transfer) conveying the explosive base, ANS, and the oxidising solution, to prevent solidification of the chemicals.

(iii) in the production houses where water is used to wash the floor, to clean the extruding, cutting and clipping machines and to cool the explosive cartridges

Each area of water use produces effluent with different characteristics. The effluents arising from the tank farm are generally oil free and consist of a fairly concentrated stream of ammomium nitrate which may contain some sodium nitrate or other process chemicals. A single combined effluent stream is discharged form the production houses. This stream is contaminated by dissolved ammonium and sodium nitrate, suspended solids, mainly waste product and by detergents and spindle oil. The waste domestic water is insignificant in volume and has minimum contamination.

This final report of the project, summarises work undertaken on selected brine and concentrate streams. A quantitative definition of a brine has been avoided, and brine has been defined as any stream of high total dissolved solids concentration which cannot be treated adequately by conventional means.

It is the policy of the Pollution Research Group to prevent or minimise pollution by in-house modifications to existing processes. Where pollution problems cannot be totally engineered out of a process, only then should an effluent treatment approach be adopted. Where this is considered necessary, the aim should be to recover and recycle water, process chemicals and heat energy within the production process. The segregation of effluent streams is central to this approach as it allows high pollution load streams to be preferentially treated without dilution by less contaminated streams. The site visits detailed in this report and the recommendations given are based within the framework of this philosophy.

Arising from this project, 2 papers and 6 conference proceedings have been published. Two patent applications have been made. They are entitled :-

(i) The Removal of Ammonium Salts from an Aqueous Medium Containing the Salt. S.A. Application No. 88/8898.

(ii) The Removal of Sulphuric Acid from an Aqueous Medium Containing the Acid. S.A. Application No. 88/5487.

Application for international patents have also been lodged.

The results obtained from Water Research Commission Project No. 203 (*The Chemical Removal of Sulphates)* were evaluated by a firm of industrial contractors and a firm of consulting engineers. Assistance was provided to these investigations under this project. The relevant reports have been submitted directly to the Water Research Commission.

2 IDENTIFICATION OF BRINE SOURCES

The Pollution Research Group contacted various organisations including Sentrachem, AECI, SASOL, ISCOR, the Chamber of Mines, ESKOM, the Department of Water Affairs and the Department of Agriculture and Water Supply. With their aid, a number of point sources of brine have been identified. The include :-

(i) regeneration liquors from anion, cation and mixed bed ion-exchange reactors,

(ii) concentrates from electrodialysis units,

(iii) concentrates from reverse osmosis units,

(iv) cooling tower blow-down streams,

(v) concentrates from evaporator units,

(vi) saline mine concentrates,

1 INTRODUCTION

Two major problems threatening water users in South Africa are :-

(i) the availability of adequate quantities of water, and

(ii) the deterioration of the quality of water resources due to increasing concentration of total dissolved solids (TDS).

In attempting to deal with these two problems of quantity and quality, increasing use has been made of water conservation and recycling technology. These measures have however, resulted in an increased production of inorganic brines and concentrates. Unless these are adequately treated, they will eventually enter the aquatic environment. The options available for controlling brine disposal into the aqueous environment include :-

(i) engineering out the source of brine,

(ii) converting the brine into a saleable product,

(iii) indirect or diffuse discharge to the environment,

(iv) deactivation or conversion to an inert substance,

(v) immobilisation or passive storage,

(vi) disposal into designated brine sink impoundments or discharge by pipeline into the sea.

The above options have been listed in terms of increasing environmental impact.

Where brine production cannot be prevented it would be advantageous to develop techniques for the on-site disposal of brines. In 1987 the Water Research Commission contracted with the Pollution Research Group, University of Natal (Project No. 201) to investigate the treatment of inorganic brines and concentrates by physical, chemical, physio-chemical and electrical techniques.

A number of point sources of brine were identified and some specific problematic streams were characterised.

Priority sources of brine include :-

(i) effluent streams generated at some AECI plants,

(ii) acid mine drainage,

(iii) cooling tower blow-down water,

(iv) saline wastes generated at SASOL 2 and 3.

(v) bottle washing effluents.

APPENDIX 10 : Visit to Lethabo Power Station, 10th March 1988 by A.E. Simpson.

APPENDIX 11 : The removal of dissolved salts from recirculating waters in the Vaal River drainage system by C.A.Buckley and R.E. Edwards.

