WATER RESEARCH COMMISSION PROJECT NO. 201

TREATMENT OF INORGANIC BRINES AND CONCENTRATES

APPENDIX 3

Visit to AECI Chemicals and Explosives Ltd at Modderfontein
4th August 1987

A Review of Efforts to Limit Effluent Arisings at the No. 4 Ammonia Plant and in the Nitrate Department

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VISIT TO AECI EXPLOSIVES AND CHEMICALS LTD AT MODDERFONTEIN,

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1. INTRODUCTION

AECI Explosives and Chemicals Ltd is making considerable effort to reduce the chemical loadings in both their strong and weak effluent streams produced at the Modderfontein factory site. Process modifications, together with the cascading and reuse of chemical and water streams have been proposed and, in some instances, have been implemented.

This report summarises some of the alternatives available for investigation which could possibly reduce effluent arisings and salt discharge from the No. 4 Ammonia and from the Nitrate Department of the factory.

2. NO. 4 AMMONIA PLANT

The No. 4 Ammonia Plant is the largest water consumer at the factory. The combined evaporative capacity of the boilers is 400 to 500 m^3/h.

The boiler feed water (160 m^3/h) is deionised in an ion-exchange system consisting of three cations exchange, three anion exchange and two mixed bed columns with a degassing unit positioned between the cation and anion columns.

The current daily consumption of chemicals for the regeneration of the ion-exchange system is 4 200 kg of 98% sulphuric acid and 2 700 kg of 100% sodium hydroxide. These amounts depend on the TDS of the raw water. At present, the waste regenerants are discharged with the weak factory effluent at a rate of 160 to 200 m^3/h.

Various possibilities addressed for reducing both the Rand Water Board (RWB) water intake to the ion-exchange system and the effluent loading from the ion-exchange system are discussed below.

2.1 Operation of the Degasser at Maximum Efficiency

The function of the degasser is to remove inorganic carbon species, as carbon dioxide, from the water before it is processed in the anion exchange column.

The adsorption selectivity of the anion exchange resin is as follows :

$$\text{Si containing anions} < CO_3^{=} < Cl^- < SO_4^{=} < OH^-$$

The commencement of a regeneration cycle is determined by the silica break-through concentration in the column eluate since this is the least strongly adsorbed species. The operating time of the anion exchange column may be extended if the silica break-through is delayed by removing carbonate, chloride or sulphate species from the feed water such that more sites are available on the anion resin for silica adsorption.

In order that the concentration of carbonate species in the feed to the anion exchange column be minimised, it is essential that the degasser be operated at maximum efficiency. This would ensure :-

(i) a delayed break-through of silica resulting in a prolonged operation time of the anion exchange column.

(ii) a lower consumption of regeneration chemicals.

2.2 Pretreatment of the Ion-Exchange System Feed Water by Cross-Flow Microfiltration and Reverse Osmosis

AECI have investigated the possibility of lengthening the period between regeneration recycles of the ion-exchange system by pretreatment of the feed water using a combination of cross-flow microfiltration (CFMF) and reverse osmosis (RO).

AECI have been quoted a budget price of R14 million for the installation of CFMF and RO equipment to purify RWB water (TDS 200 mg/l). The plant has been sized to produce 360 m^3/h of treated water (TDS 50 mg/l) approximately half of which would be used in the low pressure boilers, sited in other plants at the factory, and half of which would be used as the feed to the No. 4 Ammonia ion-exchange system.

It has been estimated that the installation of such a pretreatment sequence would reduce the consumption of regeneration chemicals in the No. 4 Ammonia ion-exchange system by 170 tons per month, a 98% savings in chemicals and a reduction in chemical loading of the resulting discharge.

If the sodium and sulphate ion loadings in the weak effluent discharge are estimated to be 120 and 350 kg/h respectively

(86 and 252 tons/month) by averaging the Winter 1986 and Summer 1986 - 1987 figures (Simpson, July 1987), then a monthly savings of 170 tons in regeneration chemicals on the No. 4 Ammonia ion-exchange system would result in a 50% reduction in the sodium and sulphate loadings in the weak effluent discharge.

Despite the chemical savings and effluent loading based advantages associated with the application of cross-flow microfiltration and reverse osmosis to the pretreatment of ion-exchange feed water, the capital cost of the system is extremely high and the reverse osmosis membrane life expectancy is unknown. In addition, CFMF is a new process and there are not many plants of similar duty in the world.

2.3 Polishing of the Ion-Exchange System Product Water by Reverse Osmosis

The possibility exists for the application of reverse osmosis as a polishing stage after demineralisation of the boiler feed water in the ion-exchange system. This possibility offers the following advantages :-

(i) the ion-exchange system offers a more than adequate pretreatment process.

