# WATER RESEARCH COMMISSION PROJECT NO. 201

# THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

## APPENDIX 12

### Visit to SASOL 2 and 3

Secunda
April 1988

Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

October 1990

CONFIDENTIAL WRC DOCUMENT NO.: 4.9/88.

# WATER RESEARCH COMMISSION PROJECT NO. 201

# TREATMENT OF INORGANIC BRINES AND CONCENTRATES

## STEERING COMMITTEE 1988

## APPENDIX 9

# VISIT TO SASOL 2 AND 3,
# SECUNDA

APRIL 1988

A.E. Simpson
Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

April 1988

WATER RESEARCH COMMISSION PROJECT NO. 201

# THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

## VISIT TO SASOL 2 AND 3

## SECUNDA

APRIL 1988

A.E. Simpson
Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

April 1988

## Table of Contents

## Table of Figures

## Table of Tables

## 1 INTRODUCTION

The raw materials to SASOL 2 and SASOL 3 are coal, water, air and chemicals, from which fertilisers, explosives, chemicals, fuel and wastes are produced. Figure 1 is a simplified flow sheet of the production process.

The overall water system is shown in Figure 2. The three basic circuits are the:

(i) raw water circuit.

(ii) ash water system.

(iii) process and cooling water circuit.

The location of the SASOL complexes in the catchment area of the Vaal Dam makes it necessary that there be a zero effluent discharge. The SASOL plants have a large number of organic and inorganic wastes as well as the normal boiler and cooling water blow-downs.

Initially investigations into the use of solar evaporation dams for the handling of all factory streams were carried out. Solar evaporation dams were not feasible since there was not sufficient land available and a reuse scheme was developed which involved the recycle of treated effluents to the cooling towers.

Saline wastes 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) ion exchange regenerants.

The origins of the salts in the brine stream are (Marriot and Brand, 1983):

(i) 42% in the raw water intake to the plant.

(ii) 33% from the coal feed.

(iii) 25% from chemicals added to aid in the removal of inorganics from various streams.

## 2 THE EFFLUENT AND WATER SYSTEM

There are two types of water treatment units at SASOL 2 and 3:

(i) Unit 66 for the evaporative recovery of water from saline effluents produced during the pretreatment of raw water for use in the boiler.

(ii) Units 52 and 252 for the recovery of water from high COD processing effluents by a combination of biological, filtration and adsorption techniques.

The effluent and water system contains 3 dams:

(i) a salty dam which is made up of two sections,

- a salty brine section for the brine from Unit 66 which has an evaporative capacity of 17 kℓ/h.