APPENDIX 12 Visit to SASOL 2 and 3, Secunda, April 1988 by A.E. Simpson

APPENDIX 13 Viait to ISCOR Newcastle, 2nd August 1988 by A.E. Simpson

APPENDIX 14 The removal of sulphuric acid from an aqueous medium containing the acid. Provisional Patent Specification

APPENDIX 15 The removal of sulphuric acid from natural and industrial waste waters by A.E. Simpson and C.A. Buckley. *Desalination* 70 (1988) pp 431-442

APPENDIX 16 Memorandum of agreement in connection with an investigation into the recovery and reuse of sodium hydroxide and water from bottle wash effluents

APPENDIX 17 Caustic recovery from bottling plant effluent by A.E. Simpson, F.G. Neytzell-de Wilde and C.A. Buckley. *Water SA*, Vol 14 No. 2 1988, pp99-104

Copies of Appendices to this Final Report may be obtained from the Water Research Commission, P.O.Box 824, Pretoria, 0001, Republic of South Africa.

LIST OF APPENDICES

APPENDIX 1 :	Explosive and Chemical production by AECI at Modderfontein and Zomerveld : Summary of a visit on 8th July 1987 by Alison E. Simpson
APPENDIX 2 :	Visit to the AECI Chemicals and Explosives Factory at Modderfontein, 27th and 28th July 1987 by Pollution Research Group.
APPENDIX 3 :	Visit to the AECI Chemicals and Explosives Factory at Modderfontein, 4th August 1987. A review of efforts to limit effluent arisings at the No.4 Ammonia Plant and in the Nitrate Department by Alison E. Simpson
APPENDIX 4 :	AECI Chemicals and Explosives Ltd., Modderfontein. Initial laboratory investigations into the treatment of effluent arising in the factory by Alison E. Simpson.
APPENDIX 5 :	Report on visit to AECI, Modderfontein, 30th November 1987 by Alison Simpson
APPENDIX 6 :	The recovery and reuse of sodium hydroxide from industrial effluents by A.E.Simpson and C.A. Buckley. A paper presented at the American Chemical Society, Division of Industrial and Engineering Chemistry meeting at the third Chemical Congress of the North American Continent, June 5-11th, 1988, Toronto, Canada.
APPENDIX 7 :	The Removal of Ammonium Salts from an Aqueous Medium Containing the Salt; Provisional Patent Specifiactions. November 1987.
APPENDIX 8 :	Ammonium nitrate removal by electrolysis : Preliminary laboratory results by A.E. Simpson.
APPENDIX 9 :	An evaluation of the technical feasibility of removing ammonium nitrate from aqueous effluents with electrolysis by W.J. Voortman.

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ACKNOWLEDGEMENTS

The work in this report was funded by the Water Research Commission, for a project entitled: *The Treatment of Inorganic Brines and Concentrates*

The financing of the project by the Water Research Commission and the contribution by the members of the Steering Committee are gratefully acknowledged.

During the course of the project, many people at the various plants and factories visited, freely gave of their time and expertise. Thanks are extended to them.

One of the most satisfactory and important aspects of this project is the relationship built up between the Pollution Research Group and the companies visited. This relationship has extended from management levels to operational levels. The different attitudes and perceptions of the same problem has enabled the Pollution Research Group to gain realistic appreciation of many problems and so produce recommendations and suggestions that have practical as well as academic merit.

Arising from this project, 2 papers and 6 conference proceedings have been published.

6 CONCLUSIONS

The treatment and disposal of brines and concentrates will continue to be a problem in South African industry. The magnitude of the problem is related to the scale of water use. Major water users are aware of their responsibility in protecting the scarce water resources of the country and have implemented or seek to implement brine-production reducing measures or responsible disposal measures. Industry has been made aware that new techniques are being developed which are tailored to South African conditions and that local expertise is available for such development. Through funding of such projects the status of the Water Research Commision is enhanced in the eyes of industry.

7 RECOMMENDATIONS

Recommendations arising from this project are :

(i) contacts made with industry should be maintained and strengthened so that future research can be market driven and thus of a practical importance.

(ii) commonly-occurring problems identified during the course of this project, for example, the general problem of unwanted precipitation, should form the basis for future research proposals.

(iii) clean technologies, waste minimisation and pollution prevention should be the first consideration in solving industrial effluent problems.

hydroxide from bottle washing effluents. The trials will be financed jointly the Water Research Commission and the National Beverage Services and will be conducted at the Peninsular Beverage Company Ltd, Parowvallei.