(ii) scaling of the reverse osmosis membranes will be minimal and a long membrane life is predicted.

(iii) since the rejection performance of reverse osmosis membranes against anionic silica species is excellent, and assuming high efficiency operation of the degasser, the anion exchange columns may be operated at a chloride break-through limit. This would significantly reduce the regeneration frequency by an amount which would need to be determined experimentally. In addition, if all the silica species are allowed to pass through the column unadsorbed, regeneration could be effectively achieved using 80 g of caustic per litre of resin, 38% less than the caustic required at present.

2.4 Reuse of Ammonium Formate Condensates from Strippers as Feed Water to the Demineralisation Unit

Figure 1 is a schematic of the ammonia plant. The condensate from the stripper is produced at a rate of 70 m^3/h. Although this stream contains some colloidal iron and small quantities of carbonates, the principle contaminant is ammonium formate (700 mg/l). In its present form, this stripper stream cannot be used as feed water to the demineralisation unit since the unit is running at maximum capacity at present and an additional salt feed would overload the system.

If this stream could be demineralised to a concentration, equal to, or below, that of RWB water, then it may be recycled as feed water to the demineralisation unit. The advantages are as follows :-

(i) the RWB water intake to the unit could be considerably reduced by approximately 30% which would, in turn, reduce the RWB water TDS loading on the system.

(ii) the loading rate on the ion-exchange system would be reduced, lowering the demand for regeneration chemicals and extending the regeneration cycle time.

(iii) the final effluent discharge volume could be reduced. In addition, if the ammonium formate was removed from the stream and not allowed to enter the effluent system, the nitrogen and COD loading of the final effluent discharge would be reduced.

(iv) this stream would not contain silica.