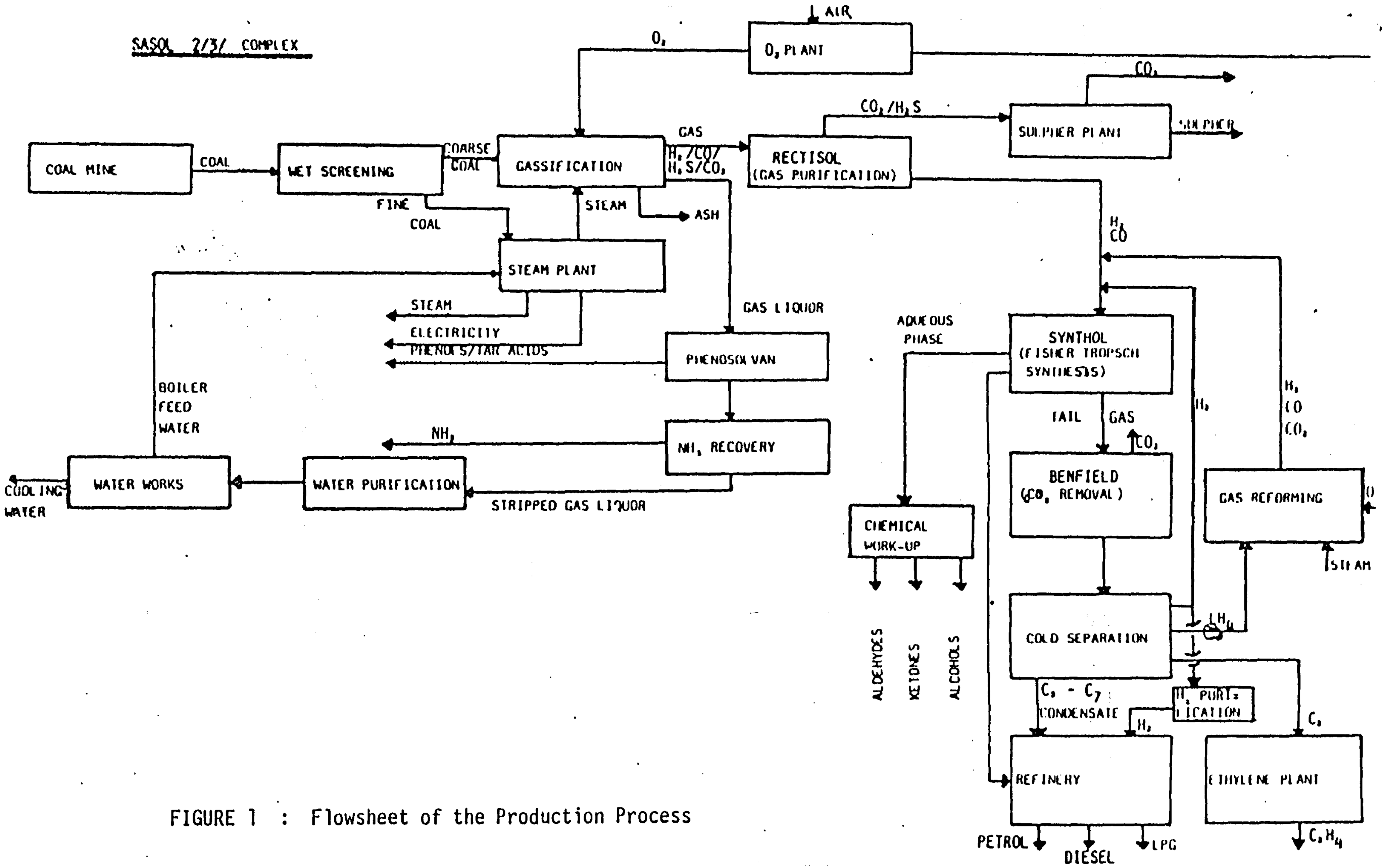


FIGURE 1 : Flowsheet of the Production Process

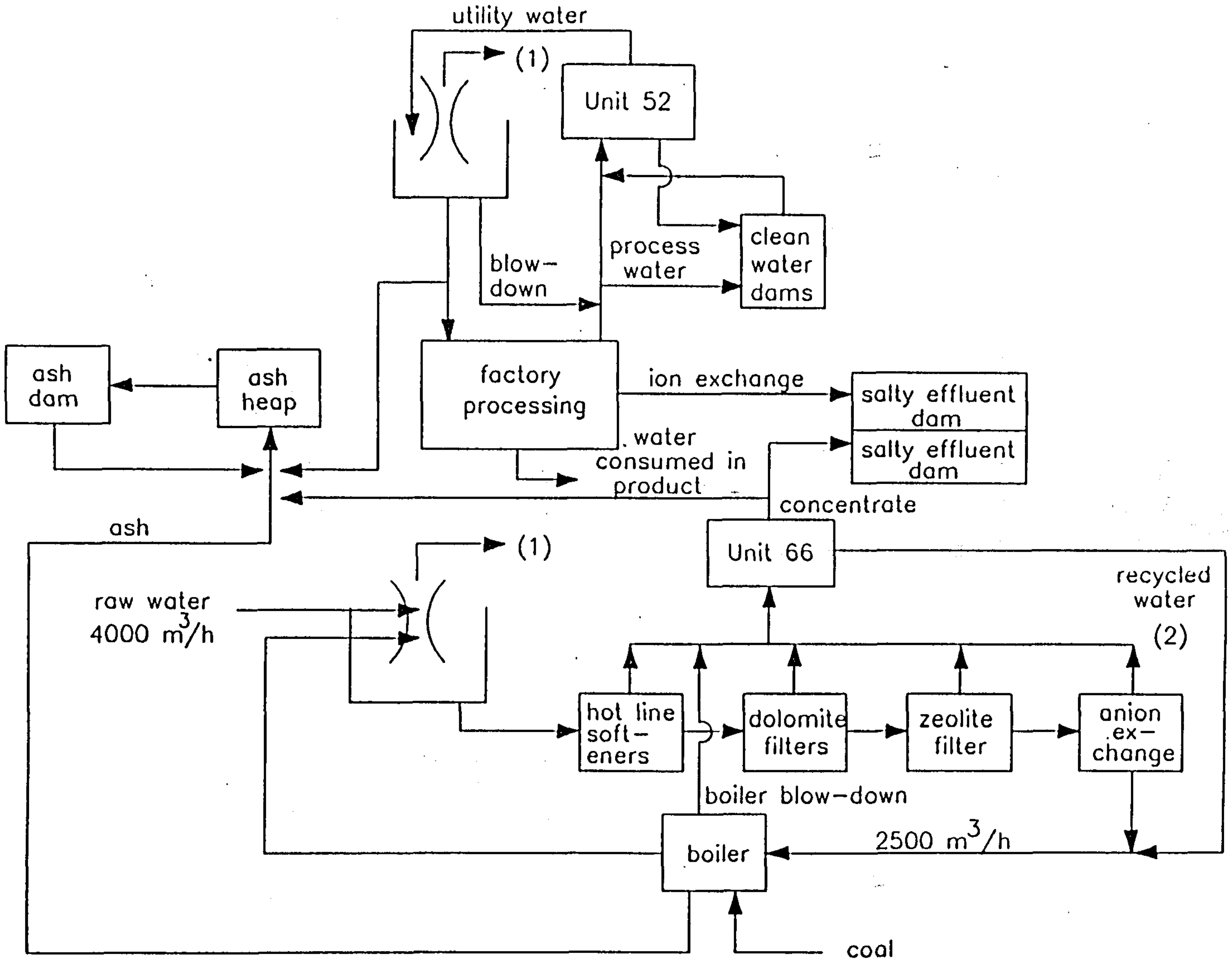


FIGURE 2 : Overall Water System

Note (1) the total cooling tower evaporation rate is 1 500 m$^3$/h
(2) the distillate from Unit 66 constitutes approximately 10% of the total intake water

  - a salty effluent section for the salty process effluents (e.g. process ion exchange regenerants by-passing Units 52 and 252) which has an evaporative capacity of 40 kℓ/h.

