WATER RESEARCH COMMISSION PROJECT NO. 201

THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

APPENDIX 6

The Recovery and Reuse of Sodium Hydroxide from Industrial Effluents

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SUMMARY

A process sequence has been developed to recover chemicals, water and heat energy from historically problematic sodium hydroxide containing effluents. The sequence combines neutralisation together with three standard membrane techniques, cross-flow microfiltration, nanofiltration and electrochemical recovery, in a novel arrangement which is economically viable and which assists in pollution abatement. In addition, the inclusion of either reverse osmosis or evaporation as an effluent concentration step is discussed.

The process separates and concentrates the effluent to produce

(i) sodium hydroxide of suitable quality and concentration for reuse (100 to 200 g/ℓ).

(ii) reusable water.

(iii) hydrogen and oxygen gases.

(iv) two low volume organic concentrates.

Results of pilot plant trials and some data for the design of a full scale plant are given.

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1 INTRODUCTION

The quality of South Africa's major water resources supplying the main industrial and economic centres of the country has gradually deteriorated with respect to salinity. The disposal of saline effluents is strictly controlled by discharge regulations and industry is under considerable pressure to desalinate wastes containing a high total dissolved solids (TDS) particularly where the impact of the type and amount of salinity on receiving water quality and river ecology is serious.

Sodium hydroxide is used extensively in various applications such as ion-exchange resin regeneration and in the pulp and paper, textile, fruit and vegetable and bottle washing industries. The total South African market is in the region of 260 000 tons per annum of 100% NaOH.

The discharge of sodium hydroxide containing effluents into the water system prejudices the potential for reuse of the water. In South Africa, discharge of these effluents into the marine environments and into solar evaporation dams is practised.

The treatment and recovery of sodium hydroxide from effluents containing the chemical is not only desirable in terms of pollution abatement, but also in terms of the potential value of the waste constituents; water, heat energy and sodium hydroxide.

The Pollution Research Group, at the University of Natal, has developed a treatment sequence, consisting of neutralisation, cross-flow microfiltration, ultrafiltration using charged membranes (nanofiltration) and electrochemical recovery, for reuse of sodium hydroxide containing effluents (1-3). Applications of this process in the textile and bottle washing industries have been considered, but the process may be adapted to treat other sodium hydroxide wastes.

2 PROCESS DEVELOPMENT

In the development of a process for the treatment of sodium hydroxide effluents, the objective was the closed loop recycle of water, chemicals and heat energy. Such a system would require the separation of the effluent into its three components; water, sodium hydroxide and an impurity fraction. Figure 1 illustrates the process.

The process involves:

(i) neutralisation using carbon dioxide gas, which is essential in the case where conventional membranes are to be used for separating impurities from the effluent.

(ii) cross-flow microfiltration (4) to remove suspended, colloidal, particulate, complexed and waxy contaminants.

(iii) nanofiltration to remove soluble impurities including organics, colour and polyvalent inorganic ions.