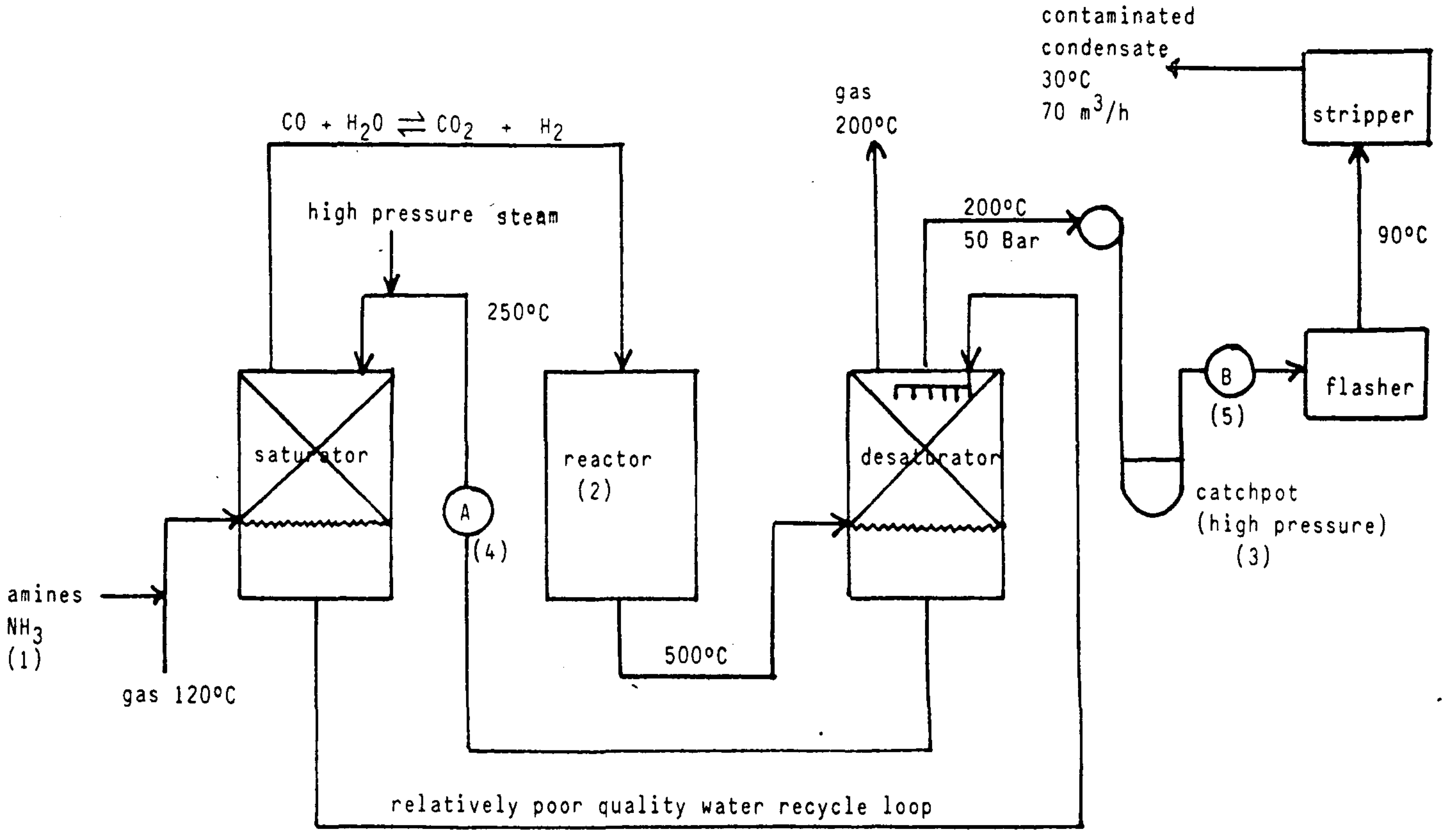

FIGURE 1 : Schematic of Ammonia Plant

Notes : (1) NH_3 is injected at this stage to raise the pH and prevent corrosion. Being volatile it protects the high parts of the reactor.

(2) formate is produced as a byproduct in the reactor and combines with the volatile ammonia to produce ammonium formate in the condensate.

(3) the high pressure condensate could be used as good quality make up water to the desaturator at this stage.

(4) possible positioning of heat exchanger to reduce steam demand.

(5) possible positioning of anion exchange unit to remove formates.

Various possible end-of-line techniques for the treatment of this stripper stream to remove ammonium formate include the following options :-

(i) reverse osmosis : AECI have had trials conducted on a sample of the stripper stream. Trials were conducted at pH 9,2 and results were dissapointing in that only 50% of the formate was retained and ammonium rejections were poor.

At high pH values, the ammonium exists in the free form and will permeate through the membrane. At low pH values, ammonium ions predominate and are rejected by the membrane. The rejection characteristics of the formate ion, however, follow the reverse trend :- a low rejection at a low pH where formic acid predominates and a higher rejection in alkaline pH where the formate ion exists.

Hence reverse osmosis cannot be expected to yield good rejections of ammonium formate solutions.

(ii) the stripper is designed to remove ammonia, but does not operate to design specifications. If the formic acid fraction could possibly be treated by a carbon adsorption or an ion-exchange process which is selective to formic acid, then the ammonia stripper would operate to specification.

(iii) biodegradation of the ammonium formates.

(iv) dissipation of ammonia by contacting the effluent with ash.

Three possible process modifications which will reduce either the contamination or the volume of the condensate stream from the stripper are :-

(i) the installation of a heat exchanger at position A in Figure 1 which would decrease the amount of steam required in the system and reduce the final contaminated condensate volume to 10 to 20 m^3/h. The estimated cost of this heat exchanger is R3 million.

(ii) modifications to the reactor to enable operation at a lower steam to gas ratio which would also lower the volume of contaminated condensate produced.

(iii) the installation of an anion exchange or activated carbon column at position B in Figure 1 which would remove the formate to produce an ammonium hydroxide solution. Efficient operation of the subsequent flasher and stripper process would remove the ammonia with the production of a water stream of suitable quality for recycle to the demineralisation unit.

2.5 Softening the Raw Water Feed to the Existing Demineralisation Unit by Pretreatment in Additional Ion-Exchangers

Figure 2 is a schematic showing the existing ion-exchange system and the proposed modifications, which could be effected at a cost of R1,5 million.

In essence, it is proposed to install two additional cation exchange and anion exchange (weak base) columns to effect a 50% removal of TDS from the feed water prior to treatment in the existing system. This additional demineralisation would produce a better quality feed to the existing system, extending the cycle time of the resin extensively and increasing the ratio of the silicates to the other anions.

It is proposed that the regeneration liquors from the existing unit be reused for regeneration of the new unit. It is estimated that the installation of the proposed modifications would halve the regeneration chemical requirements, thus reducing the salt load to drain. However, the total loading of RWB water salts in the final effluents would not be reduced.