(ii) a clean water dam interconnected to Units 52 and 252 which contains process effluent, treated and recycled, for reuse in the process cooling tower systems. The main chemical constituents of this dam are NaCl, NaF and $Na_2SO_4$. At present this dam is undersized by approximately 4 to 10 Mℓ/day.

(iii) an ash dam which receives ash heap drainage and some cooling tower blow-down. The contents of this dam are recirculated to the power station for ash transport.

## 3 UNIT 66 : EVAPORATIVE RECOVERY OF SALINE WASTES

The objectives of Unit 66 are to evaporate the brine produced during boiler water pretreatment to:

(i) reduce the volume of the brine stream requiring disposal.

(ii) produce a distillate of suitable quality for recycle to the boilers.

The initial requirements of the brine concentrator were:

(i) corrosion resistance: the occasional presence of materials such as sulphur, ammonia, cyanide and others, which are impossible to completely exclude from the effluent system, necessitated the selection of a suitable metallurgy.

(ii) scaling resistance: the high concentrations of calcium, magnesium and silica in the effluent has high scaling potential and it is essential that the heat transfer surfaces be kept clean without affecting equipment availability.

(iii) production of product water of sufficient quality: since the purpose of the evaporator was both to desalinate and to improve the water balance, it was essential that the condensate be of suitable quality for reuse.

Unit 66 contains three RCC brine concentrator trains consisting of vertical falling film vapour compression evaporators. Heat transfer takes place across titanium tubes and the recycle process is a seeded slurry one.

Figure 3 shows the layout of Unit 66.

At present only the first two trains are in operation. The third train is being refurbished as a result of condenser corrosion.

The feed to the system passes through storage tanks:

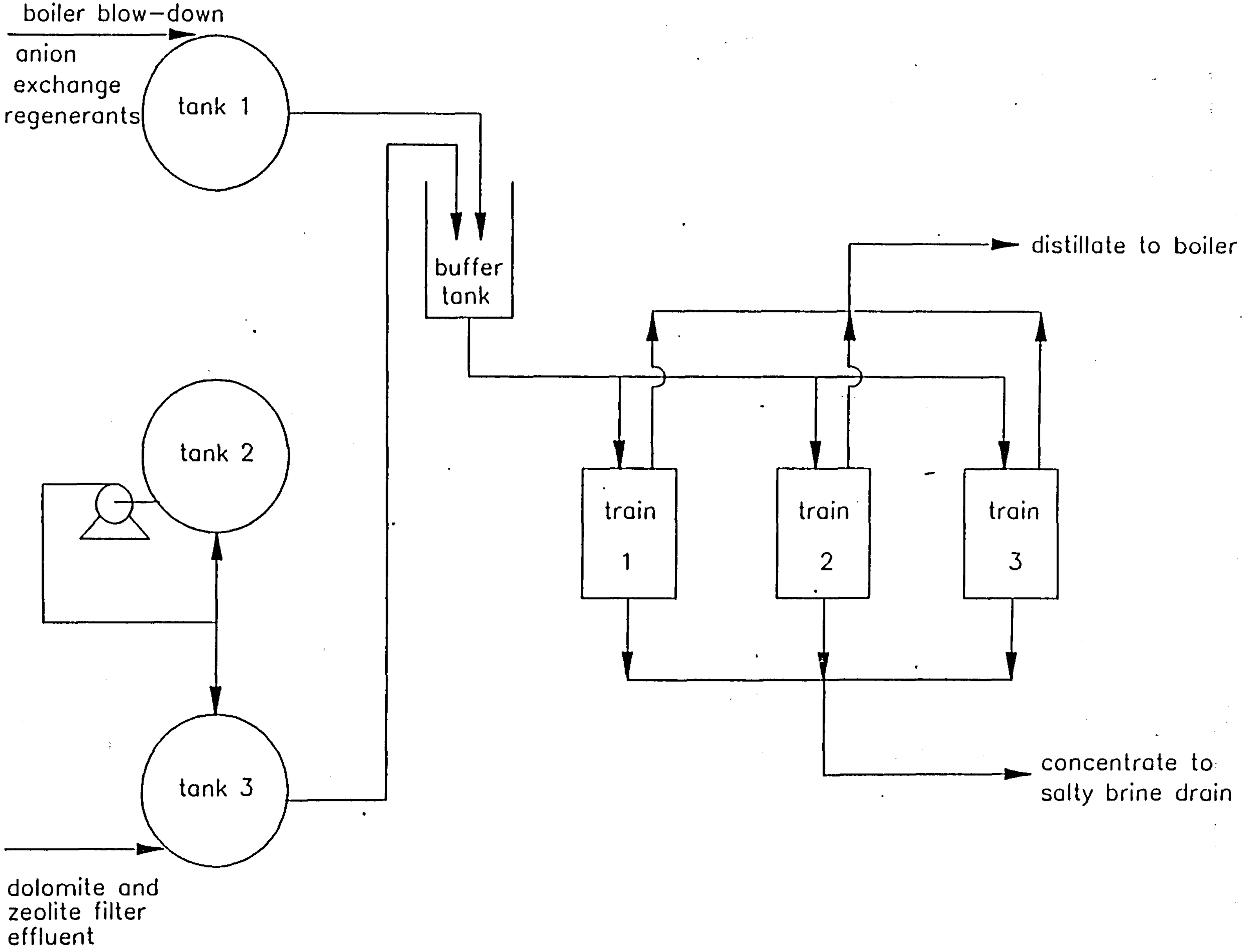


FIGURE 3 : Unit 66 - Layout

(i) the 'BBD' tank: the boiler blow-down and the anion exchange regeneration streams from the raw water circuit of SASOL 2 and SASOL 3 pass into tank 1 (the cation exchange regenerant streams are used directly in ash conditioning). The feed to tank 1 contains mainly NaOH, NaCl, $Na_2CO_3$ (the ion-exchange system does not incorporate a degasser) and $Na_2SO_4$ and the pH is between 12 and 13. There is minimal calcium in this stream. The flow of this stream is approximately 60 and 80 $m^3/h$ from SASOL 2 and SASOL 3 respectively.

(ii) the zeolite tank: the effluent from the regeneration of the zeolite and the dolomite filters (sodium softeners) in the raw water circuit is discharged into tank 2 which is interconnected with tank 3. The contents are circulated continuously to obtain better mixing and equalisation of the composition which, in the case of the zeolite effluent, is particularly inconsistent. This stream is rich in both NaCl and $CaCO_3$ and is at pH 7,8. The flow of this stream is 20 $m^3/h$ from each of SASOL 2 and SASOL 3.

Typical analyses of the two streams above are given in Tables 1 and 2.

<u>TABLE 1 : Typical Analysis of the 'BBD' Effluent</u>

(Note : all units in mg/ℓ)

| Date | Time | pH | P | M | Na | $Ca^{++}$ | $Mg^{++}$ | $Cl^-$ | $F^-$ | $SO_4$ | $NH_3$ | $PO_4$ | $SiO_2$ | TDS | TOC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/7 | 6h00 | 12,1 | 2 171 | 2 490 | 2 644 | 82 | 9 | 996 | 6,0 | 1 950 | <2 | 6,4 | 19 | 6 535 | 102 |
| | 8h00 | 12,2 | 2 239 | 2 519 | 2 544 | 70 | 4 | 1 046 | 6,5 | 1 950 | <2 | 13,2 | 22 | 6 864 | 98 |
| | 10h00 | 12,2 | 2 229 | 2 422 | 2 782 | 108 | 5 | 1 345 | 5,9 | 1 775 | <2 | 12,2 | 19 | 7 460 | 110 |
| | 12h00 | 12,1 | 1 641 | 2 007 | 3 320 | 321 | 4 | 3 138 | 4,9 | 1 575 | <2 | 9,2 | 16 | 8 996 | 81 |
| | 14h00 | 12,0 | 1 322 | 1 460 | 2 607 | 181 | 8 | 1 594 | 5,0 | 2 075 | <2 | 17,6 | 17 | 5 510 | 98 |
| | 16h00 | 12,1 | 1 341 | 1 575 | 2 519 | 120 | 2 | 1 594 | 5,0 | 1 825 | <2 | 5,2 | 17 | 6 504 | 109 |
| | 18h00 | 11,9 | 926 | 1 351 | 3 115 | 282 | 3 | 3 636 | 5,4 | 1 100 | <2 | 4,0 | 16 | 9 429 | 96 |
| | 20h00 | 12,0 | 1 351 | 1 949 | 3 285 | 282 | 2 | 3 785 | 5,9 | 1 025 | <2 | 7,2 | 13 | 8 690 | 84 |
| | 22h00 | 12,1 | 1 834 | 2 229 | 3 549 | 323 | 4 | 3 487 | 5,9 | 1 425 | <2 | 2,0 | 18 | 7 495 | 78 |
| | 24h00 | 12,2 | 1 853 | 2 210 | 2 500 | 124 | 9 | 797 | 5,4 | 2 375 | <2 | 14,8 | 22 | 5 844 | 110 |
| 11/7 | 02h00 | 12,2 | 1 824 | 2 104 | 2 430 | 104 | 10 | 797 | 5,7 | 2 350 | <2 | 23,6 | 20 | 6 025 | 105 |
| | 04h00 | 12,2 | 1 814 | 2 094 | 2 430 | 161 | 13 | 747 | 5,4 | 2 475 | <2 | 22,4 | 20 | 6 723 | 107 |

The contents of tank 1 and tanks 2 and 3 are stored separately to prevent calcium precipitation and are combined in the buffer tank before feeding to the brine concentrators. The pH of the brine is adjusted to 5,5 using sulphuric acid to destroy the carbonate alkalinity and the brine is then preheated using sensible heat from the distillate exiting the concentrator.

