Simultaneous electrosynthesis of alkaline hydrogen peroxide and sodium chlorate

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Simultaneous electrosynthesis of alkaline hydrogen peroxide and sodium chlorate in the same cell was investigated. The alkaline hydrogen peroxide was obtained by the electroreduction of oxygen in NaOH on a fixed carbon bed while the chlorate was obtained by the reaction of anodic electrogenerated hypochlorite and hypochlorous acid in an external reactor. An anion membrane, protected on the anode side with an asbestos diaphragm, was used as the separator between the two chambers of the cell. The trickle bed electrode of dimensions 0.23 m high $\times$ 0.0362 m wide $\times$ 0.003 m thick was used on the cathode side. The anolyte chamber of the cell, 0.23 m high $\times$ 0.0362 m wide $\times$ 0.003 m thick was operated at a fixed anolyte flow of 2.0 $\times$ 10^{-6} m^3 s^{-1} while the oxygen loadings in the trickle bed was kept constant at 0.102 kg m^{-2} s^{-1}. Other operating conditions include inlet and outlet temperatures of 27-33° C (anode side), 20-29° C (cathode side), cell voltages of 3.0-4.2 V (at current density of 1.2-2.4 kA m^{-2}) and a fixed temperature of 70° C in the anolyte tank.

The effects of superficial current density, NaOH concentration (0.5-2.0 M) and catholyte liquid loadings (0.92-4.6 kg m^{-2} s^{-1}) on the chlorate and peroxide current efficiencies were measured. The effect of peroxy to hydroxyl mole ratio on the chlorate current efficiency was also determined.

Depending on the conditions, alkaline peroxide solution and sodium chlorate were cogenerated at peroxide current efficiency between 20.0 and 86.0%; chlorate current efficiency between 51.0 and 80.6% and peroxide concentration ranging from 0.069 to 0.80 M. The cogeneration of the two chemicals was carried out at both concentrated (2.4-2.8 M) and dilute (0-0.5 M) chlorate solutions. A relative improvement on the current efficiencies at concentrated chlorate was observed. A chloride balance indicated a less than 0.4% chloride loss to the catholyte. The results are interpreted in terms of the electrochemistry, chemical kinetics and the hydrodynamics of the cell.

Nomenclature

C_i concentration of species i (mol m^{-3})
F Faraday constant (96 500 C mol^{-1})

I current (A)
Q catholyte flow rate (m^3 s^{-1})
τ total time of cell operation (s)
η_i current efficiency of species i (%)

1. Introduction

Sodium chlorate and hydrogen peroxide are strong oxidizing agents used in pulp bleaching processes. While sodium chlorate is used in generating chlorine dioxide for the bleaching processes, greater use is now being made of alkaline hydrogen peroxide as both a brightening and extractive agent. Direct use of hydrogen peroxide is not limited to only mechanical pulps (for brightening purposes), but also it is used as a complement of chlorine dioxide (in chemical pulp bleaching) in one or more sequences [1].

At the low alkaline peroxide to caustic concentration ratio required for pulp extraction, an on-site generation of the peroxide can be considered as an alternative method of obtaining cheaper alkaline peroxide in pulp mills. Electrochemical reduction of oxygen in an alkaline solution not only produces

perhydroxyl (peroxy) ions, but also there is an increase in hydroxy ion concentration (i.e. the process is a net alkali producer, if anode reactions are disregarded). The typical reactions in a peroxide producing cell are given in Equations 1-3 (below). When the stoichiometry of oxygen reduction in an alkaline medium, Equation 1, is considered with anodic oxidation of chloride (which requires hydroxyl ion to maintain the desired pH for chlorate formation, Equations 5-10), a simultaneous production of alkaline peroxide in the cathode chamber and chlorate in the anode chamber of a divided cell seems an idea worthy of investigation. In such an arrangement, the cathode reactions of a traditional chlorate cell (Equations 11-13) are suppressed in favour of oxygen reduction for peroxide formation. Similarly, the anode reactions of a typical peroxide cell are prevented from occurring in preference to chlorine generation. The combined peroxide/

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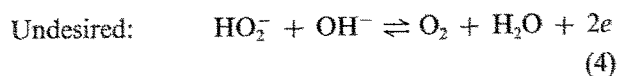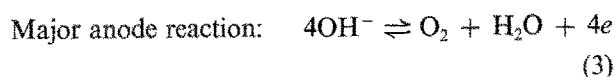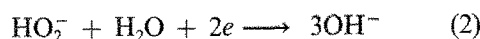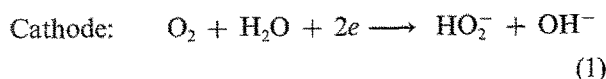
chlorate cell would involve Reaction 14 on the cathode for peroxide generation and Reaction 15 in the anode and associated recirculation tank for chlorate generation. An efficiency loss reaction in such a cell would involve Reaction 16 which may occur in the catholyte and/or anolyte chamber.