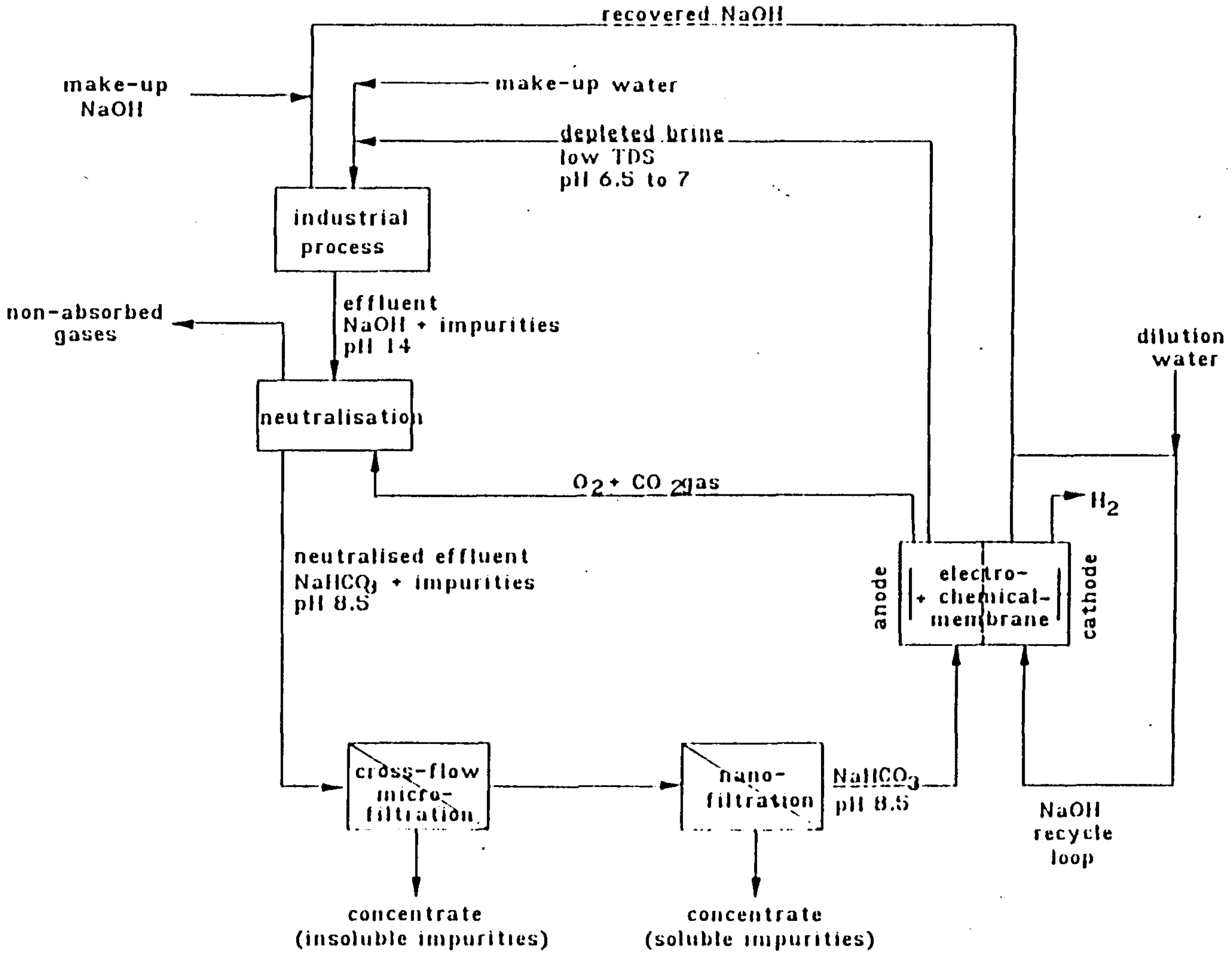

Figure 1 : Schematic of Sodium Hydroxide Recovery Process

(iv) electrochemical depletion of the sodium salt in a membrane stack with the recovery of sodium hydroxide and carbon dioxide. The carbon dioxide is recycled within the treatment process; the recovered sodium hydroxide and the depleted brine are recycled for reuse in the industrial process.

PROCESS CHEMISTRY

Carbonate Chemistry

The successful application of the process is dependent, to a large extent, on the chemistry of the carbonate species in solution. Figure 2 shows the various ionic species co-existing in carbonate solutions at a range of pH values.

Absorption of carbon dioxide gas by a hydroxide solution reduces the pH of the solution with the formation of carbonate ions. As more carbon dioxide is absorbed, bicarbonate ions are formed. These ions predominate in solution between pH values of 10,5 and 6,5. Below a pH value of 8,6 the bicarbonate ions exist in equilibrium with dissolved carbon dioxide or carbonic acid.

Neutralisation

The neutralisation reaction, in which hydroxide species are converted to bicarbonate ions, proceeds rapidly and efficiently due to the chemical absorption of carbon dioxide. The pH of the neutralised effluent should be controlled at pH 8,5 to 8,6. At this pH value bicarbonate ions are the predominant species, at lower pH values carbon dioxide is not absorbed efficiently.

Neutralisation of sodium hydroxide effluents may result in the formation of suspended matter, which is soluble at high pH values but which becomes insoluble as the effluent is neutralised.

Cross-flow Microfiltration

Cross-flow microfiltration is a pressure driven filtration process in which the direction of product flow is perpendicular to the direction of feed flow. The support may be a woven tube, with or without a filtration precoat laid down from a slurry of kaolin, limestone or bentonite.

Cross-flow microfiltration removes all turbidity from the effluent. In general substances such as waxes, colloidal and suspended material and particles are retained. In addition, interactions of some inorganic species, either with the suspended and colloidal organics or with the precoat, result in their preclusion from permeating the filter.

