ELECTROCHEMICAL CONCENTRATOR FOR CAUSTIC CONCENTRATION

K ASOKAN AND S KRISHNAMURTHY

Chlor-Alkali Division, Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

10.5 lakh tonnes of caustic soda is produced in India based on the membrane cell technology. Though membrane cells require 700 KWh lesser electrical energy per tonne of caustic, they produce caustic of concentration 32-33 wt%, which has to be concentrated to 45-46 wt% to meet the needs of the consumers. Concentration is now being done by thermal evaporators. Every tonne of 32-33 wt% caustic requires 0.75 tonne of steam for concentration. 8 lakh tonnes of steam is being consumed per annum for this purpose. In the present paper an electrochemical concentrator is proposed to replace the thermal evaporators.

INTRODUCTION

Chlor-alkali industry is one of the major electrochemical industries in India. Present installed capacity for caustic soda production is 22.51 lakh tonnes per annum. During 1999-2000, 15.14 lakh tonnes of caustic soda and 13.33 lakh tonnes of chlorine were produced [1]. It is an energy intensive industry and consumes large quantities of both electricity and steam. 460 crore KWh electrical energy and 7.8 lakh tonnes of steam (equivalent to 2 crore KWh electrical energy) are used per annum. Hence development and implementation of any technology to reduce the electrical and thermal requirements of the chlor-alkali process would have a significant impact on the country's energy industry.

Two conventional processes are available for the electrolytic production of caustic soda and chlorine. They are the diaphragm cell process and the mercury cell process. Diaphragm cell process involves the carcinogenic asbestos as a separator, consumes more energy and produces a weak impure caustic liquor. Amalgam cells use the hazardous pollutant mercury as cathode but give high purity concentrated caustic at the expense of higher electrical energy. Due to increasing awareness for energy conserving and environment friendly technologies, expansion of existing caustic production facilities and new installations have been adopting the modern membrane cell technology only.

Diaphragm cells have been phased out of the Indian chlor-alkali scene recently. Even mercury cells are being replaced by membrane cells. Now 68% of caustic production in the country 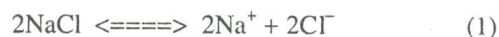is based on membrane cells. They account for 10.5 lakh tonnes of caustic per annum [1]. Though membrane cells require about 700 KWh lesser electrical energy per tonne of caustic, they produce caustic of concentration 32-33 wt% which has to be concentrated to 45-46 wt% to meet the needs of consumers. Concentration is now being done by thermal evaporators. Every tonne of 32-33 wt% caustic soda requires 0.75 tonne of steam for concentration. 7.8 lakh tonnes of steam is required for this per annum. In the present paper an electrochemical concentrator is proposed to replace thermal evaporators. Concentration of caustic by electrochemical means is achieved by coupling the membrane cell to a membrane alkaline fuel cell.

EXPERIMENTAL DETAILS

Chlor-Alkali Membrane Cell (CMC)

In the membrane Chlor-alkali cell [2], the cation exchange membrane separates the anode and cathode compartments (Fig. 1). Ultra pure brine fed to the anode compartment is electrolyzed to produce chlorine, which leaves along with depleted brine. 28-30 wt% caustic liquor is passed through the cathode compartment where water is reduced to produce hydroxide ions and hydrogen gas. The cation exchange membrane transports Na^+ ions from the anode to cathode compartment. Na^+ ions combine with hydroxide ions and NaOH is formed in the cathode compartment. 32-33 wt% caustic solution flows out of the cathode compartment.
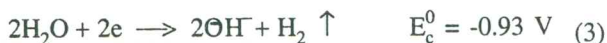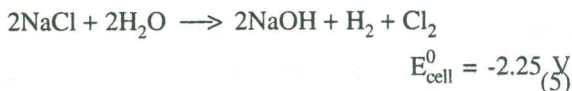
The electrode reactions are:

$$2NaCl \Longleftrightarrow 2Na^+ + 2Cl^- \qquad (1)$$

Anode

$$2Cl^- \longrightarrow Cl_2 \uparrow + 2e \qquad E_a^0 = -1.32 \text{ V} \qquad (2)$$

Cathode

$$2H_2O + 2e \longrightarrow 2OH^- + H_2 \uparrow \qquad E_c^0 = -0.93 \text{ V} \qquad (3)$$

$$2Na^+ + 2OH^- \longrightarrow 2NaOH \qquad (4)$$

Overall

$$2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2$$
$$E_{cell}^0 = -2.25 \text{ V} \quad (5)$$

Hence the products of the overall process are H_2, Cl_2 and NaOH.

