

WATER RESEARCH COMMISSION PROJECT NO. 201

THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

APPENDIX 17

Caustic Recovery from Bottling Plant Effluent

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Abstract

The treatment process employed by most bottle washing plants for the recovery and recycle of water from sodium hydroxide bottle washer effluent involves filtration, activated carbon adsorption and ion exchange. The major disadvantage of the ion-exchange system is that the total dissolved solids load in the final discharge is actually increased above that of the effluent due to the regeneration chemicals.

An alternative treatment process for the recovery and recycle of water from bottle washer effluent has been proposed and involves filtration, carbonation and reverse osmosis. In addition a final stage involving the electrolysis of the reverse osmosis brine concentrate in an electrochemical membrane cell has been proposed. This will allow for the recovery and reuse of the sodium hydroxide and will minimise the total dissolved solids which are discharged to the wash drain.

Investigations, reported elsewhere, on the use of electrochemical techniques for caustic recovery from textile effluents have been successful. It is suggested that similar techniques used for the treatment of bottle washer effluent will be successful. The technical operating parameters and the economics of the process are therefore not discussed in this paper.

Introduction

South Africa is a water-scarce country that faces two major water-related problems, viz. a critical water shortage by the year 2020 AD; and the salination of existing water supplies due to the discharge of industrial contaminants into our waterways (Kriel, 1975).

The Water Research Commission has since 1971 sponsored research in connection with water management and effluent treatment, in order to assist industry and protect the quality of our water resources. This has led also to the development of groups/research centres with expertise in the treatment of industrial effluents, such as the Pollution Research Group at the University of Natal. Emphasis has been placed on the total recycle of effluents, in which water is recovered and purified for reuse; and processing chemicals are separated from effluents for reuse, thus eliminating or significantly reducing the unnecessary discharge of total dissolved solids to waste drains.

The Coca-Cola Export Corporation** is extremely conscious of environmental and water quality protection and has developed and installed treatment methods for the recovery and reuse of water from processing streams within bottling plants. At a number of bottling units, the waste-water recovery and reconditioning plants involve the use of ion-exchange systems. Strong acid is used to regenerate the cation-exchange resin resulting in an increase in total solids leaving the factory site. More recently a system has been installed at a bottling plant involving carbonation of the effluent, ion exchange and regeneration with brine (Preston-Whyte, 1986).

The Pollution Research Group was approached to examine additional water and chemical recovery potential at various bottling plants in South Africa. After initial examination of effluent arisings at two bottling plants, the Pollution Research Group selected bottle washer effluent for further investigation since the discharge of this effluent constitutes an important stream from the point of view of volume and total dissolved solids content.

Typically, effluent produced from the bottle washer comprises 75 to 85% of the total bottling plant effluent. Of particular

importance to bottling plants is the sodium ion concentration in this effluent stream, since there exists the potential for the recovery and reuse of both water and sodium hydroxide.

The bottle washing process

During bottle washing, process conditions specified by the Coca-Cola Export Corporation are followed to ensure that washed empty bottles are clean, sterile and sodium hydroxide free. Fig. 1 shows the general flow diagram for a typical bottle washing machine and reclamation plant. Essentially, in the bottle washing machines, the bottles are prewarmed before entering the sodium hydroxide tanks where contact is made with the sodium hydroxide solution for 5 min at a concentration of 2.5% NaOH at 60°C or 3.0% NaOH at 57°C.

Some sodium hydroxide is dragged out on the bottles to the rinse range. The approximate carry-over in a typical bottle washing plant handling 30 000 cases/d (8 to 24 bottles/case depending on bottle size) is equivalent to 1 to 2 t of 100% NaOH per week. The spread of results of analysis of the two rinse-water streams from a bottle washing plant over 15 d is given in Table 1.

Table 1 also contains the results of the analysis of samples of the 'clean' effluent taken from a buffer tank over ten days, which show a much smaller spread and would be more representative.