The simultaneous production of peroxide and chlorate in the same cell has been given little consideration according to the literature. It was only recently that a Japanese patent [2] was granted on such a process using an organic compound in the cathode of a divided cell. Although a simultaneous production of alkaline hydrogen peroxide and chlorate in the same cell is not a new principle of electrosynthesis, it is appealing and the principle could be applied to other electrochemical systems where one of the electrode reaction products is cheaper or less useful than the possible alternative reaction product.
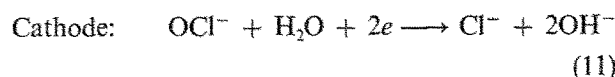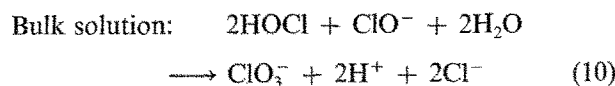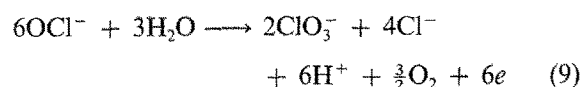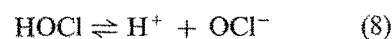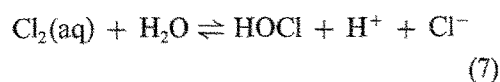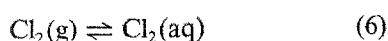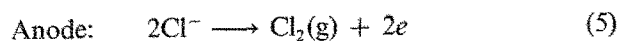
Problems in overcoming simultaneous production of alkaline hydrogen peroxide and sodium chlorate include the identification of an ideal long lasting separator that would selectively allow hydroxyl ion passage or transfer from the cathode to the anode side and be stable in the anode side oxidative hypochlorite/chlorate environment. The present work was undertaken to explore the possibility of making alkaline peroxide and sodium chlorate simultaneously in the same electrochemical cell using an anion selective membrane or an ordinary diaphragm separator. The primary factors for the process were investigated.

The use of an oxygen depolarized cathode in the chlorate synthesis could mean an energy reduction per ton of chlorate and the success of such a process could eliminate the use of chromate in chlorate generation at pulp mills generating chlorate on site. Depending on the NaOH feed concentration and net OH^- depletion due to transfer across the membrane, a weight ratio of $NaOH:H_2O_2$ of $2:1$ could be obtained and thus qualifies such alkaline peroxide for the extraction stages and some bleaching sequences where peroxide is used along with chlorine dioxide or oxygen. The non-production of hydrogen could mean a loss of heating fuels (for those pulp mills not flaring their H_2 produced in the chlorate generation).
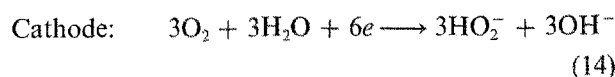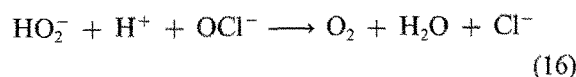
Typical peroxide cell

Cathode: $O_2 + H_2O + 2e \longrightarrow HO_2^- + OH^-$

$$(1)$$

$$HO_2^- + H_2O + 2e \longrightarrow 3OH^- \qquad (2)$$

Major anode reaction: $4OH^- \rightleftharpoons O_2 + H_2O + 4e$

$$(3)$$

Undesired: $HO_2^- + OH^- \rightleftharpoons O_2 + H_2O + 2e$

$$(4)$$

Typical chlorate cell

Anode: $2Cl^- \longrightarrow Cl_2(g) + 2e \qquad (5)$

$$Cl_2(g) \rightleftharpoons Cl_2(aq) \qquad (6)$$

$$Cl_2(aq) + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
$$(7)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (8)$$

$$6OCl^- + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^-$$
$$+ 6H^+ + \tfrac{3}{2}O_2 + 6e \qquad (9)$$

Bulk solution: $2HOCl + ClO^- + 2H_2O$

$$\longrightarrow ClO_3^- + 2H^+ + 2Cl^- \qquad (10)$$

Cathode: $OCl^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-$
$$(11)$$

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \qquad (12)$$

$$3H_2O + ClO_3^- + 6e \longrightarrow Cl^- + 6OH^- \qquad (13)$$

Combined peroxide/chlorate cell

Cathode: $3O_2 + 3H_2O + 6e \longrightarrow 3HO_2^- + 3OH^-$
$$(14)$$

Anode side:

$$Cl^- + 6OH^- \longrightarrow ClO_3^- + 3H_2O + 6e \qquad (15)$$

Peroxy/chlorate cell efficiency loss reaction:

$$HO_2^- + H^+ + OCl^- \longrightarrow O_2 + H_2O + Cl^-$$
$$(16)$$

2. Principles of the peroxy-chlorate cell

Figure 1 shows schematically the basic reactions in a membrane peroxy-chlorate cell. The ion transport across the membrane underlies the basic process principle. Net flux of ions across the membrane will depend on the relative magnitude of the concentration and migrational potentials; successful production of chlorate and peroxide in the same cell will depend on the selective transport of OH^- over HO_2^- ions across the separator from the catholyte to the anolyte; thus selective transport of OH^- over HO_2^- ions will depend on both the differences between their diffusion coef-
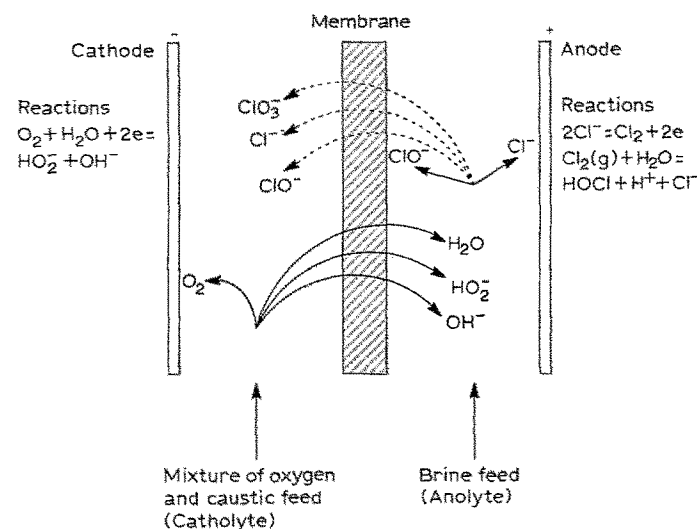