4.8 TEXTILE DYE EFFLUENT

A closed-loop recycle system using a charged ultrafiltration membrane to decolourise reactive dye effluents from a textile yarn and fabric dyeing process was developed by a research student. The concentration of sodium chloride in a reactive dyebath ranges from 50 to 100 g/ℓ.

The value of the electrolyte, sodium chloride, in the permeate ranges from R10 to R20 per kℓ. A pilot plant has been designed for installation at Ninian and Lester's Pinetown factory. This plant will handle the concentrated dye effluent from one machine. The plant should be operational by the end of 1989.

5 REALISATION OF PROJECT OBJECTIVES

Point sources of brine production have been identified. Insight has been gained on the processes from which these brines originate and on the nature and characteristics of brine streams whose chemistry is particularly problematical in seeking a treatment method. At most sites visited various water and chemical saving measures were recommended and received favourably by the companies concerned. The extent to which these recommendations have been acted upon has been dependant on changing factory requirements and economic constraints.

Options for controlling brine disposal into the aqueous system have been identified. These options have formed the basis of the evolving Pollution Research Group philosophy on waste minimisation and pollution prevention. In this regard, the project has played an important development and capacity building role. The direct benefits of this are difficult to quantify at this stage but sufficient people have interacted in this project to ensure that there is a pool of young researchers with an awareness of the difficulties involved in the treatment and disposal of brines and that future new industrial developments should take effluent production and treatment options into account at the planning and development stage of a new venture.

Where the prevention of brine production proved unavoidable, new techniques have been developed for on-site disposal. Arising from the development of these techniques, two patent applications have been made. They are entitled :-

(i) The Removal of Ammonium Salts from an Aqueous Medium Containing the Salt. S.A. Application No. 88/8898.

(ii) The Removal of Sulphuric Acid from an Aqueous Medium Containing the Acid. S.A. Application No. 88/5487.

Application for international patents have also been lodged.

(i) recoverable water,
(ii) irrigation effluent,
(iii) evaporation effluent,
(iv) storm water.

An evaporator has been installed to concentrate the evaporation effluent which is of such poor quality that neither discharge nor irrigation is allowed.

Oil is a general contaminant around the plant and efforts should be made to improve the performance of the oil removal systems that are in place and to install additional ones.

Recommendations were made to improve the performance of the demineralisation plant, and to reduce the load of regeneration chemicals used. Suggestions were given as to how chemicals could be extracted from certain waste streams, purified and reused.

4.6 Acid Mine Water and Sulphuric Acid-containing Wastewater

Sulphuric acid, because of its relative low cost and availibility, is used widely in industry where acidic or anhydrous conditions are required. In addition , the weathering of sulphide bearing rocks and the extraction and beneficiation of sulphide containing ores, leads to the production of acid mine water. The treatment of these wastes by conventional technologies such as, lime softening, electrodialysis and seeded slurry evaporation is limited by the precipitation of calcium sulphate.

A process was developed to neutralise sulphuric acid and remove sulphates from an effluent stream, without the addition of further chemicals to the system.

The electromembrane process is similar to that developed for the denitrification of ammonium nitrate solutions except that :-

(i) sulphate ions migrate across the membrane instead of nitrate ions,
(ii) only hydrogen gas is evolved from the cathode,
(iii) calcium sulphate is formed in the anolyte, precipitates, and is separated by filtration.

Laboratory trials were undertaken on acidic ion exchange regenerant wastes and on acidic mine drainage waters. A provisional South African patent has been assigned to the Water Research Commission for this process. Applications for international patents have also been lodged.

4.7 NATIONAL BEVERAGE SERVICES

Following a meeting with National Beverages Services, a proposal has been prepared for the pilot plant evaluation of an electrochemical system for the recovery of sodium

It was envisaged that the sulphur produced by the process from the combined mine waters and cooling tower blow-down streams, approximately 24 tons/day as sulphate, could be converted to sulphur trioxide for use in the Lethabo boiler stacks to increase the conductivity of the waste flue gas in the electrostatic precipitators. Each boiler requires approximately 6 tons/day of sulphur as sulphur trioxide.

The results obtained from Water Research Commission Project No. 203 (*The Chemical Removal of Sulphates)* were evaluated by a firm of industrial contractors and a firm of consulting engineers. Assistance was provided to these investigations under this project. The relevant reports have been submitted directly to the Water Research Commission.