The specific water usage during washing varies from 1.5 to 4 l/litre bottle depending on the age of the bottling plant. The caustic/detergent consumption is between 1.5 and 2.0 g/litre bottle. The chemical contribution to the total dissolved solids (TDS) of the effluent is approximately 1.1 g/l. The bottle washer effluent is the major contributor to the TDS load in the final plant effluent, hence treatment is desirable.

The Coca-Cola Export Corporation has taken action to recover water for recycling by the installation of ion-exchange water recovery units. Approximately 80 to 85% of the bottle washer effluent is processed in the recovery unit. The remaining 15 to 20% from the initial rinsing is discharged to the waste drain. The recovery process consists of sand and carbon filtration, followed by ion exchange. The ion-exchange system is used to neutralise the effluent prior to reuse. Unfortunately, however, the ion-exchange system does not reduce the total dissolved solids load in the resulting effluent to drain, but in fact increases the load due to the regeneration chemicals used in the system.

The Pollution Research Group has undertaken preliminary investigations into the treatment of bottle washer effluent by ex-

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** Now known as The National Beverage Services.

TABLE 1
SPREAD OF RESULTS FOR SAMPLES FROM BOTTLE WASHING MACHINES

Analysis		'Unclean' 15% from initial rinsing.	'Clean' 85% from final rinsing	
			Spot samples	Buffer tank samples
pH		13 - 10,2	12 - 9,3	11,1 - 10,7
Conductivity	(mS/cm)	75,6 - 0,55	6,35 - 0,30	1,63 - 0,55
Total organic carbon	(mg/l)	3 600* - 19	343 - 11	56 - 15
NaOH	(mg/l)	14 000** - 0	1 375 ** - 0	38 - 0
Na ₂ CO ₃	(mg/l)	22 557** - 93	806 - 8	416 - 42
NaHCO ₃	(mg/l)	1 109 - 0	66 - 0	104 - 0
Na	(mg/l)	10 900 - 40	1 158 - 3	230 - 18
Calcium	(mg/l)	22,2 - 3,2	22,2 - 3,0	10 - 4,3
Magnesium	(mg/l)	2,2 - 0	2,7 - 0	1,6 - 0

* Several bottles contaminated by a hydrocarbon such as paraffin on one day

** Unusually high values

aming the application of technologies which are alternatives to ion exchange and which do not add to the total dissolved solids content of the discharge in the manner in which an ion-exchange system does.

Description of proposed treatment process

The proposed sequence for the treatment of the 80 to 85 % fraction of the bottle washer effluent is shown in Fig. 2. The sequence involves the recovery and recycle of water and chemicals from the sodium hydroxide effluent stream and comprises:

- filtration and activated carbon adsorption to remove suspended and organic matter and residual chlorine;
- carbonation to reduce the alkalinity;
- reverse osmosis with the production of high quality water; and
- electrolytic recovery of sodium hydroxide from the reverse osmosis concentrate.

Each of the above unit operations is described more fully below.

Filtration

The existing filtration procedure will still be applicable. The sand/anthracite filters will remove suspended solids and the carbon filters will remove residual chlorine and organic matter.

An alternative pretreatment stage of cross-flow microfiltration (Groves *et al.*, 1985) could be investigated as a replacement for the sand/anthracite and carbon filter combination in new recovery plants.

Carbonation

The principle objective of the carbonation stage of the process sequence is to reduce the hydroxide alkalinity of the filtered sodium hydroxide effluent stream.

The high pH of any sodium hydroxide or sodium carbonate solution prevents the use of concentration processes based on the conventional membrane technologies of reverse osmosis and electrodialysis because of damage to the membrane at high pH values. Improved membranes are being developed in these areas.

However, if the pH of the effluent could be controlled below pH 10, then the concentration of the salts by such membrane processes would be possible and high quality water would be available for recycle.

Carbonation of the filtered effluent is achieved by contacting the effluent with carbon dioxide gas in an absorption column. Fig. 3 shows the distribution of species which are present in a carbonate solution at various pH values.