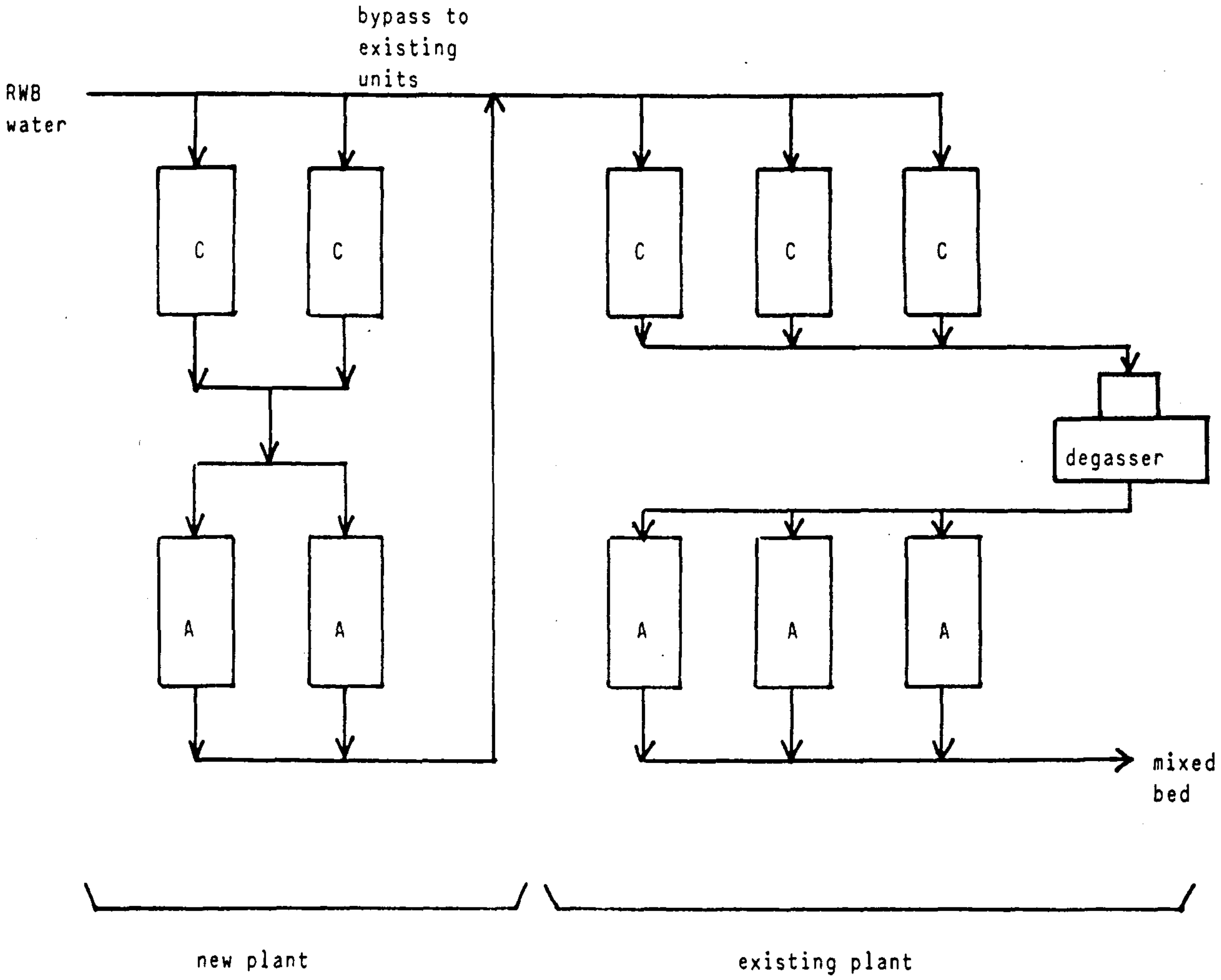

FIGURE 2 : Schematic of existing ion-exchange units and the proposed modifications

2.6 Prevention of Sludge Build-Up in the Demineralisation Unit by Cross-Flow Microfiltration Pretreatment

At present the feed water to the existing demineralisation unit is not pretreated to remove colloidal, particulate or suspended matter. This is partially trapped within the ion-exchange units and is removed by a backwashing process prior to regeneration. A build-up of sludge in the boiler condensate system has been observed.

It is suspected that the presence of colloidal particles in the ion-exchange bed would cause irreversible fouling of the resin beads and thus reduce the life and capacity of the resin. In addition, sludge build-up on the bead surface would impede the kinetics of the adsorption process.

The option exists for the installation of a cross-flow microfilter in front of the demineralisation unit, which will significantly reduce sludge build-up within the ion-exchange column and overcome the need for a backwashing stage during regeneration. This, in turn, would decrease the volume of the effluent produced from the demineralisation unit but would not directly reduce the TDS load.

The installation of a cross-flow microfilter prior to ion-exchange could be used to assess the reliability and suitability of this process as a pretreatment for reverse osmosis in a non critical application.