Alkaline Fuel Cell (AFC)

Alkaline Fuel cell consists two gas diffusion electrodes - a porous hydrogen oxidation anode and a porous oxygen reduction cathode with gas chambers and a common electrolyte compartment (**Fig. 2**), filled with caustic solution. H_2 fed to the anode gas chamber diffuses through the porous anode and gets oxidised to water while oxygen from the cathode gas chamber diffuses through the porous cathode and gets reduced to hydroxide ions. The individual electrode reactions are:

Anode

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e \qquad E_a^0 = +0.83 \text{ V} \quad (6)$$

Cathode

$$(O) + H_2O + 2e \longrightarrow 2OH^- \qquad E_c^0 = +0.40 \text{ V} \quad (7)$$

Overall

$$H_2 + (O) \longrightarrow H_2O \qquad E = 1.23 \text{ V} \quad (8)$$

The reversible cell voltage of alkaline fuel cell is 1.23 V

Electrochemical concentrator (ECC)

It consists of an AFC with a Cation Exchange Membrane (CEM) placed between the gas diffusion anode and cathode (Fig. 3). 32-33 wt% caustic from the CMC enters the anode and cathode compartments of ECC. H_2 from CMC and oxygen from air react at the gas diffusion anode and cathode respectively.

The individual electrode reactions are:

Anode

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e \qquad (9)$$

Cathode

$$(O) + H_2O + 2e \longrightarrow 2OH^- \qquad (10)$$

Due to the presence of CEM, Na^+ ions flow from the anode to the cathode compartment. The consumption of water and generation of hydroxide ions at the cathode combined with the selective transport of Na^+ ions from anode to cathode compartment result in increasing the caustic concentration in the cathode compartment. Conversely generation of water at the anode and depletion of Na^+ ions through membrane transport result in diluting the anolyte stream. Concentrated caustic can be withdrawn as the product, while the depleted caustic may be recycled to the CMC.

Electrodes

Electrodes were porous gas diffusion electrodes, exposed to gas on one side and the electrolyte on the other. The electrodes were made up of very high surface area ($> 1000 \text{ m}^2/\text{g}$) activated carbon dispersed with finely divided electrocatalyst. Anode electrocatalyst was silver and cathode electrocatalyst was platinum. The performance of the electrocatalyst is affected by the choice of the carbon support, choice of catalyst, mechanism of
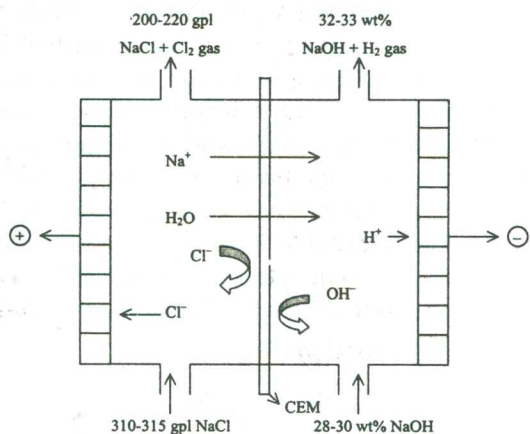