Fig. 1. Schematic diagram of a membrane peroxy-chlorate cell showing electrode conditions and transport processes.
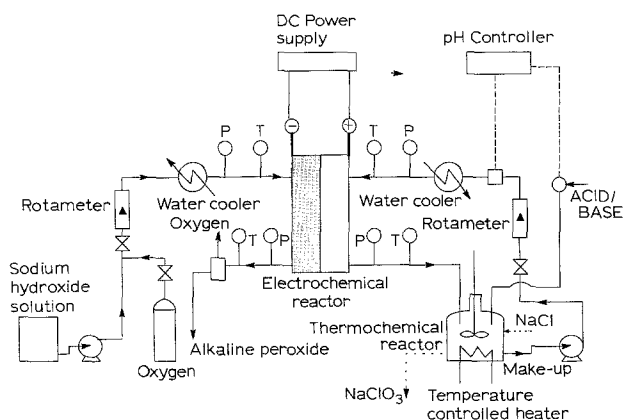
Fig. 2. Process for the simultaneous electrosynthesis of alkaline peroxide and sodium chlorate.

ficients in the membranes and concentration gradients. The hydroxyl ion has a diffusion coefficient about four times that of the perhydroxyl ion in 1.0 M caustic (Reaction 4). It is therefore likely that OH$^-$ ions are the major current carrier in the process, making it possible to generate both peroxide and chlorate in the reactor.

3. Experimental details and procedures

This work was carried out using a bench scale continuous 'flow-by' single cell electrochemical reactor. The reactor consisted of a cathode bed sandwiched between a flat feeder electrode plate, an anion membrane and an anode chamber. The cell was fed from the top with separate anolyte and catholyte solutions (co-current flow in the cell). A line diagram of the equipment is given in Fig. 2.

A monopole chlorine electrode, (DSA, Electrode Corp., USA) was employed as anode. The anode chamber was contained in a neoprene gasket with PVC mesh support (mesh size 10, Cole Parmer, USA). The anion membrane, 'RAIPORE 1035' (Electrosynthesis Co. Inc., NY, USA), was protected on the

Table 1. Dimensions of a peroxy-chlorate cell

Cell component	Dimensions
Compression plates	43.2×10^{-2} m long by 12.7×10^{-2} wide and 2.54×10^{-2} m thick
DSA Chlorine electrode (anode) RuO$_2$ coated titanium	48.3×10^{-2} m long by 12.7×10^{-2} m wide by 3.0×10^{-2} m thick
Effective superficial area of membrane	83.3×10^{-4} m^2
Anode chamber	23×10^{-2} m long by 3.62×10^{-2} m wide by 3×10^{-3} m thick
Cathode bed (compressed)	23×10^{-2} m long by 3.62×10^{-2} m wide by 3×10^{-3} m thick
PVC mesh membrane support (mesh size: 10)	23×10^{-2} m by 3.6×10^{-2} m (2 used)

anode side by an asbestos diaphragm (Albion Ind. Prod. Ltd., Vancouver). The cathode bed consisted of a fixed bed of graphite felt (Graphite felt Grade GF, Carborundum Corp., NY, USA). The felt was pre-treated by soaking in 5.0% nitric acid for 2 h or more and then washed with distilled water. The cathode feeder electrode was a plate of 316 stainless steel. The cathode bed was contained in a neoprene rubber gasket. Some important dimensions of the cell are given in Table 1.

Metered flow of anolyte was recycled through the anode chamber from a 2.2 l reaction tank. The anolyte tank was thermostated to a constant temperature while a meter/controller monitored and controlled the pH of the tank solution. The pH value of the outflow from the tank (or anolyte feed to the cell) was controlled and maintained constant to ± 0.3 pH unit by adding 1.0 M HCl (or 2.12 M HCl for some runs) or 1.0 M NaOH to the tank (in the event of excess addition of HCl) from the automatic pH controller. The catholyte was delivered from a 20 l tank and passed once through the cell and was then sampled before disposal to the drains. Oxygen was metered to a T-junction in the catholyte feed. Both the anolyte and catholyte were pre-cooled before the cell by passing through water cooled titanium coolers. The cell was not cooled. Rotameters, controlled manually through needle valves, were used in measuring the flows of the anolyte, catholyte and oxygen. A d.c. power supply with a maximum power output of 1.0 kVA and capable of either voltage or current controls up to 40.0 V or 25.0 A was used.

All parts in contact with the anolyte were made of either polypropylene, polyethelene, Teflon, glass or Plexiglass while for the catholyte, glass, polypropylene, stainless steel or Plexiglass were used. No corrosion was observed during the experimental program. The anolyte and catholyte were laboratory grade sodium chloride and sodium hydroxide respectively, both in deionized water. Oxygen was of $\geqslant 99\%$ purity.