Nanofiltration

The nanofiltration membrane is a negatively charged ultrafiltration membrane which selectively rejects organics on a size exclusion basis and inorganics on a charge discrimination basis (5). Monovalent ions, of low charge density, permeate the membrane but divalent and polyvalent ions are excluded.

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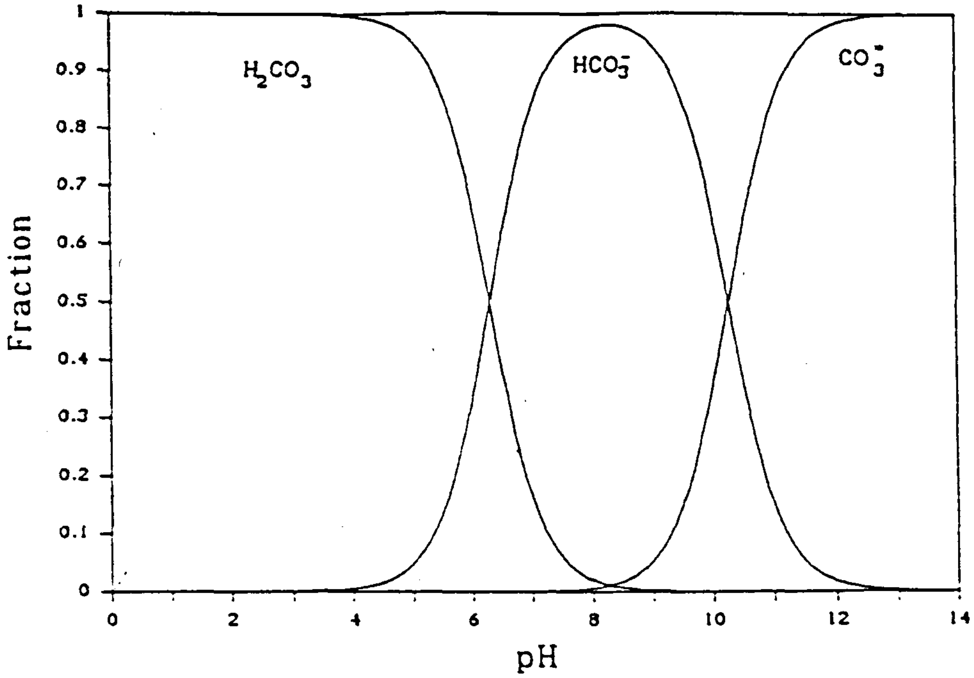

Figure 2: Distribution of Inorganic Carbon Species with pH

The unique exclusion properties of this membrane allow its performance against some ionic solutions to be tailored in such a way as to enable either their permeation or their exclusion. In the application under consideration, nanofiltration is used as a softener for the separation of divalent hardness ions from the monovalent sodium species.

The control of the pH of the nanofiltration feed is the major factor determining the effectiveness of the desired separation (6). At pH 8,6, sodium ions and bicarbonate ions pass through the membrane and are recovered in the permeate stream. If the pH of the feed is allowed to increase above 8,6 monovalent bicarbonate ions are converted to divalent carbonate ions. The carbonate ions are excluded and the requirements of electroneutrality prescribe rejection of sodium, thus lowering the potential for its recovery and conversion to sodium hydroxide. The nanofiltration membrane rejection performance, as a function of feed pH and concentration is illustrated in Figure 3 (6).

The removal of impurities, particularly calcium and magnesium, from the effluent during pretreatment is very important since these elements are potentially scaling to the membrane in the electrochemical recovery stage.

3.5 Electrochemical Recovery

The chemistry of the electrochemical recovery stage is shown in Figure 4. The anode and cathode compartments are separated by a highly selective cation permeable membrane. Under an applied potential:

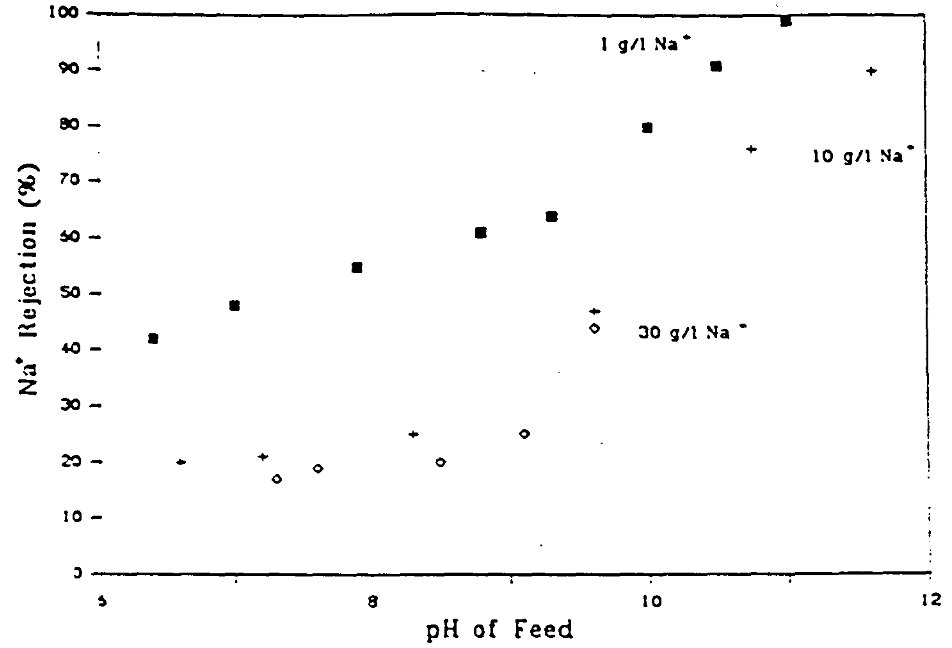

Figure 3: Nanofiltration Performance : Dependence of Rejection on pH and Concentration

(i) the sodium bicarbonate salt in the pretreated effluent which is passed through the anolyte compartment is split and the sodium ions migrate into the catholyte.

(ii) water is reduced at the cathode and hydrogen gas is liberated.

(iii) water is oxidised at the anode and the resulting acidity in the anolyte causes a shift in the equilibrium of the carbonate species with the release of carbon dioxide gas, which is recycled to the neutralisation stage.

4 EXAMPLES OF INDUSTRIAL APPLICATIONS

4.1 Treatment of Cotton Scour Effluent

In the textile industry the non-cellulosic contaminants of cotton are removed from the fibre during a process known as scouring. Scouring involves the saponification of the waxes, pectins and other contaminants using sodium hydroxide. A large fraction of the sodium hydroxide used is not consumed in the chemical reaction and is washed from the fibre after scouring. The effluent so produced contains approximately 25 g/ℓ NaOH and 20 g/ℓ chemical oxygen demand (COD). Typically it constitutes 10% of the volume of the total factory discharge and contains 20 to 25% of the pollution load of the total factory discharge.

4.1.1 Pilot Plant Results

Pilot plant trials at a local factory indicated that the process could be successfully implemented for the treatment of cotton scour effluent. Typical results are given in Table 1.

Neutralisation converted the hydroxide ions in the effluent to bicarbonate ions and lowered the pH to 8,6.

Cross-flow microfiltration removed approximately 30% of the total solids and 60% of the chemical oxygen demand from the neutralised effluent. Limestone was the most favourable precoat in terms of flux and rejection performance. Using a limestone precoat, fluxes were high (50 ℓ/m²h, 25°C, 300 kPa) and the flux decline was minimal. Rejections of calcium were above 90% and the magnesium concentrations were reduced to below 2 mg/ℓ. Waxy and colloidal deposits on the tubes were successfully removed by rinsing with a solution of sodium hydroxide and process detergent.

The nanofiltration membrane used was a spiral wrap type manufactured by FilmTec (FT40). The flux and rejection performance of the nanofiltration membrane was dependent on pH. The fluxes were increased eight fold, from 4 ℓ/m²h to 30 ℓ/m²h (1 MPa, 28°C), when the pH of the feed was lowered from 9,7 to 3,0. This was a result of an increase in the permeation of ionic species through the membrane at lower pH values, which lowered the osmotic pressure gradient across the membrane. Nanofiltration removed all the residual colour from the effluent and further lowered the calcium and magnesium ion concentrations. When the pH of the feed was maintained between 8,0 and 8,5, approximately 90 to 95% of the sodium could be recovered in the permeate. No membrane fouling was observed.