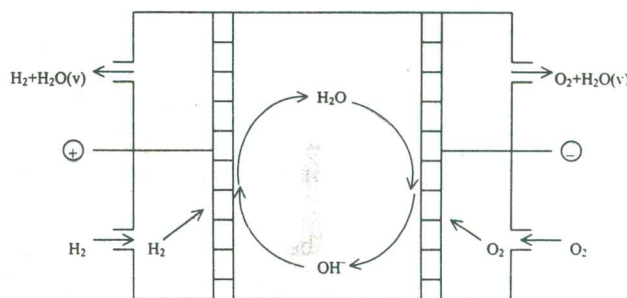
Fig. 1: Chlor-alkali membrane cell

Fig. 2: Alkaline fuel cell

catalyst dispersion, catalyst particle size and catalyst loading. Electrocatalyst was blended with a hydrophobic binder (PTFE), formed and sintered to yield the electrodes. The binder content, sintering temperature, catalyst loading and thickness also affect the performance of the electrodes. Normal catalyst loading ranges from 0.5-2 mg/ cm^2.

Cation exchange membranes

CEM consists of a perfluorinated carbon backbone structure for chemical stability with cation exchange groups attached. The cation exchange groups are carboxylic, sulphonic or a combination of both. Perfluorinated carboxlyate membranes exhibit excellent permselectivity but poor conductivity. Perfluorinated sulphonate membranes exhibit good conductivity but poor permselectivity. Recent membranes are bilayer membranes which combine the advantage of both the above types. They contain a thin carboxylate layer for permselectivity and a thick sulphonate layer for mechanical strength and optimum conductivity. For the present work, Dupont's bilayer membrane, Nafion 961 was used.

Techniques

A two compartment cell constructed entirely of teflon was used for determining IR drop across the CEM. The membrane was positioned between the two electrolyte compartments. Exposed area of the membrane was 10 cm^2. Anode and cathode compartments were filled with 32 wt% and 46% caustic solution respectively. A constant current was applied across the CEM through platinum screen electrodes using PAR 273 Potentiostat/Galvanostat. Potential drop across the CEM was measured as a function of current density using two Luggin capillary probes kept on either side of the membrane. These probes provided solution contact with dynamic hydrogen electrodes.

Sodium ion transport number and water transport properties of the CEM was determined in the ECC itself. Anode and cathode compartments were filled with caustic solutions of known flow rate and concentration. A constant current was applied to the cell for a definite time. The anolyte and catholyte effluent solutions were collected separately and their weights and concentrations were determined. From the electrolyte weight change, the concentration change and the amount of charge passed, sodium ion transport number and electroosmatic water flux (number of water molecules accompanying each sodium ion transported across CEM) were determined by a judicious material balance.

RESULTS AND DISCUSSION

The characteristics of the CEM affect the performance of the ECC. As in the case of CMC, the Na$^+$ ion transport and OH$^-$ ion rejection properties of the membrane determine the current efficiency of the ECC. Electroosmatic water flux from the anode to cathode compartment limits the caustic concentrating ability of the system. The variation of IR drop across the membrane with current density in a typical ECC is given in Table I and the same data is shown as a plot in Fig. 4. To enable ECC, to concentrate caustic, power output of the AFC should be atleast sufficient to compensate for the IR drop data across the CEM. The point of intersection of the membrane IR drop data and AFC performance data represents the operating current density that would result in zero net power. At higher current
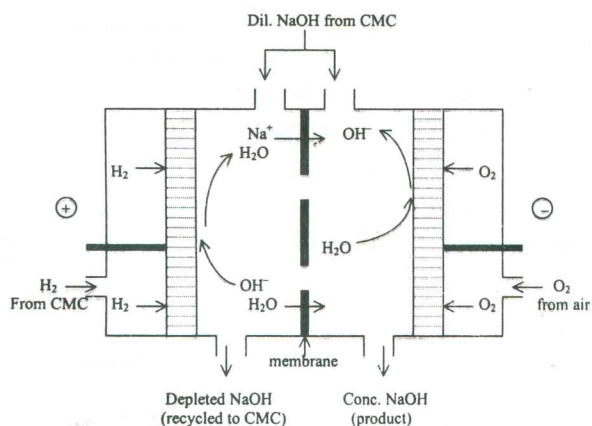

Fig. 3: Electrochemical concentrator

TABLE I: IR drop of CEM and power output of AFC vs current density

Current density (mA.cm^{-2})	Power output of AFC (mV)	IR drop of CEM (mV)
50	915	152
100	842	317
150	790	400
200	705	562
250	600	700
300	550	950