After exploratory experiments (involving the identification of a separator and process condition) indicated that sodium chlorate and hydrogen peroxide could be made simultaneously in the same electrochemical cell, a series of experimental runs were carried out. Experiments of between 120 to 180 min duration were carried out over a range of conditions to examine the effects of several variables on the reactor performance. The major independent variables were catholyte liquid loadings of 0.92–4.6 kg m^{-2} s^{-1} (corresponding to (0.1–0.5) $\times$ 10^{-6} m^3 s^{-1}), NaOH concentration of 0.5–2.0 M and current of 10.0–20.0 A or 1.2–2.4 kA m^{-2}. The anolyte rate through the cell was set at 2.0 $\times$ 10^{-6} m^3 s^{-1} and the oxygen gas load to the cathode was kept constant at 0.102 kg m^{-2} s^{-1}. Samples of the catholyte product were taken at intervals for analysis of peroxide concentration. A conventional titration method using potassium permanganate (0.10 N) as titrant and sulphuric acid for the acidification of the sample before titration was employed. A potentiometric titration method, based on a modified

method due to Norkus and Prokopchik [3], was used to determine the concentrations of active chlorine (sum of hypochlorite, hypochlorous acid and dissolved molecular chlorine) and chlorate, methodological details of which are given in [4]. Cl^- analysis was carried out by the Mohr titration method.

3.1. Selection of independent variables

In the initial stage of this work, nine possible process factors were screened by a Plackett–Burman design with each factor at two levels [5]. The factors examined included: sodium hydroxide concentration (0.2 to 2.0 M); catholyte loading (0.92 to $9.20\,kg\,m^{-2}\,s^{-1}$); oxygen loading (0.024 to $0.12\,kg\,m^{-2}\,s^{-1}$); sodium chloride concentration (1.0 to 5.0 M); anolyte flow (5.0×10^{-7} to $3.0 \times 10^{-6}\,m^3\,s^{-1}$); sodium chlorate concentration (0.0 to 0.2 M); anolyte temperature (40 to 70° C); anolyte tank pH (5.5 to 7.5); and current (5.0 to 25 A).

These tests showed that sodium hydroxide concentration, sodium chlorate concentration and anolyte pH probably affect the current efficiency for chlorate while sodium chloride concentration and current affect the current efficiency for peroxide. Since previous investigators [6, 7] had shown a strong effect of catholyte load for the electrosynthesis of peroxide in a trickle-bed, it was decided to limit further investigation of the coupled process to the following four independent variables:

(i)   sodium hydroxide concentration in the catholyte;
(ii) catholyte loading;
(iii) sodium chlorate concentration in the anolyte;
(iv) current.

4. Results and discussion

Current efficiencies of the products were used as a measure of the system performance. Chloride ion oxidation on the anode, Equation 5, is the basic anodic process. The chlorine formed from the chloride ion oxidation is dissolved in the aqueous solution, Equation 6, and subsequently hydrolysed, yielding hypochlorous species (hypochlorous acid and hypochlorite) as in Equations 7 and 8. The active chlorine could be converted to chlorate in two parallel ways: viz. the chemical route in the external reactor, Equation 10, or the electrochemical route in the cell, Equation 9. In evaluating the sodium chlorate current efficiency, an assumption was made that all the chlorate produced was through the chemical route. This assumption is justified based on the experimental conditions adopted which favour the chemical route of chlorate formation. Thus the overall chlorate formation is represented by Equation 10. According to the overall equation for chlorate formation, the production of chlorate requires $6 \times 96\,500\,C\,mol^{-1}$. Thus the chlorate percentage current efficiency was defined as

$$\eta_{ClO_3^-} = \frac{600FC_{ClO_3^-}}{I\tau} \qquad (17)$$

In a similar way, the cathodic reduction of oxygen to hydrogen peroxide has the peroxide current efficiency expressed in the form:

$$\eta_{HO_2^-} = \frac{200FQC_{HO_2^-}}{I} \qquad (18)$$

Thus the chemistry of the process, operating conditions and the design of the cell determine the current efficiency.

Using the results of the variable screening experiments, factorial experiments were carried out to elucidate the effects of catholyte flow or loading, sodium hydroxide concentration and current density.

4.1. Factorial experiments

The factorial experiments were carried out at two different anolyte chlorate concentrations: viz. the low chlorate concentration run, where the initial anolyte chlorate concentration was less than 1.0 M, and the high chlorate concentration run in which an initial chlorate concentration greater than 1.0 M was used. The experimental conditions common to all the runs are shown in Table 2. The low chlorate results are shown in Tables 3 and 4 for sodium chlorate and alkaline hydrogen peroxide while the results for the high chlorate runs are shown in Tables 5 and 6 for the chlorate and peroxide. Discussion in the next four sections is based on the results of low chlorate runs.

4.1.1. Effect of current density. The effects of current (i.e. current density based on the active area of metal current feeder plates or the separator) are shown in Tables 3 and 4. As can be seen in Table 3, the chlorate current efficiency increases with increase in the current density at any given caustic concentration. Other principal features of the results are: (i) an increase in the chlorate current efficiency with an increase in catholyte loading rate at a given current density; (ii) a fall in peroxide current efficiency, at any given caustic concentration and catholyte loading, with an increase in current density (see Table 4); (iii) a rise in peroxide current efficiency with increased catholyte loading at any given current density.