At Matimba Power station, problems were being experienced with iron contamination of the boiler feed water and its effect on the ion exchange resins. Suggestions were made to improve the system and to solve the problem.

4.4 SASOL

A visit was made to the SASOL 2 and SASOL 3 plants at Secunda. The Sasol plants have a large number of organic and inorganic wastes, as well as the conventional boiler and cooling water blow-down streams.

Saline waters are segregated and handled separately from other wastes. The three major sources of inorganic wastes are :-

(i) regenerant streams from boiler feed water pretreatment,

(ii) boiler blow-down,

(iii) process water ion-exchange regenerants.

The saline effluents are treated in one of three vapour compression evaporators operating in a seeded slurry mode. The condensate is reused in processing. Some of the concentrate is used for ash quenching and ash transport; the remainder is discharged to solar evaporation dams. Some problems, mainly operational, are being experienced.

The cooling tower blow-down and organic wastes are treated biologically and then settled, clarified and filtered through sand, carbon and ion-exchange columns before reuse.

Recommendations were made regarding the operation of the treatment units and the water and effluent handling system in general.

4.5 ISCOR

A visit was made to Iscor Iron and Steel Works at Newcastle. The works produces a range of iron and steel alloys and by-products such as ammonium sulphate, sulphuric acid, tar and oil.

Waste liquid effluents from the plant are divided into four stream :-

being concentrated to dryness. Results indicated that process could be tailored to produce a concentrate stream of either calcium nitrate or ammonium nitrate, both of which have resale or reuse potential.

4.3 ESKOM

Site visits were made to Lethabo and Matimba Power Stations. Lethabo is a wet-cooled power station wheras Matimba is a dry-cooled station. Each type of ststion presents different problems. For their wet-cooled stations, Eskom have adopted a zero liquid discharge philosophy and have implemented a number of water recovery measures at their newer power stations. These include either reverse osmosis or electrodialysis reversal for the treatment of cooling water blow-down, further brine concentration and condensate recovery in evaporators, sludge thickening and sludge dewatering to recover water from clarifier underflow. The brines produced by these various measures are disposed of in the ash system which acts as a salt sink, thus no brine concentrate leaves the power station.

At Lethabo Power station, the various water and effluent reticulation systems were examined and insight was gained into the water management strategies employed on a power station. As a major water user Eskom have identified the increasing salinity of Vaal River water as an issue of concern and investigations by ESKOM are constantly in progress to develop techniques for reducing the salt load of their various water circuits. A sulphate removal process, developed at the University of Natal under contract to the Water Research Commission, (WRC Project No. 203, *The Chemical Removal of Sulphates*) was of particular interest to them. The process which could be based at a power station such as Lethabo, could be operated on a regional scale. The process involves precipitation of the sulphates as barium sulphate, using barium carbonate. The barium sulphate is reduced to barium sulphide using coal in a rotary kiln. The barium sulphide is then leached and converted to insoluble barium carbonate by contacting the solution with carbon dioxide. The barium carbonate is recycled at 95 % recovery and the sulphide is liberated as hydrogen sulphide gas. The conversion of this gas to sulphur and/or subsequently to sulphur tri- or dioxide gas is conventional technology.

It was envisaged that the sulphate rich wastes at Lethabo could be desulphonated and recycled. In addition, the acid mine waters from the surrounding mines could be treated at Lethabo. It was estimated that the total sulphate loading of the mine waters would be approximately 50 to 70 tons/day as sulphate. The sulphate loading of Lethabo wastes is a function of the raw water concentration and, assuming a sulphate level of 20 mg/ℓ, and a water consumption 150 Mℓ/day, was estimated to be 3 ton/day as sulphate.

(vii) leachates from ash disposal sites,
(viii) concentrates from industrial manufacturing processes.

Priority sources of brine include :-

(i) effluent streams generated at some AECI plants,
(ii) acid mine drainage,
(iii) cooling tower blow-down water,in particular that arising from power station cooling towers,
(iv) saline wastes generated at SASOL 2 and 3.
(v) bottle washing effluents.

Site visits were made to a number of organisations to gain first hand experience and appreciation of the processes leading to the generation of particular brines and concentrates. These are described and investigations summarised. Where results are of a confidential nature, this has been noted.

4.2 AECI

The AECI plants at Zommerveld and Modderfontein manufacture mining explosives. An effluent is produced which contains approximately 3 g/ℓ of ammonium nitrate, the discharge of which is problematical because of the high TDS (8,5 g/ℓ) and nitrogen content.