## TABLE 2 : Typical Analysis of the 'Zeolite Waste' Stream

(Note : All units as mg/ℓ)

| Date | Time | pH | P | M | Na | Ca | Mg | Cl | F | $SO_4$ | $NH_3$ | $PO_4$ | $SiO_2$ | TDS | TOC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11/7 | 06h00 | 9,4 | 10 | 37 | 2 975 | 511 | 122 | 2 988 | 0,35 | 50 | <2 | 4,2 | 1,1 | 10 556 | 18 |
| | 08h00 | 9,6 | 6 | 35 | 2 660 | 468 | 109 | 996 | 0,37 | 46 | <2 | 4,2 | 0,8 | 9 705 | 16 |
| | 10h00 | 9,9 | 17 | 66 | 3 895 | 871 | 159 | 3 985 | 0,42 | 47 | <2 | 0,5 | 0,8 | 15 411 | 16 |
| | 12h00 | 10,2 | 23 | 73 | 2 877 | 662 | 109 | 2 988 | 0,46 | 35 | <2 | 0,5 | 0,8 | 10 396 | 12 |
| | 14h00 | 10,2 | 19 | 69 | 2 809 | 605 | 103 | 2 988 | 0,45 | 32 | <2 | 0,4 | 0,8 | 9 783 | 12 |
| | 16h00 | 9,6 | 21 | 87 | 5 247 | 1 170 | 251 | 8 965 | 0,47 | 54 | <2 | 1,4 | 0,8 | 20 995 | 18 |
| | 18h00 | 9,6 | 17 | 77 | 5 272 | 1 195 | 245 | 8 965 | 0,4 | 65 | <2 | 0,9 | 0,8 | 23 310 | 12 |
| | 20h00 | 10,0 | 19 | 52 | 2 524 | 732 | 105 | 2 988 | 0,37 | 30 | <2 | 0,4 | 1,2 | 9 649 | 20 |
| | 22h00 | 9,9 | 21 | 44 | 2 469 | 633 | 102 | 996 | 0,38 | 27 | <2 | 0,4 | 1,2 | 9 244 | 18 |
| | 24h00 | 9,6 | 17 | 54 | 3 320 | 862 | 151 | 3 985 | 0,58 | 30 | <2 | 0,2 | 1,2 | 13 545 | 14 |
| 12/7 | 02h00 | 9,6 | 17 | 52 | 3 320 | 789 | 151 | 9 961 | 0,4 | 35 | <2 | 0,2 | 1,2 | 12 289 | 12 |
| | 04h00 | 9,6 | 17 | 52 | 3 333 | 816 | 153 | 4 981 | 0,38 | 35 | <2 | 0,2 | 1,2 | 12 170 | 12 |

After preheating and deaeration the brine feed is transferred to the top of the evaporator, from where it passes through specially designed distributors and flows as a thin film down titanium tubes.

The steam, generated in the tubes, passes through a demister and is compressed in an electrically driven centrifugal compressor, thus supplying driving energy to the entire process. The distillate is collected in the condenser and is recycled to the boiler after heating the incoming evaporator feed.

Scale formation on the heat exchange surface is inhibited by use of a calcium sulphate seed, which is maintained in suspension and onto which further precipitation of various salts occurs. The desired level of suspended solids is maintained by use of hydrocyclones which are used to remove and recover crystals from the waste brine for recycle.

Salt removal occurs at a rate of approximately 70 tons/day, the energy requirements being approximately 23 kW/m$^3$ of product water.

The chemical composition of the evaporator feed is approximately as follows:

TS = 9 to 13 g/ℓ
Na = 7 g/ℓ
Ca = 2 g/ℓ

The design flow is approximately 120 kℓ/h per train. However, the actual total flow to Unit 66 is only about 200 kℓ/h.

The cycles of concentration which are achieved by Unit 66 are maintained between 14 and 20. The determining factor in the water recovery of the unit is the precipitation of the double salt, $CaSO_4.Na_2SO_4$, which scales the heat exchange surfaces. The precipitation of this salt is dependent on the chemical composition of the reticulating brine rather than on its solids concentration.

The product from the evaporator consists of a slurry containing 120 to 200 g/ℓ of solids, 40 to 60 g/ℓ of which is suspended, mainly as calcium sulphate with some silica and sodium sulphate. The flow of this concentrate is 16 to 17 kℓ/h.

The concentrate is discharged to the salty brine dam along with equipment wash water and waste condensate. Some of this concentrate is used for ash quenching and ash transport.

The main operational problems associated with Unit 66 are as follows:

(i) breakage of the pH probes: probes robust enough to withstand the conditions within the system are difficult to obtain. In addition, the probes must be removed every 8 to 24 hours in order to mechanically scrape the salty precipitate from the membrane surface.

(ii) rapid and unexpected changes in feedwater composition can lead to scaling.