TABLE II: Operating data of ECC

Anolyte inlet		Anolyte outlet		Catholyte inlet		Catholyte outlet		t_{Na^+}	T_{H_2O}
Concn wt%	Feed rate ml/h	Concn wt%	Flow rate ml/h	Concn wt%	Feed rate ml/h	Concn wt%	Flow rate ml/h		
32	8.7	29.02	6.09	32	5.65	35.42	7.48	0.65	3.22
32	10.53	30.07	9.08	32	10.00	36.72	11.70	0.60	3.56
32	8.51	28.18	5.69	32	7.21	37.81	8.71	0.56	4.12
32	8.25	27.88	6.81	32	5.93	38.73	7.11	0.53	4.39
32	5.88	27.78	4.39	32	1.97	39.76	3.70	0.49	4.87
32	9.92	30.83	8.44	32	1.42	41.69	2.88	0.46	5.12
32	12.99	29.65	12.24	32	2.31	43.84	2.91	0.43	5.49

Catalyst loading - Anode: 1 mg/ cm^2 Pt; Cathode: 1 mg/ cm^2 Ag

Active area of electrodes - 21.72 cm^2 Current density: 200 mA/ cm^2

t_{Na^+} Sodium ion transport number T_{H_2O} Electroosmatic water flux

densities external power is required by ECC. At lower current densities, power is generated in addition to caustic concentration.

For the present studies, Nafion 961 membrane was used. Concentration of caustic fed to ECC was kept constant throughout at 32 wt%. The ECC was operated at different anolyte and catholyte feed rates. NaOH concentration in the anolyte outlet, catholyte outlet, Na^+ ion transport number, electroosmatic water flux, IR drops across the membrane were measured. Results are given in Table II. Anolyte outlet flow rate was found to be lower than feed rate, due to water molecules accompanying Na^+ ions transported across the membrane. Catholyte outlet flow rate was higher than the feed rate because of water molecules associated with Na^+ ions migrated through the membrane. Sodium ion transport number, electroosmatic water flux were dependent on anolyte and catholyte outlet concentrations. With increase in catholyte concentration, Na^+ ion transport number decreases most probably due to reduced OH^- ion rejection ability of membrane at higher hydroxide ion gradient across the membrane. On the other hand, transport number for water increases due to osmatic effect.

With Nafion 961 membrane, caustic could not be concentrated beyond 44 wt% and there was no power output from ECC. As Nafion 961, is as reinforced bilayer membrane, with sulphonic and carboxylic functional group on opposite sides, IR drop is higher and no dc power output can be expected. For concentration of caustic to 46wt% unreinforced sulphonic acid membrane has to be used.

CONCLUSION

Concentration of caustic without the expense of energy is possible with ECC. By proper selection of electrode materials, cation exchange membrane and operating current density, dc power can be generated in addition to caustic concentration.
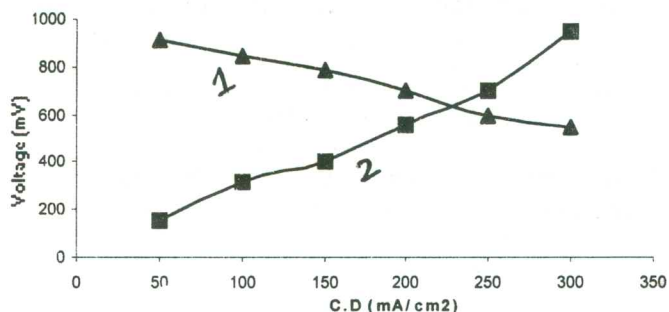
Fig. 4: Variation of IR drop of CEM and power output of AFC with current density
(1) Power output of AFC (mV)
(2) IR drop of CEM (mV)

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1. *Alkali Manufacturers' Association Annual Report 1999-2000*

2. S Krishnamurthy, V Arumugam, K Subramanian, K Asokan, P Subbiah and K I Vasu, *Bull Electrochem,* **6** (1990) 427