If a solution containing carbonate and/or sodium hydroxide is

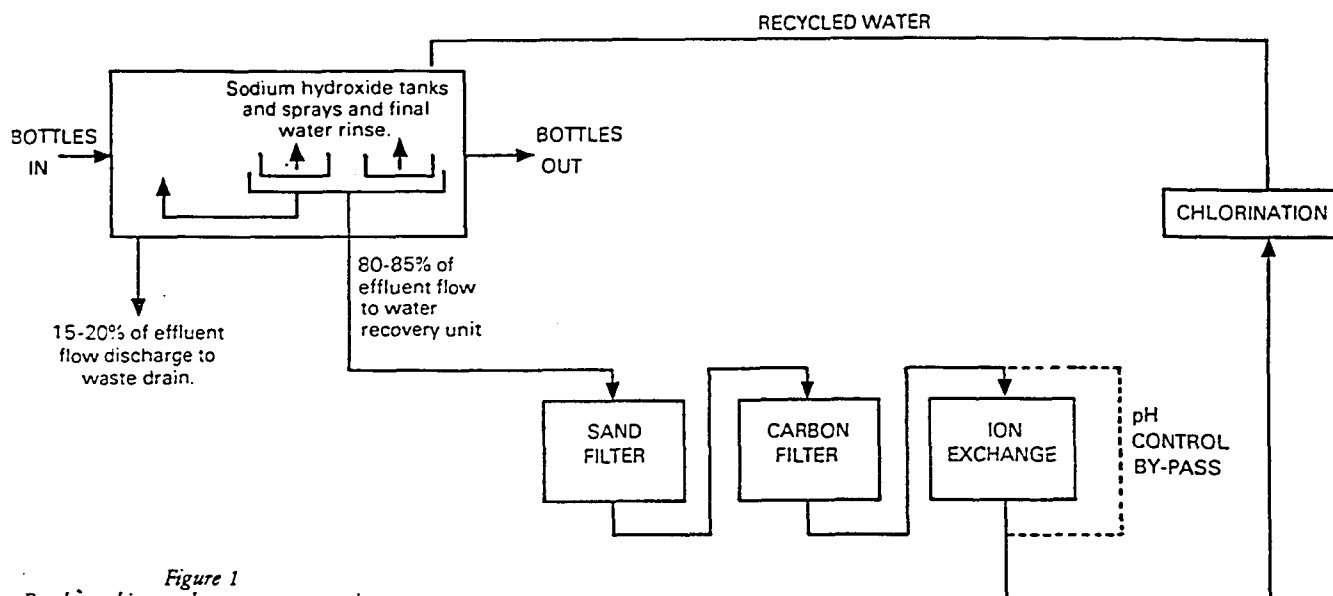


Figure 1
Bottle washing and water recovery units.