The increase in current density increases the rate of gas evolution, the mass transfer rate and the number

Table 2. Range of common process conditions for all runs

Quantity	Range		Units
	Anode side	Cathode side	
Cell temp. (In/Out)	28/33	22/30	°C
NaCl Conc.	3.5–4.2	–	M
Anolyte tank temp.	68–82	–	°C
Anolyte vol.	2.15–2.2	–	litres
Cell pressure	0–58.6	0–48.6	kPa
Oxygen loading	–	0.102	$kg\,m^{-2}\,s^{-1}$
Voltage across cell	3.0–4.2	3.0–4.2	V

Table 3. Chlorate current efficiency and concentration at low chlorate runs

Current density $(kA\,m^{-2})$	Catholyte loading $(kg\,m^{-2}\,s^{-1})$	Catholyte (NaOH concentration, M)			
		0.5		2.0	
		Chlorate current efficiency (%)	ClO_3^- conc. Initial/Final (M)	Chlorate current efficiency (%)	ClO_3^- conc. Initial/Final (M)
1.2 (10 A)	0.92	53.0	0.0/0.049	53.2	0.0/0.033
	4.60	68.5	0.258/0.322	70.3	0.0/0.044
2.4 (20 A)	0.92	69.1	0.0/0.129	62.6	0.099/0.190
	4.60	78.0	0.225/0.370	72.9	0.102/0.193

of moles of hypochlorite to be converted to chlorate in the chemical reactor. These effects of increasing current density result in an increase in the homogeneous chemical chlorate formation and an increase in the electrical transference flux of the OH^- and HO_2^- anions into the anolyte. The data in Table 3 indicate that at any given catholyte loading and NaOH concentration, the balance between HO_2^- flux and OCl^- generation becomes more favourable to OCl^- with increased current density, thereby resulting in chlorate current efficiency increase. Table 4 shows further than an increase in the current density at any given catholyte loading and NaOH concentration results in a decrease in peroxide current efficiency and an increase in peroxide concentration. An increase in the current density results in higher peroxide concentration and leads to a higher HO_2^- migration to the anolyte and higher rate of peroxide reduction (due to increase in the negative cathode potential). The combined result of the current density effect is a loss in peroxide current efficiency (Equation 2). Compared to the Oloman and Watkinson [8] results of 84.0% current efficiency in peroxide at $0.5\,kA\,m^{-2}$ (peroxide concentration = 0.3 M) and 60.0% at $1.5\,kA\,m^{-2}$ (peroxide concentration = 0.70 M) under a pressure of 930 kPa and NaOH concentration of 2.0 M, the present results show that peroxide current efficiency decreases from 86.0% (peroxide concentration = 0.446 M) at $1.2\,kA\,m^{-2}$ to 53.0% (peroxide concentration = 0.520 M) at $2.4\,kA\,m^{-2}$ for a catholyte loading of $0.92\,kg\,m^{-2}\,s^{-1}$. It is thus an improvement over the results obtained by

Oloman and Watkinson, who produced only alkaline peroxide.

4.1.2. Effect of catholyte loading.

The effect of catholyte loading on the process is as shown in Table 3 for the chlorate side and Table 4 for the peroxide side. The chlorate current efficiency increases with catholyte loadings which could be attributed to the lower peroxide concentration that results with higher loadings of the cathlyte. The lower peroxide concentration means a lower peroxide migration and diffusion into the anolyte thus resulting to a lower loss in hypochlorite and hence a higher chlorate production.

In Table 4, it is observed that the peroxide current efficiency at 0.5 M NaOH increases as the catholyte loadings increase. However, at 2.0 M NaOH, the peroxide current efficiency decreases with catholyte loadings.

The result at 2.0 M caustic contrasts with that of Oloman and Watkinson [8], in which they observed a rise in peroxide current efficiency with increase in catholyte loadings. Although they operated a similar cell as the one used in this work, they used a cationic membrane as the separator and generated oxygen on the anode at a current density range of $0.4-1.6\,kA\,m^{-2}$. The observation in this work underlies the interacting effect of the anode side reactions to the cathode side reactions. Kalu [4], has suggested that the hydrodynamics affect the loss mechanisms and hence the importance of catholyte flow or loading in the peroxide current efficiency.

Table 4. Peroxide current efficiency and concentration at low chlorate runs

Current density $(kA\,m^{-2})$	Catholyte loading $(kg\,m^{-2}\,s^{-1})$	Catholyte (NaOH concentration, M)			
		0.5		2.0	
		Peroxide current efficiency (%)	Peroxide conc. (M)	Peroxide current efficiency (%)	Peroxide conc. (M)
1.2 (10 A)	0.92	29.5	0.153	86.1	0.446
	4.60	62.0	0.064	66.2	0.069
2.4 (20 A)	0.92	15.9	0.145	52.7	0.520
	4.60	39.5	0.082	37.7	0.077

4.1.3. Effect of NaOH concentration.

The following features are observed in Table 3: (a) at a current density of $1.2\,kA\,m^{-2}$, the chlorate current efficiency remains constant with increase in NaOH concentration, and (b) at $2.4\,kA\,m^{-2}$, the chlorate current efficiency falls with rise in NaOH concentration. The latter contrasts with (a) and thus suggests an interaction between the effects of current density and NaOH concentration.

Observations made in (a) may be explained, in part, by the electrical transference flux term at given current density and diffusion flux. The observation made in (b) is also partly accounted for by the increased importance of migration and concentration of peroxide at $2.4\,kA\,m^{-2}$ relative to $1.2\,kA\,m^{-2}$.