(iii) the system has spare evaporative capacity which cannot be used since the degree of brine concentration is inhibited by the double salt precipitation on the heat exchange surface.

(iv) a substantial amount of energy is required to produce as concentrated a stream as possible. This stream is then rediluted to 25% of its concentration by equipment wash water and waste condensate before discharge to the salty brine dam.

(v) besides the precipitation of the double salt, the permissible water recovery is also determined by the flow requirements of the 4 km pipeline conveying waste brine to the salt brine dam. The velocity in the three inch diameter pipeline must be maintained above at least 1,1 m/s (equivalent to a flow of 18 $m^3$/h) to prevent settling of the undissolved solids in the pipeline.

## 4 UNITS 52 AND 252 : PROCESS EFFLUENT RECOVERY

Units 52 and 252 upgrade all the process effluent streams including the stripped gas liquor (SGL), the synthol reaction water, the API liquor and the cooling tower blow-down. The synthol reaction water has a low pH and is segregated from the other effluents. The treated water is recycled as cooling tower water.

Units 52 and 252 consist of:

(i) five anearobic biological digestion ponds.
(ii) settlers.
(iii) clarifiers.
(iv) sand filters.
(v) carbon absorption.
(vi) anion exchange columns.

Table 3 gives the flow and composition of the main streams upgraded by Units 52 and 252. The total flow to each biological digester is approximately 600 to 1 200 kℓ/h of backflow from the aerobic basin, 300 kℓ/h of synthol reaction water and 600 kℓ/h of other process waters. Phosphoric acid is used as a nutrient and is added to the streams before biological treatment.

TABLE 3 : Typical Characteristics of Effluent Streams to Units 52 and 252
(Note: All analsyis in mg/ℓ)

| Parameter | Stream | | | |
|---|---|---|---|---|
| | SGL | API | Reaction Water | Cooling tower blow-down |
| Total flow (kℓ/month) | 1 000 000 | 650 000 | 335 000 | 120 000 |
| Hourly flow (kℓ/h) | 1 400 | 790 | 400 | 150 |
| Bypass to dams (%) | 0 | 8 | 10 | 10 |
| pH | - | 8 | 2,9 | - |
| COD | 2 250 | 1 100 | 19 000 | 2 000 |
| TOC | 750 | 200 | 6 500 | 200 |
| $Cl^-$ | 60 | 200 | - | 400 |
| Na | 30 | 255 | - | 4 |
| S as $SO_4$ | 400 | 700 | - | 1 760 |
| TKN-N | 400 | 300 | - | 880 |
| $NO_3$-N | - | - | - | 830 |
| $NH_3$-N | 270 | - | - | 4 |
| F | 100 | 120 | - | 360 |
| Volatile acids | - | - | 11 000 | - |
| Fatty acids | - | - | 12 000 | - |
| $PO_4$ | - | - | - | 3 |
| $CrO_4$ | - | - | - | 5 |

The biggest flow is the SGL, typically 1 400 kℓ/h which constitutes just less than 50% of the total flow of these streams.

The COD loading of the process streams to Unit 52 can reach 30 tons/day. The largest contributor to the COD loading is the synthol reaction water, which contains nearly 50% of the total COD entering the unit.

The residence time in the biological digester is 20 to 30 hours during which time the COD concentration is reduced by approximately 87%. A thick black sludge is produced during the digestion process, which is collected and burnt in an incinerator.

Bentonite is added to the clarifiers as a flocculant aid. The carbon adsorption process does not appear to be functioning well and the average COD decrease of the effluent by treatment with carbon adsorption is 0,7%. In some cases both the COD and solids concentration appear to be higher in the eluant than in the feed. In Unit 252 the carbon filters are bypassed.

In both Units 52 and 252 the anion exchange columns are bypassed unless an intolerably high (300 mg/ℓ) chloride concentration is reached. Operation of these columns under normal circumstances requires that regeneration be carried out after each 400 to 800 $m^3$ of effluent is treated. Thus large amounts of regenerant chemicals are required, the disposal of which cannot be handled.

The product water from Units 52 and 252 is reused in the cooling tower. Its COD averages 400 to 600 mg/ℓ and it contains 150 to 300 g/ℓ of dissolved solids.

## 5 SYNTHOL REACTION WATER - AEROBIC TREATMENT

The synthol reaction water is clear and contains mostly volatile and fatty acids with very little inorganic salts. Pilot plant trials have indicated that aerobic treatment of this effluent will reduce its COD to a level suitable for discharge into a nearby river. The installation of a full scale plant is planned which will reduce the flow of the process water to Units 52 and 252 by approximately 25% but will reduce the COD loading on these units by nearly 50%.