2.7 Removal of Precipitated Salts from the Regeneration Liquors Prior to Dilution and Resolution

The initial sulphuric acid waste regeneration stream contains insoluble calcium sulphate salts. It would be beneficial, in terms of the final effluent chemical loading, if the insoluble salts were to be removed from the system prior to dilution and resolution.

The possibility of using a filtration technique, for example cross-flow microfiltration, to effect the removal of insoluble salts could be investigated.

2.8 Reduction of the TDS Loadings in the Cation Exchange Column Regeneration Waste Stream by Precipitation Techniques

It has been suggested that the sulphuric acid regeneration stream from the first strong wash should be neutralised with lime. This neutralisation procedure would convert the sulphuric acid to calcium sulphate which has a solubility limit of 1 900 mg/l. The insoluble salt must be removed by filtration techniques and the resulting solution, saturated with calcium sulphate would have a TDS loading significantly below the TDS loading of the first strong wash acid stream.

2.9 Cascading the Anion Exchange Column Regeneration Waste Stream to Alternative Process within the Factory

It has been estimated that a 20 mg/l reduction of the sodium concentration in the final weak effluent discharge could be effected if some of the caustic regeneration waste from the anion exchange columns was reused in the cotton kiering section of the fusing factory. Using this figure of 20 mg/l sodium, and assuming a final weak effluent discharge of 1 000 m^3/h, this translates to a kiering caustic consumption of 0,8 tons of 100% NaOH per day.

Two further developments from this suggestion are that :-

(i) the price of cotton, already kiered to specification by a textile factory e.g. John Grant, be investigated with the view to terminating kiering operations at the Modderfontein site.

(ii) modifications to the existing kiering process be investigated to enable kiering to be achieved at high temperatures and pressures. The resulting effect would be that kiering could be achieved at considerably lower sodium hydroxide usages and residence times.

Surveys conducted by the Pollution Research Group at various textile factories in Southern Africa indicate typical caustic consumption for efficient kiering and scouring of various cotton grades (Table 1).

TABLE 1 : **Typical Caustic Consumption During Kiering and Scouring of Cotton**

Process	**Cotton type**	**Cotton quality**	**Caustic consumption g/kg cotton**
Batch scouring			
(i) atmospheric	cotton wool	high	38
	cotton wool	commercial	53
(ii) pressurised	cotton wool	high	14
	cotton wool	commercial	20
Batch kiering high pressure, 120°C	fabric	high	23 to 53*
Continuous scouring steam atmosphere	fabric	high	56 to 96

Note * in this case potassium hydroxide was used in place of sodium hydroxide for kiering.

Assuming a caustic consumption of 53 g/kg cotton then the production of kiered cotton would be 15 ton per day.

2.10 Recovering Sodium Hydroxide from the Anion Exchange Column Regeneration Waste for Reuse

The Pollution Research Group have developed and patented (through the WRC) a four stage treatment sequence (Figure 3) involving :-

(i) neutralisation
(ii) cross-flow microfiltration
(iii) nanofiltration and
(iv) electrochemical sodium hydroxide recovery

which will enable the treatment of sodium hydroxide containing effluents with the recovery of :-

(i) heat energy
(ii) low quality water (TDS = 500 mg/l)
(iii) high purity sodium hydroxide at any required concentration from 5 to 40%.

Pilot-plant trials conducted at a local textile mill indicated that sodium hydroxide could be recovered at a power cost of R150 to R200/ton (at R0,05/kWh). The Pollution Research Group is in the process of designing a plant to recover 1 ton/day of sodium hydroxide from a caustic textile effluent.

Pending the economic viability of the process and the performance of the full-scale unit to be installed at the textile factory, it is suggested that AECI investigate the possibility of applying the proposed treatment sequence to the recovery and reuse of caustic anion-exchange regeneration liquors.

2.11 Reducing the Chemical Usage During Regeneration of the Existing Demineralisation Unit

It has been suggested that a detailed survey of the composition of the eluted regeneration streams be conducted to determine :-