The effects of NaOH concentration on the peroxide current efficiency and concentration in Table 4 indicate (i) that the peroxide concentation and current efficiency increases with increase in NaOH concentration, and (ii) that this observation, with respect to peroxide efficiency, is consistent with low catholyte loads. As the catholyte loading increases, the peroxide current efficiency does not rise as rapidly as it does at lower catholyte loading. In fact it is observed that at a loading of $4.6\,kg\,m^{-2}\,s^{-1}$, both the current efficiency and peroxide concentration fall with increase in caustic concentration.

As observed by Oloman and Watkinson [8] for a peroxide cell (current density $0.2-0.8\,kA\,m^{-2}$), peroxide concentration and current efficiency increases with increase in NaOH concentration. It was suggested that high initial NaOH concentration could protect the peroxide from subsequent cathode reactions. It might well be that in the present process, at high catholyte loadings and high NaOH concentration, the interacting effects of flow, current and NaOH concentation on peroxide loss to the anolyte become more pronounced than the influence of other factors that favour a rise in peroxide current efficiency.

4.1.4. Effect of peroxy-hydroxy mole ratio.

Alkaline peroxide reacts with hypochlorite or dissolved elemental chlorine, Equation 16, which are important intermediates in the chlorate synthesis. Hydrolysis of chlorine and the formation of OCl^- require the presence of OH^- ions in the environment, Equation 7. It was thus important to study the effect of the HO_2^-/OH^- ratio on the chlorate current efficiency in a coupled peroxy-chlorate process. These effects are illustrated in Figs 3 and 4.

Although peroxide concentration is not an independent variable in this process, Figs 3 and 4 are not simply the inverse of the effect of the hydroxide concentration on chlorate current efficiency. Hydroxyl ion concentration used in computing the mole ratio is the NaOH feed concentration into the cell. The following observations are made from the peroxy-hydroxy mole ratio plots: (a) that the chlorate current efficiency falls with rise in the peroxy-hydroxy mole ratio, and (b) that chlorate current efficiency at $2.4\,kA\,m^{-2}$ is greater than that at $1.2\,kA\,m^{-2}$.
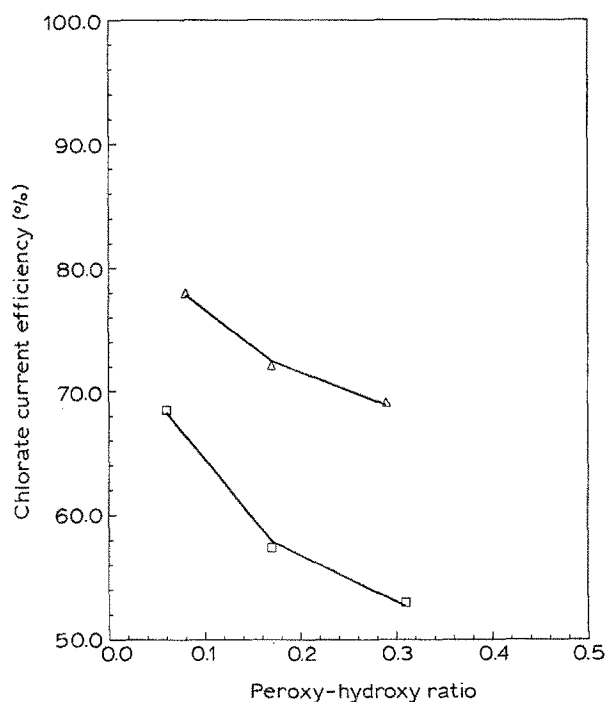

Fig. 3. Effect of HO_2^-/OH^- mole ratio on the chlorate current efficiency at $0.5\,M$ NaOH. Current densities: (□) $1.20\,kA\,m^{-2}$; (△) $2.40\,kA\,m^{-2}$.

The trends observed are in line with the explanation that as the HO_2^- ion concentration increases, more of the peroxide ions are transported across the membrane to deplete the chlorate forming intermediates. The linearized plot, when extended to the peroxy-hydroxy ratio-axis, gives the value of peroxy-hydroxy ratio above which it would likely be (theoretically) impossible to make chlorate. More experimental points at higher peroxy-hydroxy ratio would be required to con-
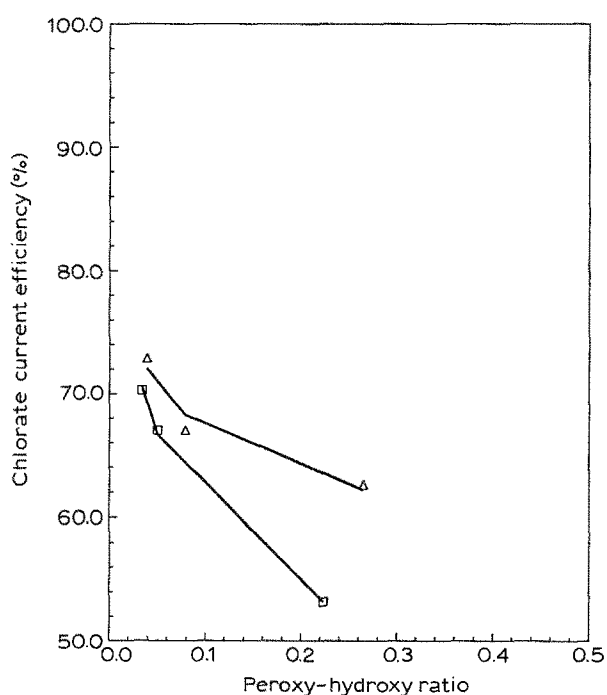

Fig. 4. Effect of HO_2^-/OH^- mole ratio on the chlorate current efficiency at $2.0\,M$ NaOH. Current densities: (□) $1.20\,kA\,m^{-2}$; (△) $2.40\,kA\,m^{-2}$.