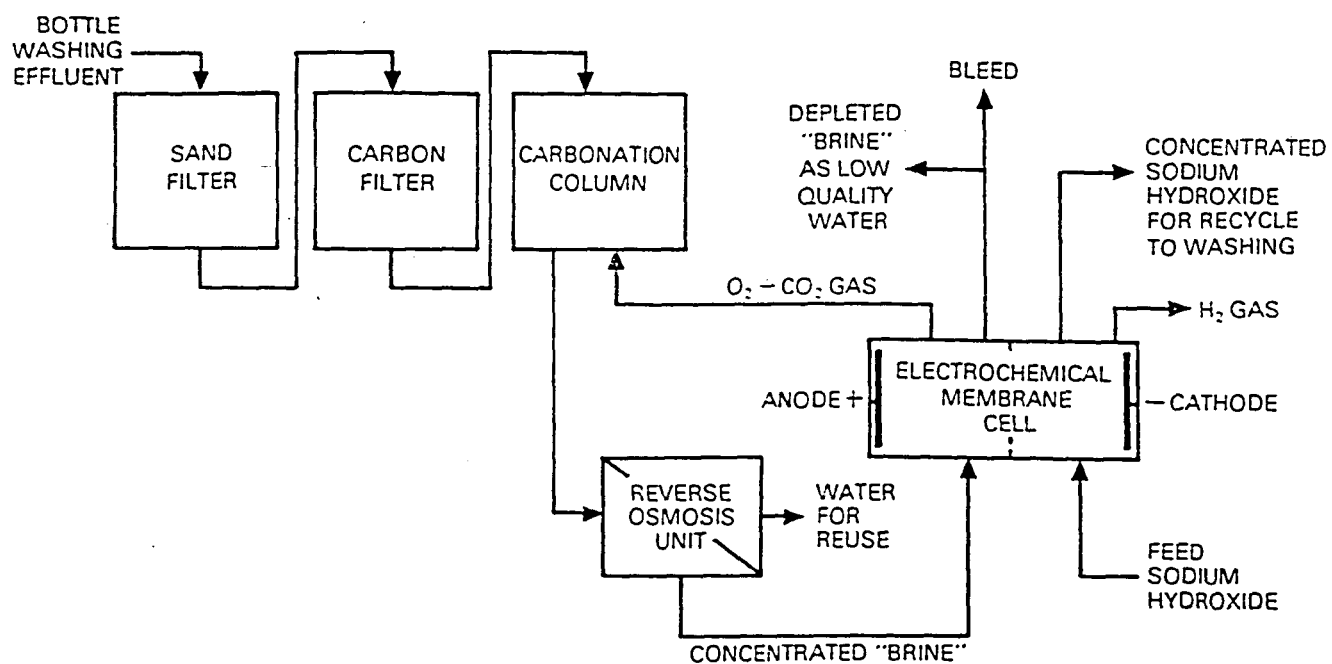


Figure 2
Proposed treatment of bottle washing effluent.