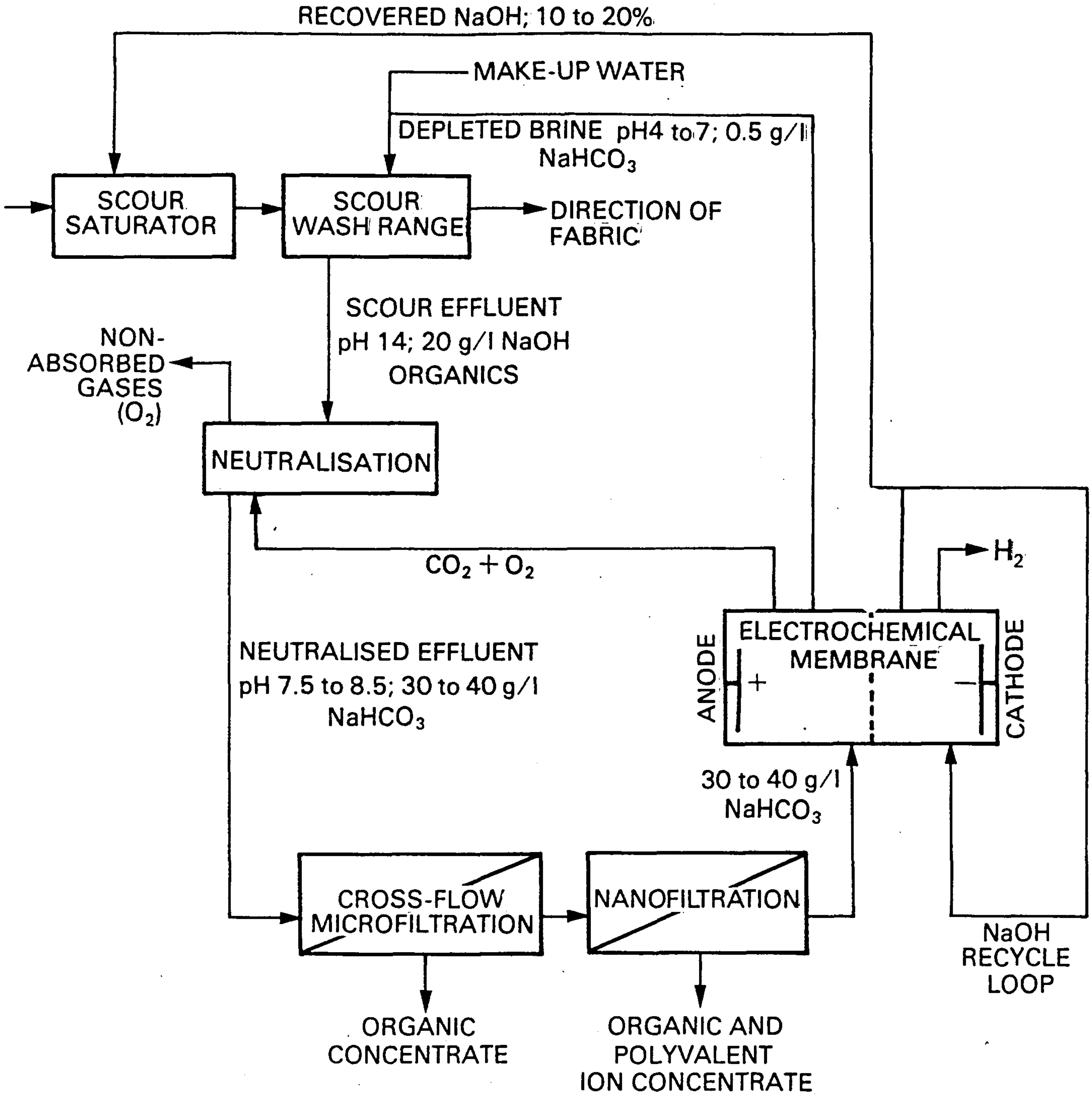

FIGURE 3 : Process sequence for the recovery and recycle of sodium hydroxide effluents

(i) the rate of removal of the contaminants from the ion-exchange resin.

(ii) the point at which the ratio between regeneration chemical usage and contaminant removal becomes unacceptable high.

(iii) whether the chemical consumption and the regeneration time may be decreased with minimal effects on restored ion-exchange capacity.

3. NITRATE DEPARTMENT

The Nitrate Department includes the plants which produce nitric acid, ammonium nitrate solutions (ANS) prilled ammonium nitrate and limed ammonium nitrate (LAN).

In terms of effluent arisings, the priority areas to be addressed include :-

(i) cooling tower blowdowns
(ii) demineralisation discharges
(iii) pump gland seal leaks
(iv) drainage system modifications
(v) dry cleaning techniques and subsequent washing down procedures
(vi) potential uses for contaminated condensates from steam traps
(vii) potential uses for ammonium nitrate fall-out in the prilling plant.
(viii) potential uses for floor sweepings.

3.1 Cooling Tower Blowdowns

Cooling tower blowdown and purges present the largest TDS problem. Cooling tower blowdown occurs to remove :-

(i) corroding contaminants
(ii) suspended solids
(iii) scaling and/or fouling contaminants from the system

Where water recovery is limited by suspended solids build-up, cross-flow microfiltration of cooling tower blowdowns could find application.

If desalination is required, reverse osmosis is an option. High quality water for reuse in the boilers would be produced. However, problems associated with the disposal of a low volume concentrate stream high in TDS, would need to be addressed.