At Zomerveld, a comprehensive water and effluent survey was conducted, and recommendations were made to enable the rescheduling and recycling of various process streams. Suggestiions were given to minimise contamination of the final effluent by oils, suspended solids and dissolved salts, particularly ammonium nitrate.

At Modderfontein, a series of investigations were carried out in conjunction with the Environmental Services Department at AECI Chemicals and Explosives Ltd. Particular attention was paid to ion-exchange regeneration wastes as these streams contain heavy salt loads. Opportunities for the purification and recovery of sodium hydroxide from caustic regeneration waste by electrochemical means were noted. In addition the precipitation potential of selected effluent streams was examined. This information was required to ascetrain what treatment options might be appropiate and to determine to what degree streams could be concentrated before precipitation would commence.

The treatment and disposal of nitrogenous effluents was examined. A pilot plant study was undertaken to evaluate the treatment of such streams in an electrochemical membrane process. The products of such a process are gas streams, (ammonia, hydrogen and oxygen), an aqueous stream of relatively good quality water, and a stream capable of

(ii) acid mine drainage,

(iii) cooling tower blow-down water,

(iv) saline wastes generated at SASOL 2 and 3.

(v) bottle washing effluents.

This final report of the project, summarises work undertaken on selected brine and concentrate streams.

2 PROJECT AIMS

The aims of this project were to:

(i) identify point sources of brine and to characterise those with a particulatly problematic chemistry,

(ii) identify options for controlling brine disposal into the aqueous environment,

(iii) develop techniques for on-site disposal of brines in situations were brine production was unavoidable.

3 PROJECT OBJECTIVES

The aims of the project were to be realised by initially undertaking a series of site visits to identify and characterise problematical brine streams. At each site, the brine-producing process or processes would be examined and where possible measures to reduce brine volumes would be suggested. Where appropiate, new treatment methods would be explored or novel application of existing technology treatment options would be recommended.

4 SUMMARY OF RESULTS

4.1 Identification of Brine Sources

Various organisations including Sentrachem, AECI, Sasol, Iscor, the Chamber of Mines, Eskom, the Department of Water Affairs and the Department of Agriculture and Water Supply were contacted With their aid, a number of point sources of brine have been identified. They include :-

(i) regeneration liquors from anion, cation and mixed bed ion-exchange reactors,

(ii) concentrates from electrodialysis units,

(iii) concentrates from reverse osmosis units,

(iv) cooling tower blow-down streams,

(v) concentrates from evaporator units,

(vi) saline mine concentrates,

EXECUTIVE SUMMARY

1 BACKGROUND TO THE PROJECT

Two major problems threatening water users in South Africa are :-

(i) the availability of adequate quantities of water, and

(ii) the deterioration of the quality of water resources due to increasing concentration of total dissolved solids (TDS).

In attempting to deal with these two problems of quantity and quality, increasing use has been made of water conservation and recycling technology. These measures have however, resulted in an increased production of inorganic brines and concentrates. For the purpose of this report, a quantitative definition of a brine has been avoided, and brine has been defined as any stream of high total dissolved solids concentration which cannot be treated adequately by conventional means.

Treatment and/or responsible disposal is however essential for these streams as unless these are adequately treated, they will eventually enter the aquatic environment, threatening the quality of both surface and groundwaters.

The basis of this research project was to provide a framework of information which would enable brine producers to assess the best treatment options for their brine and be aware of the latest technology available to them.

The options available for controlling brine disposal into the aqueous environment include :-

(i) engineering out the source of brine,

(ii) converting the brine into a saleable product,

(iii) indirect or diffuse discharge to the environment,

(iv) deactivation or conversion to an inert substance,

(v) immobilisation or passive storage,

(vi) disposal into designated brine sink impoundments or discharge by pipeline into the sea.

The above options have been listed in terms of increasing environmental impact.

Where brine production cannot be prevented it would be advantageous to develop techniques for the on-site disposal of brines. The Water Research Commission contracted with the Pollution Research Group, University of Natal (Project No. 201) to investigate the treatment of inorganic brines and concentrates by physical, chemical, physio-chemical and electrical techniques.

A number of point sources of brine were identified and some specific problematic streams were characterised.

Priority sources of brine include :-

(i) effluent streams generated at some AECI plants,

RESEARCH INTO THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

Final Report

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