<u>TABLE 1 : Typical Results of the Pilot Plant</u>

Analysis		Scour effluent	After neutralisation	After CFMF	After NF	After electrolysis	Recovered NaOH
pH		13,5	8,6	8,4	8,6	5,5	14,0
Total carbon	g/ℓ	6,8	13,4	13,0	10,0	0,4	-
Inorganic carbon	g/ℓ	0,4	7,3	7,8	8,8	0	-
Organic carbon	g/ℓ	6,4	6,1	5,2	1,2	0,4	-
Chemical oxygen demand	g/ℓ	14,0	14,0	9,0	0,5	0,5	-
Hydroxide	g/ℓ	7,0	0	0	0	0	70,0
Carbonate	g/ℓ	4,4	1,9	2,0	3,4	0	1,5
Bicarbonate	g/ℓ	0	27,4	28,0	19,6	0	0
Sodium	g/ℓ	14,0	14,0	14,0	12,2	0,3	97,0
Calcium	mg/ℓ	45	45	3	2	2	-
Magnesium	mg/ℓ	7	7	2	1	1	-
Total solids	g/ℓ	37	37	34	-	0,5	-

The combined pretreatment sequence lowered the chemical oxygen demand of the effluent by 85 to 90% and removed over 95% of the calcium and magnesium.

The cation exchange electromembrane used in the electrochemical recovery stage was manufactured by Du Pont Co. (Nation 324). The composition of the depleted brine solution produced in the electrochemical cell was a function of the degree of electrolysis. The sodium concentration could be depleted to 500 mg/ℓ, with a 98% recovery of sodium as sodium hydroxide. The pH of the brine at this level of depletion was 5,5.

At optimum operating conditions, the sodium could be recovered at a 70 to 80% current efficiency and at a power consumption of 3 500 kWh/ton 100% NaOH. Maximum current efficiency was maintained by ensuring that polarisation was prevented by operation of the cell stack below the limiting current density. The current density is a function of the electrolyte flows and conductivities, the latter being dependent on temperature.

The experimentally determined correlation between the limiting current density and the temperature corrected conductivity was:

$$\lim i(T) = 26\,A/Sm \times conductivity(T)$$

where the conductivity is in S/m and the limiting current density (i) is in A/m^2.

Operation of the cell at current densities above the limiting value caused polarisation at the anolyte surface of the electromembrane. This in turn created an alkaline environment in the vicinity of the membrane resulting in calcium carbonate deposition. The scale was removed effectively by acid flushing and the electromembrane performance was restored to its original levels.

Although the anolyte concentration of calcium and magnesium was an order of magnitude greater than those recommended by the manufacturers of the membrane, fouling was minimal. It is hypothesised that the chelation of the ions by small organics in the industrial effluents prevent their migration in the presence of an electric field.

4.1.2 Plant Design

In the full scale design of an electrochemical recovery system to treat scour effluent, an evaporation stage has been incorporated to concentrate the scour effluent by a factor of four prior to treatment by the proposed process. The mass balance of the proposed system is illustrated in Figure 5.

The membrane area requirements for the design example are:

(i) cross-flow microfiltration (35°C) : 14 m^2.

(ii) nanofiltration (35°C) : 8,5 m^2.

(iii) electrochemical recovery (70°C) : 7 m^2.

The process is designed to recover 75% or (0,3 tons/day) of the sodium hydroxide in the effluent and 95% of the water.

Finally pilot plant evaporation trials have indicated that fouling of the heat exchange surface during concentration of scour effluent does not occur.

4.2 Treatment of Bottle Washing Effluent

The bottle washing process involves contacting the bottles with a sodium hydroxide solution for five minutes at a concentration of 25 g/ℓ. Some sodium hydroxide is carried over on the bottles to the rinse range. Typical bottle washing effluent contains up to 1 500 mg/ℓ of sodium in the form of sodium hydroxide and sodium and carbonate.