3.2 Demineralisation Unit Discharges

The demineralisation unit on the No. 11 Nitric Acid plant is technically similar to that on the No. 4 Ammonia plant. It is 0,1 times the size of the No. 4 Ammonium demineralisation unit and the waste regeneration chemicals are discharged with the strong effluent at a rate of 10 m^3/h.

At present the demineralisation plant is oversized, yielding spare capacity. The product water is used in low pressure boilers and hence the quality of the water produced by the No. 11 Nitric Acid demineralisation unit does not need to be as high as that produced by the No. 4 Ammonia demineralisation unit. For this reason it has been suggested that the No. 4 Ammonia demineralisation unit be operated after break-through has occurred and that all demineralised water thereafter be fed to the No. 11 Nitric Acid plant. Regeneration of the No. 4 Ammonia demineralisation unit would be effected only when the product stream was too high in TDS for use in the No. 11 Nitric Acid plant boilers.

Implementation of this proposal would reduce the chemical contributions by the demineralisation unit to the final factory effluents but is not practically feasible at present since the No. 4 Ammonium demineralisation unit is operating at full capacity.

3.3 Pump Gland Seal Leaks

Leaks of ammonium nitrate and other chemicals from gland seals result from mechanical faults and should be prevented where possible.

3.4 Drainage System Modifications

It has been proposed that all drains be interconnected, the effluents collected and returned to the plant for reuse, either as a solution, or in the dry form as a low quality fertilizer.

3.5 Dry Cleaning Techniques and Washing Down Procedures

Dry cleaning should be done regularly and effectively. Potential uses for fall-outs and floor sweepings should be investigated. Effluent production volumes should be minimized during washing down by ensuring minimum usage of liquid carrier. The application of cross-flow microfiltration to upgrade the quality of floor washings for subsequent use at Kynoch could be investigated.

3.6 Potential Uses for Contaminated Condensates

Condensate produced in the ANS plant and contaminated with 1% ammonium nitric is :-

(i) recycled at a rate of 8 to 10 m^3/h to the nitric acid plants when these plants are operating (Figure 4). Make-up water from the demineralisation unit is required at a rate of approximately 10 m^3/h. (One nitric acid plant, normally No. 9, is always operated on demineralised water only, since this acid is used for nitroglycerine production and contaminants must be maintained at minimum levels).

(ii) used for diluting the ANS product from 96% to 88% for transport to Kynoch, where further dilution to 60% is carried out during liquid fertilizer production.

(iii) used for washing down.

(iv) if 96% ANS could be produced, the necessity of evaporation would be alleviated and the production of contaminated concentrate avoided (see footnote 3, Figure 4).

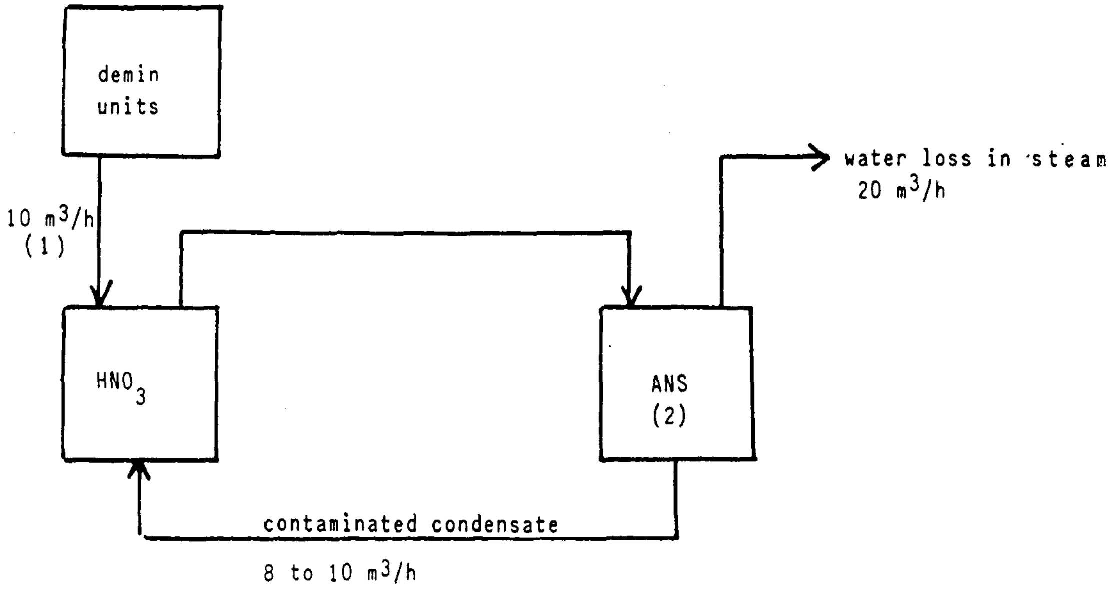

FIGURE 4 : Contaminated condensate recycle

Notes : (1) the process water consumed in the production of HNO_3 must contain less than 100 mg/l of chlorides. At higher chloride levels chloride corrosion occurs and aqua regia is formed in the absorption column.