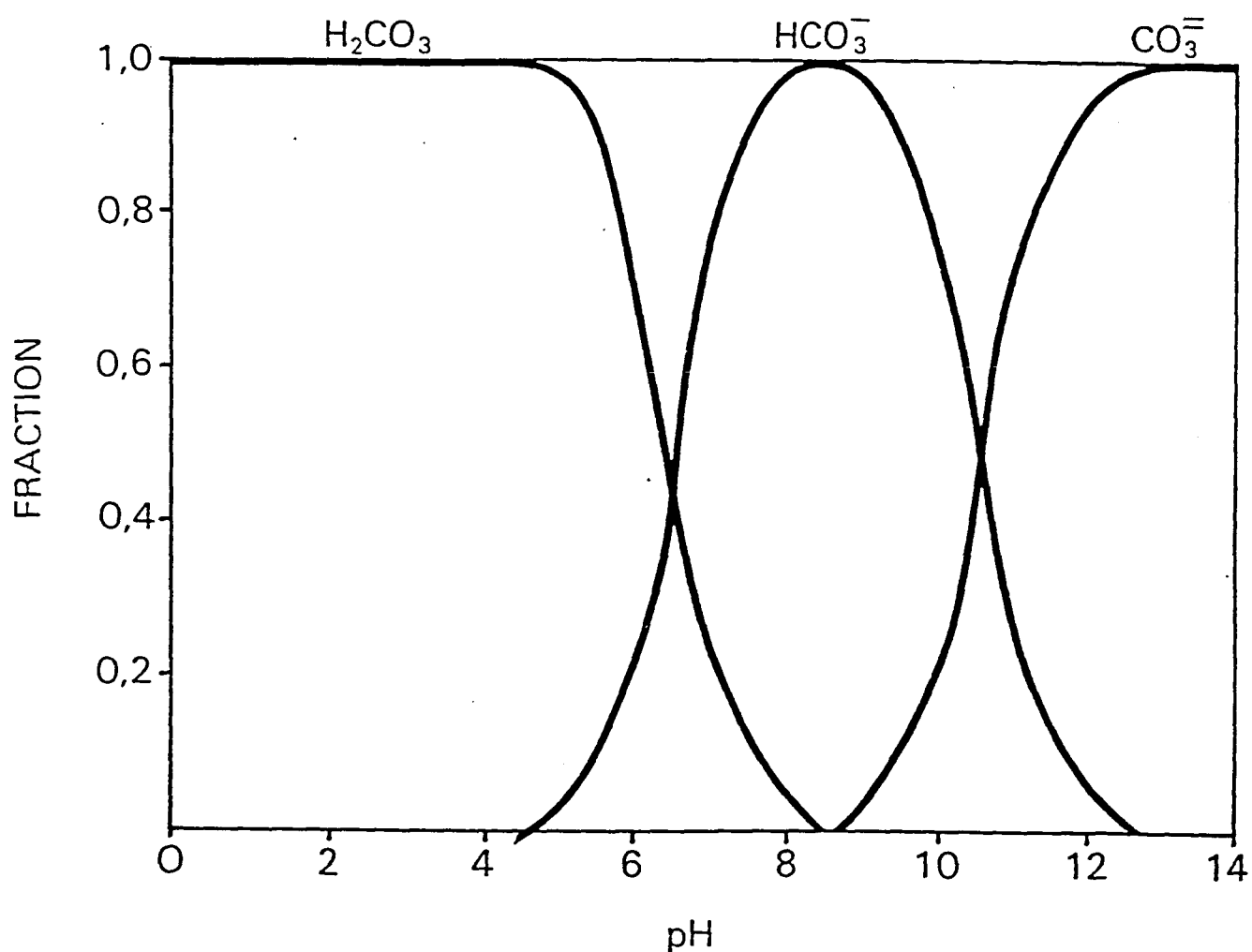


Figure 3
Distribution of carbonate species with pH.

carbonated by passing carbon dioxide gas into the solution, all the sodium will be in the ionic form while the 'carbon dioxide' will be either in the ionic form in solution or as carbon dioxide in water.

The amounts of H^+ , OH^- , CO_3^{2-} and HCO_3^- ions present and the amounts of CO_2 and H_2CO_3 present are regulated by the equilibrium constants.

Consideration of the theoretical aspects of the carbonate/bicarbonate/carbonic acid equilibrium together with consideration of the practical aspects of conventional membrane concentration techniques indicate that:

- Carbonation of the effluent to pH 9 would be optimum. Fig. 4, which has been constructed from equilibrium data (Harned and Davies, 1943; Harned and Scholes, 1941 and Wissbrun *et al.*, 1954) shows that at pH 9 the ratio of $CO_3^{2-} : HCO_3^-$ is 0.04 : 1 and that there is virtually no other form of inorganic carbon in the solution. At lower pH values free carbon dioxide is evolved causing unnecessary loss of carbon dioxide and pH changes on concentration; and
- Concentrations of carbonate effluent should be achieved using high-rejection reverse osmosis membranes which would not significantly alter the pH of the feed solution. If low-rejection membranes were used, bicarbonate ions would pass through into the permeate, increasing the $CO_3^{2-} : HCO_3^-$ ratio and causing a pH increase in the feed.

Reverse osmosis

Reverse osmosis is a pressure-driven membrane separation process which retains salts and most organics but allows water to permeate the membrane. In the envisaged process, a high volume stream of high quality water is produced which may be recycled to processing. The low volume concentrate, high in TDS (sodium carbonate and sodium bicarbonate) may be:

- discharged to drain; or
- passed to an electrochemical membrane cell where separation of the component ions occurs with the production of sodium hydroxide. The specialised membranes installed in electrolysis cells can be used in the presence of high concentrations of sodium hydroxide (5 to 35%)

Since the membrane electrolysis of concentrated solutions is more efficient than the electrolysis of dilute solutions, it is important that the pressure-driven membrane process should be operated to achieve as high a water recovery as possible without precipitation of either the carbonate or the bicarbonate species.

Membrane electrolysis

Fig. 5 is a diagram of an electrochemical membrane cell used for the electrolysis of a sodium carbonate/sodium bicarbonate solution.