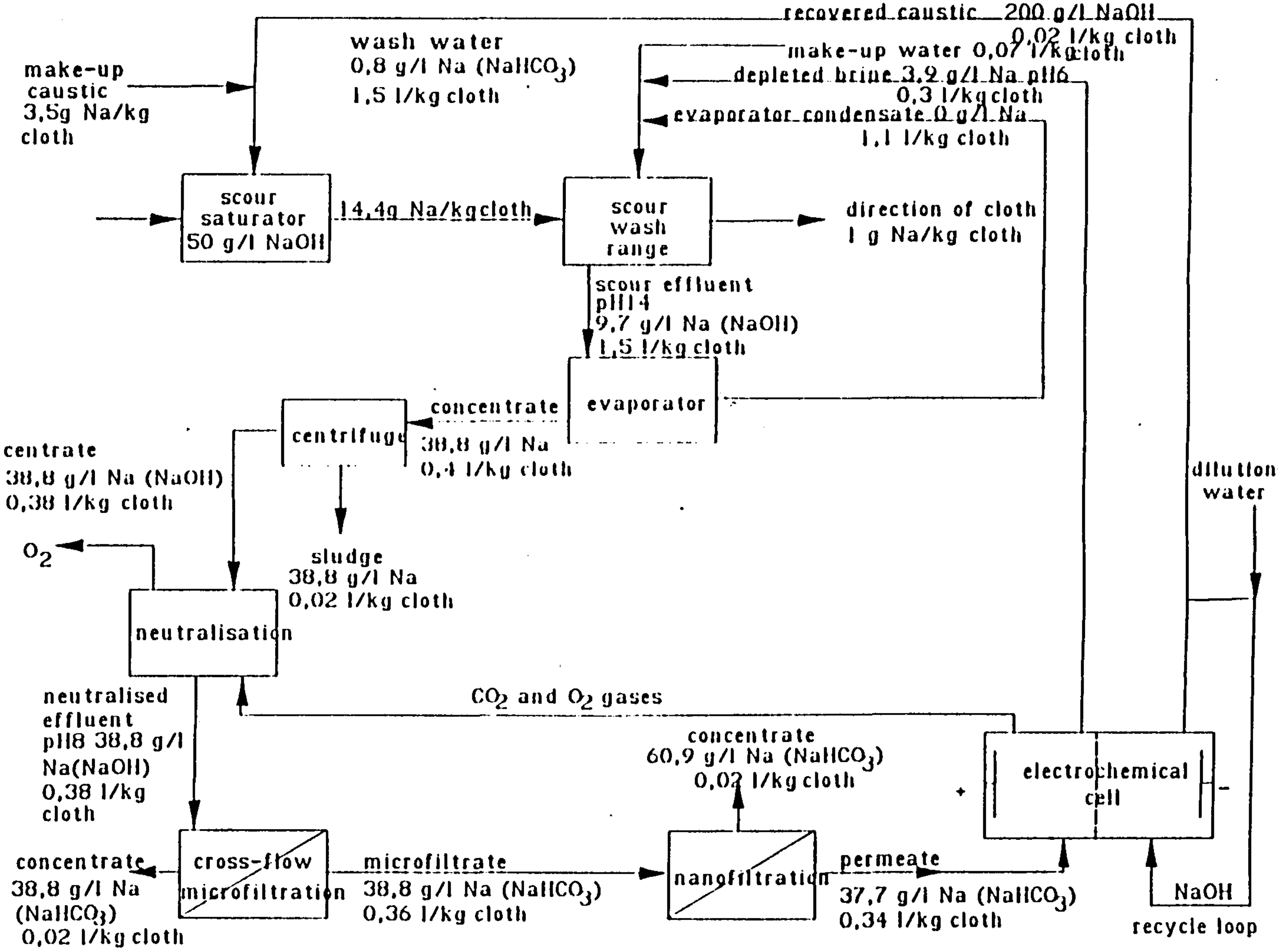

Figure 5 : Mass Balance of Recycle Process

The treatment of bottle washing effluent (7) for the electrochemical recovery of sodium hydroxide includes an additional reverse osmosis stage, after nanofiltration, to increase the concentration of the pretreated effluent to a level suitable for electrochemical processing.

Pilot plant trials are being conducted to evaluate the performance of the process for the treatment of this effluent.

5 PROCESS ADVANTAGES

The process makes indirect use of available and standard water treatment and industrial technologies, combining these technologies in a novel fashion to enable the recovery of water, chemicals and heat energy from an historically problematic type of effluent.

The process recovers sodium hydroxide at a suitable concentration for reuse, is economically viable and aids in pollution abatement.

The oxy-alkali electrochemical stage is an adaptation of chlor-alkali technology. The standard method for salt purification using lime soda softening and ion exchange has been replaced by two membrane techniques: cross-flow microfiltration and nanofiltration. The rejection of hardness ions by cross-flow microfiltration and nanofiltration is enhanced by the presence of sequestrants. Although calcium and magnesium concentrations in the electrochemical unit feed are not as low as are obtained by conventional pretreatment, fouling is controlled by the prevention of polarisation and by the presence of sequestrants.

6 ACKNOWLEDGEMENTS

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