## 6 CONCLUSIONS AND RECOMMENDATIONS

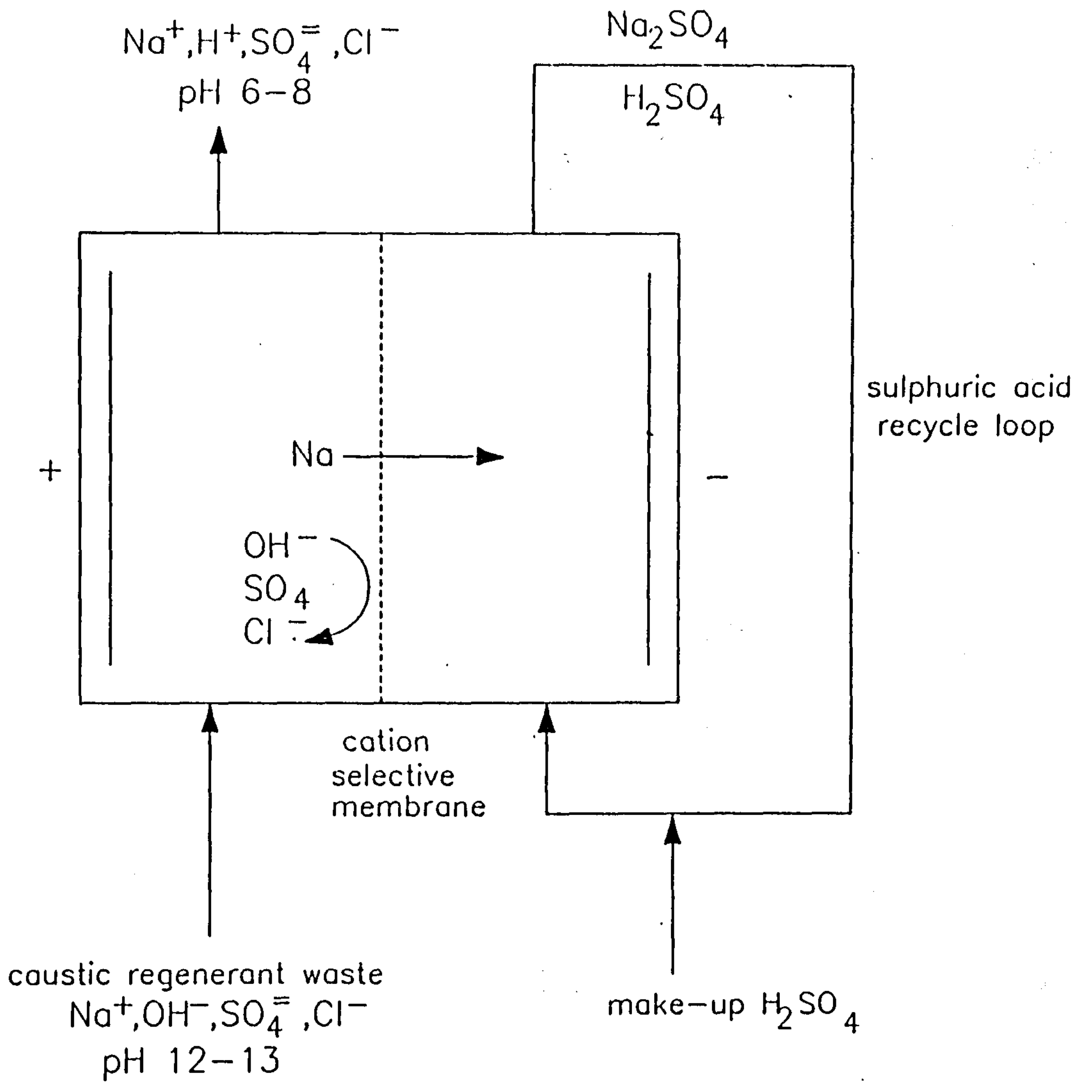
(i) The major problem associated with Unit 66 appears to be operational rather than technical in that the brine concentrate is diluted to 25% of its original concentration prior to discharge to the dam.

(ii) The major water recovery limitation is the precipitation of the double salt, $CaSO_4.Na_2SO_4$ which may be inhibited by ensuring that the concentration of sodium sulphate in the liquor be maintained at minimum levels.

A major contributor to the sodium sulphate in the brine concentrator feed is the sulphuric acid neutralisation of the anion exchange waste regenerant caustic stream in the buffer tank. It would be advantageous if neutralisation could be achieved without further addition to the dissolved solids loading in the effluent. Such a system is illustrated in Figure 4 and makes use of electrolytic principles to neutralise the caustic stream, by replacing the sodium ions with hydrogen ions.

The sodium ions are transported across the cation selective electro-membrane under the influence of a potential. Hydrogen ions are produced at the positive anode by oxidation of water, contributing to the neutralisation of the caustic stream; reduction of water occurs at the cathode. The catholyte solution is recycled continuously and the neutralised anolyte or effluent stream, reduced in sodium concentration, is evaporated in the brine concentrator, with less double salt precipitation.