Table 5. Chlorate current efficiency and concentration at low chlorate runs

Current density (kA m⁻²)	Catholyte loading (kg m⁻² s⁻¹)	Catholyte (NaOH concentration, M)			
		1.0		2.0	
		ClO_3^- current efficiency (%)	ClO_3^- conc. Initial/Final (M)	ClO_3^- current efficiency (%)	ClO_3^- conc. Initial/Final (M)
1.2	0.92	61.1	2.700/2.738	77.3	2.890/2.942
(10 A)	4.60	69.0	2.700/2.744	67.0	2.723/2.788
2.4	0.92	66.4	2.523/2.589	72.8	2.890/3.021
(20 A)	4.60	80.6	2.903/3.015	51.0	2.836/2.883

firm the postulated behaviour. An alternative approach to the elucidation of the effects of the peroxy-hydroxy ratio on the process is a mathematical simulation of the system. A mathematical model of the system will be the subject of our next communication.

4.2. High chlorate concentration runs

The experimental results at high chlorate concentration are shown in Tables 5 and 6. In comparing the high and low chlorate runs, it may be inferred that:

(i) the chlorate current efficiencies at 0.92 kg m⁻² s⁻¹ and 1.2 kA m⁻² for both 1.0 and 2.0 M NaOH are higher for the high chlorate concentration than the low chlorate run. At 4.6 kg m⁻² s⁻¹ catholyte loadings, similar results are obtained. At 2.4 kA m⁻², the trend observed at 1.2 kA m⁻² is not repeated.

(ii) the peroxide current efficiency and concentration at high chlorate runs show an improvement over the results at low chlorate runs. The role of chlorate concentration in the peroxide current efficiency may be attributed to interactions of process variables.

4.3. Cell voltage and energy consumption

The cell voltage was observed to increase linearly with current density from 3.0 V at 1.2 kA m⁻² to 3.9 V at 2.4 kA m⁻² for a catholyte load of 0.92 kg m⁻² s⁻¹. At 2.4 kA m⁻², the cell voltage increased by 0.3 V as catholyte load was raised from 0.92 to 4.60 kg m⁻² s⁻¹ and this is presumed to be due to membrane bulging

or deterioration with increased catholyte load. Since the cogeneration cell is effectively a chlorate cell with an oxygen depolarized cathode, it appears that the decrease in voltage from cathode depolarization is more than offset by the voltage drop through the separator. The cell voltage could probably be reduced by increasing temperature and pressure or by using a more conductive separator.

Cogeneration of peroxide and chlorate, both with current efficiency of 70% at a current density of 2.4 kA m⁻² and 4.2 V per cell gives an energy consumption of 9 k Wh for the production of 1.0 kg of sodium chlorate plus 1 kg of hydrogen peroxide. For comparison, conventional chlorate cells typically operate around 5 kWh kg⁻¹ sodium chlorate [10] while the electrosynthesis of hydrogen peroxide in the H-D Tech. process runs at 0.6 kA m⁻² and 2.0 V, 80% current efficiency with specific energy around 4.0 k Wh kg⁻¹ hydrogen peroxide [6, 11]. The energy consumption of the experimental coupled cell is thus about the same as that of the separate commercial processes and there are prospects for reducing the cogeneration energy by optimization.

4.4. Membrane stability

The membrane stability affects the current efficiencies of both products and the cell voltage. An asbestos diaphragm on the anode side was used to protect and prolong the membrane life. Since no physical or chemical tests were carried out on the membrane in

Table 6. Peroxide current efficiency and concentration at low chlorate runs

Current density (kA m⁻²)	Catholyte loading (kg m⁻² s⁻¹)	Catholyte (NaOH concentration, M)			
		1.0		2.0	
		Peroxide current efficiency (%)	Peroxide conc. (M)	Peroxide current efficiency (%)	Peroxide conc. (M)
1.2 (10 A)	0.92	60.0	0.311	73.0	0.378
	4.60	77.2	0.080	96.5	0.100
2.4 (20 A)	0.92	36.2	0.375	78.2	0.810
	4.60	63.7	0.132	61.4	0.127

order to evaluate its levels of deterioration, the reproducibility of the product current efficiencies and changes in the cell voltage with time were used as a yardstick for measuring the membrane stability.

To be able to assess the extent of a typical membrane degradation in the process, the cell voltage was followed with time. A typical result obtained for a membrane that had been in use for over 20 h is as shown in Fig. 5 (the 3 h run implies an additional 3 h over its 20 h usage). The variation in the cell voltage did not indicate a serious membrane damage (or increase in resistance) — at least in the first 23 h of the use of the membrane. The cell voltage at the first hour of use of this particular membrane was 3.0 V at $1.2\,kA\,m^{-2}$ (current density) and a catholyte loadings of $0.92\,kg\,m^{-2}\,s^{-1}$.

The product current efficiencies were compared at two or more different times of a particular membrane usage. All the experimental conditions were the same. Observations made in the experimental runs included the colouration of the anolyte stream for each use of a 'new membrane'. The pink colouration observed for each use of a new membrane was not pronounced nor was it observed in subsequent runs using the same membrane. This slight colouration may be due to the wear of the membrane — most probably as a result of reaction between the generated chlorate intermediates and membrane backbone materials. This wear did not manifest itself in the cell voltage results (which could have increased with older and deteriorated membranes) neither did it show in subsequent runs using the same membrane.