(2) in the existing process nitric acid at 60% is used to produce ANS at 90% which is then evaporated to a concentration of 96%. It is estimated that if the nitric acid was reacted at 63% then the ANS would be produced at 96%, thus alleviating the necessity of evaporation and the production of a contaminated condensate.

At present, if the nitric acid plants are down due to problems of an intermittent nature most of the contaminated condensate is dumped and discharged from the factory with the strong effluent. In the event of this occurring (a 25 day/month running time is budgetted per plant) it has been suggested that :-

(i) a concentration system as shown in Figure 5 be investigated to increase the concentration of the ammonium nitrate in the contaminated condensate to a level which would enable reuse.

(ii) the additional transport costs resulting in the dilution of the ANS transported to Kynoch to 60% using contaminated condensate, and not 88%, be investigated.

(iii) the supply of diluted ANS to explosive customers be investigated.

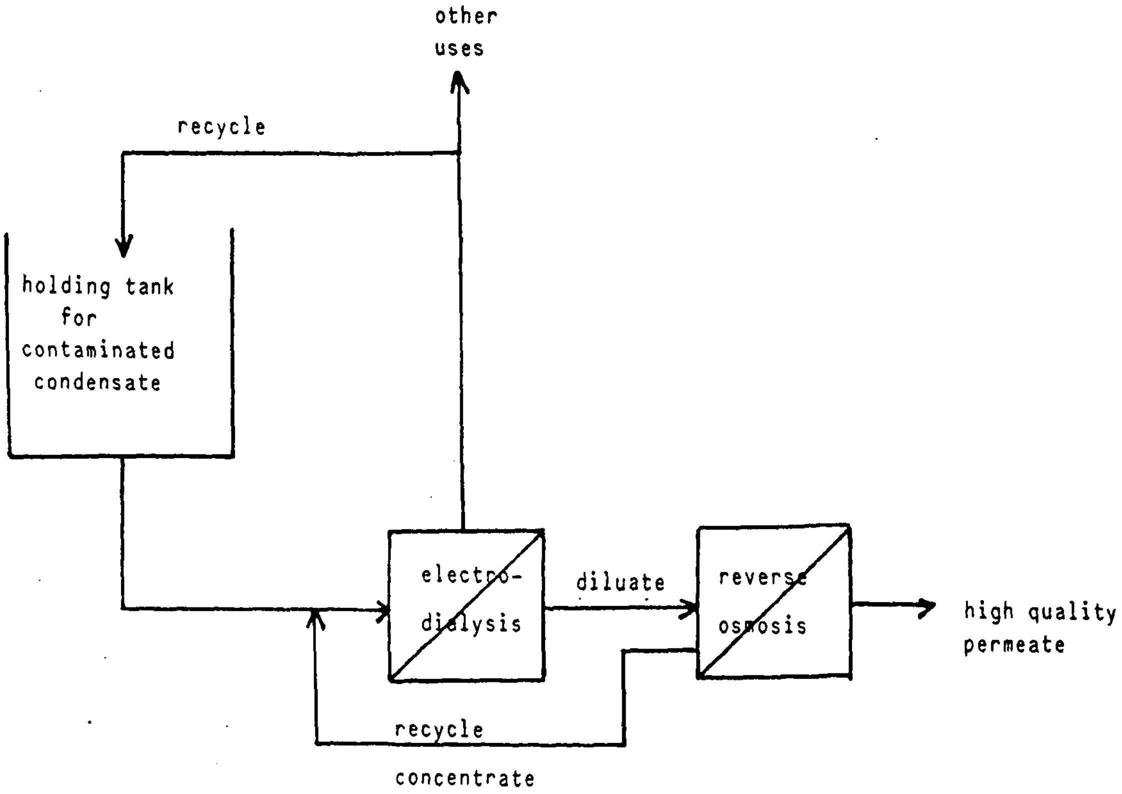

FIGURE 5 : Possible treatment sequence for the concentration and reuse of contaminated condensate from the ANS plant when the nitric acid plant is not in operation

REFERENCE

Simpson, A.E., 'Visit to AECI Explosives and Chemical Factory at Modderfontein, 27th and 28th July 1987'.