In this system the anode and cathode compartments are separated by a cation-exchange membrane. The reverse osmosis brine concentrate is passed through the anode compartment where oxidation of water occurs, resulting in the evolution of oxygen and the simultaneous formation of hydrogen ions:



The increase in the acidity shifts the equilibrium of the solution in a direction which favours the release of carbon dioxide gas. This gas is used to neutralise bottle washer effluent in the absorption column.

During electrolysis sodium ions are transported through the

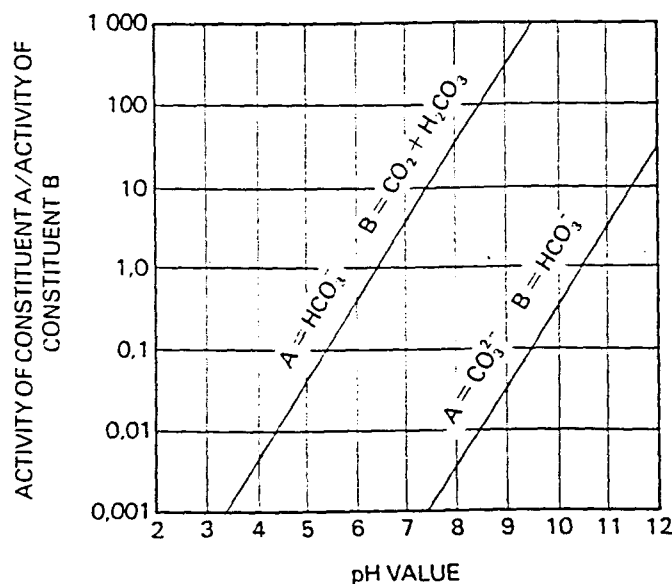
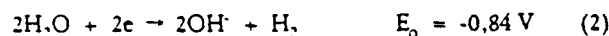


Figure 4
Fractional activities of carbonate species in solutions at 20°C.

membrane from the anode compartment to the cathode compartment where they combine with hydroxide ions formed by the reduction of water at the cathode:



Hydrogen gas is evolved from the catholyte and vented to the atmosphere.

The three main products of membrane electrolysis are:

- a neutral depleted brine solution for recycling as low quality process water;
- concentrated sodium hydroxide for recycling to the bottle washing process; and
- carbon dioxide gas for the neutralisation of filtered bottle washing effluent.

Conclusions

The integrated process, involving carbonation, reverse osmosis and membrane electrolysis (Fig. 2) will thus yield:

- high quality water for recycle;
- sodium hydroxide solution for recycle; and
- an effluent resulting from a bleed from the circuit to maintain low organic carbon in the liquors and an effluent resulting from batch washing of the filter circuit.

The bottle washer effluent is the major contributor to the TDS in the final plant discharge. It is estimated that the recovery and reuse of chemicals and water from this stream will significantly reduce the total pollution load from bottling plants.

The Pollution Research Group has been investigating the closed loop recycling of sodium hydroxide effluents since 1983. Two pilot plants have been successfully operated at factory sites for the recovery of sodium hydroxide from caustic textile effluents using the electrochemical membrane cell principle (Buckley and Simpson, 1986). Typical operating parameters of the electrochemical membrane cell are given in Table 2. Full-scale plants are being planned for installation during 1988.