(iii) If recovery and direct reuse of sodium chloride regenerant stream from the zeolite filters could be achieved the solids loading of the brine concentrate would be reduced.



anode reaction:
$H_2O - 2e \longrightarrow 2\ H^+ + 1/2\ O_2$

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

FIGURE 4 : Electrolytic Neutralisation of Caustic Anion Exchange Waste Regenerant

- It is possible that a treatment and direct reuse system as shown in Figure 5 could be applicable to the sodium chloride rich zeolite regenerant. The regenerant and rinse streams are purified and/or concentrated in situ using nanofiltration or reverse osmosis techniques and returned for reuse. Two low volume nanofiltration concentrate streams will be produced which can be further treated by evaporation.
- Brine reclamation and reuse was studied (Burton and Kreusch, 1974) at a regeneration plant for ion exchange water softeners. The process was a modified lime-soda softening process which produced a sodium chloride brine of 95% purity at 160 g/ℓ. This brine was suitable for reuse as a regenerant brine after neutralisation with HCl. The lime-soda softening sludge, the volume of which was 11% of the waste brine, was the only waste.

## 7 REFERENCES

Marriot, J.N. and Brand, J.J., Disposal of Saline Waste Waters at SASOL Two and Three. Paper Presented at Symposium on Desalination: New Developments and Industrial Application, CSIR Conference Centre, Pretoria, 27 October 1983.

Burton, J. and Kreusch, E., Industrial Water Softener Waste Brine Reclamation. U.S. EPA Project No. 12120 GLE, Report EPA-660/2-74-007, February 1974.

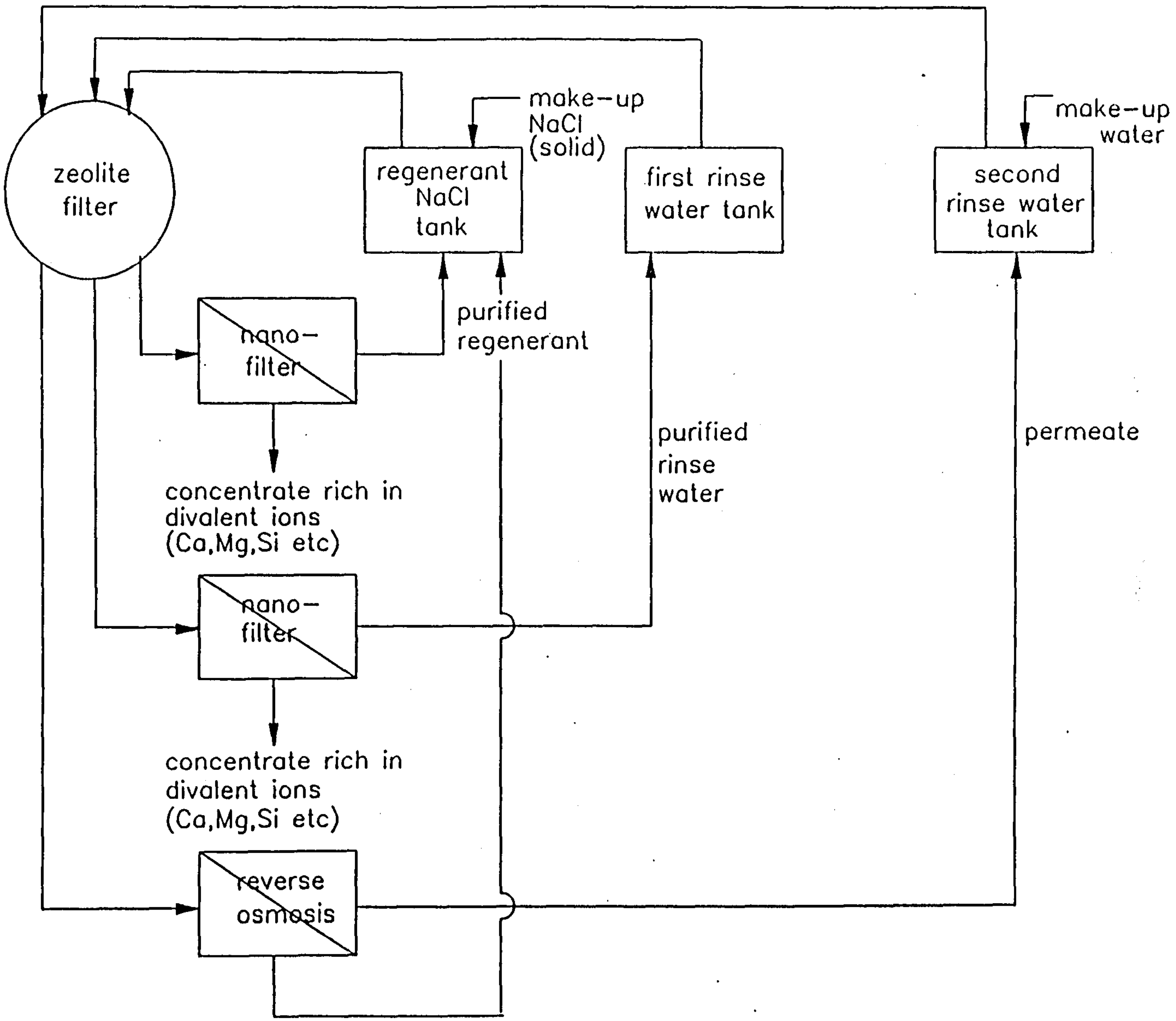


FIGURE 5 : Direct Reuse of the Zeolite Regenerant Streams