No condition which will interfere with the successful applica-

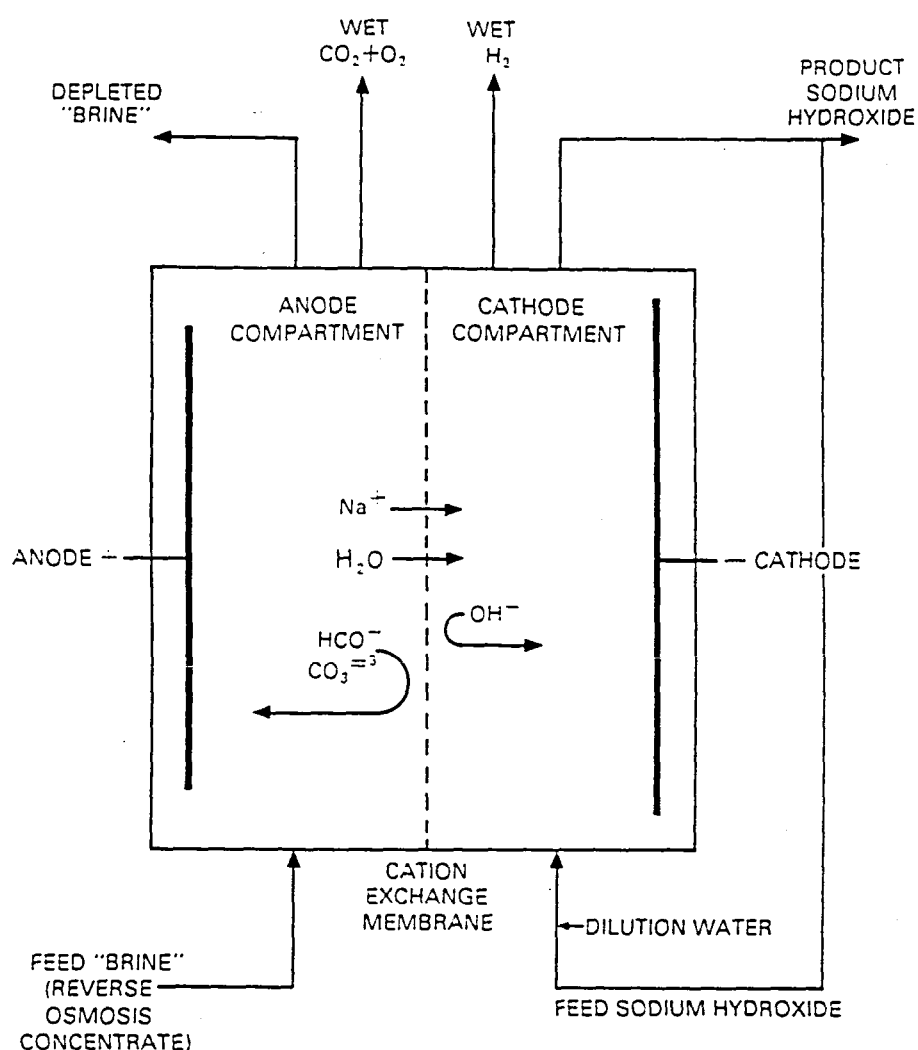
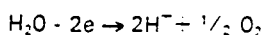


Figure 5
The electrochemical membrane cell.

Anode reaction



Cathode reaction

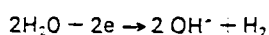


TABLE 2
TYPICAL OPERATING PARAMETERS FOR SODIUM
HYDROXIDE RECOVERY FROM TEXTILE WASTE
STREAMS USING A PILOT PLANT
ELECTROCHEMICAL MEMBRANE CELL

Parameter	Description
Cell type	Steedley DEM D2 (PVC frame), 0.1 m ²
Electromembrane type	Nafion 324 (Du Pont)
Operational mode	Batch from high anolyte concentration (12g/l Na ⁺) to low anolyte concentration (0.2 g/l Na ⁺)
Product sodium hydroxide	10 to 20%
Operating temperature	55°C
Potential	4 to 8 V per cell
Current density	Up to 6 000 A/m ²
Electrical current efficiency	60 to 80%
Electrical power requirement	4 000 kW.h/t 100% NaOH

tion of the electrolysis stage is envisaged for the carbonated bottle washer effluent. The effluents from textile scouring processes are extremely complex and the electrolysis stage on the carbonated effluent has operated successfully as indicated above.

Acknowledgements

The research work leading to the development of the electrochemical membrane cell method for the recovery and recycling of sodium hydroxide from caustic effluents was undertaken in terms of a contract with the Water Research Commission entitled Water Management and Effluent Treatment in the Textile Industry - Treatment of Scouring and Bleaching Effluents. The contribution by the management and staff of the Coca-Cola Export Corporation and its associated bottlers is acknowledged. An early draft of the paper was presented at the Coca-Cola Export Corporation Water Management Seminar, Johannesburg, 1986.

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