A typical result is shown in Table 7. Run A_2 is a repeat of A_1 while B_2 is a repeat of B_1. The variation between A_1 and A_2 is negligible and cannot be attributed to membrane degradation. While those of B_1 and B_2 differ, the variation is probably due to experimental errors.

4.5. HCl addition

According to Equations 14 and 15, the amount of OH^- furnished by the peroxide formation reaction (Reaction 14) is insufficient to make a mole of chlorate for a passage of 6 moles of electricity. Thus the reactions, 14 and 15, suggest that a simultaneous synthesis

of alkaline peroxide and chlorate in the same cell would require alkaline addition from an external source into the anolyte to maintain the optimum pH required for chlorate production. In the present work, the catholyte was the only external source that furnished the required alkality. The cathode chamber acts as an efficient external alkali source for anolyte pH level control because either Reaction 14 is carried out in alkaline media, hence sufficient OH^- ions are available to make up for the required OH^- or other side reactions producing OH^- ions occur as well as Reaction 14, for example Reaction 2, also, HO_2^- will also neutralize H^+ as in Equation 16.

In this work, HCl addition to the anolyte was used to keep and control and anolyte tank pH level. This indicates that sufficient OH^- was obtained in the anolyte with the catholyte acting as an external source of alkality to satisfy the requirements of Equations 14 and 15.

4.6. Chloride balance

The membrane serves to separate and thereby prevent the mixing of the anolyte and catholyte. Ideally, only negative ions move through the anion exchange membrane while the two parts of the cell are sealed from each other. The anions in the anolyte are favoured under the influence of diffusion potential to diffuse into the catholyte. Thus, the Cl^-, ClO_3^-, ClO^- and Cl_3^- ions in the anolyte tend to diffuse into the catholyte. To assess the loss of efficiency due to the diffusion term, a material balance was carried out on the chloride in the system. In the material balance no attempt was made to account for chloride loss in the form of undissolved chlorine gas (vented out) and chlorate in the catholyte.

A typical chloride balance result is shown in Table 8. These results indicate that little chloride was lost to the catholyte.

Table 7. Age of membrane and its effects on product current efficiency

	1.2 $(kA\,m^{-2})$		2.4 $(kA\,m^{-2})$	
	A_1	A_2	B_1	B_2
ClO_3^- current efficiency (%)	73.0	77.3	60.0	80.6
HO_2^- current efficiency (%)	78.0	73.0	70.0	70.0
Peroxide conc. (M)	0.404	0.378	0.146	0.146
Age of membrane (h)	3.0	25.0	12.0	28.0

Table 8. Typical chloride balance on the process

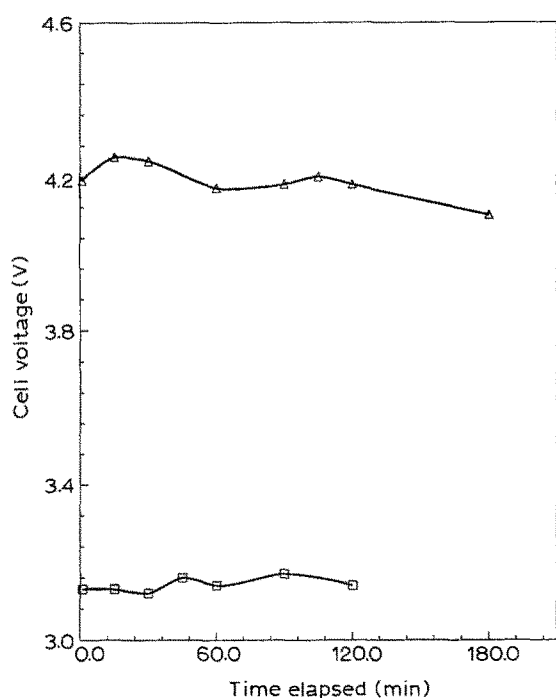| Chloride balance	Input	Output
Moles of Cl in Anolyte NaCl	6.46	6.29
Moles of Cl in Anolyte $NaClO_3$	5.84	5.95
Moles of Cl in Anolyte OCl^-	–	0.02
Moles of Cl in added HCl	0.01	–
Moles of Cl in catholyte	–	0.01
Total moles of Cl	12.31	12.27

Fig. 5. Typical cell voltage variation with time. Current densities: (□) 1.20 kA m^{-2}; (△) 2.40 kA m^{-2}.

4.7. Water transport across the membrane

An increase in the anolyte volume was observed in most of the experimental runs. This increase was due to water transport from the catholyte and the addition of HCl for pH control. The transport of water molecules across the membrane is a function of the current denisty, hydration number of ions and membrane structure. George et al. [9] observed that water transport across an ion exchange membrane is markedly higher at low current densities than at higher current densities.

In the present work, no attempt was made to study the relationship between the amount of water transported and the experimental conditions. The only observation made was that, the increase in solution volume in the anolyte leads to a lower chlorate concentration than would have obtained had the anolyte volume remained constant.

5. Conclusion

Alkaline hydrogen peroxide and sodium chlorate were successfully synthesized simultaneously in the same electrochemical cell using a combination of an anion membrane and an asbestos diaphragm as the separator. In the operation of a continuous electrochemical reactor, the effects of current density, catholyte loading and sodium hydroxide concentration on the peroxide and chlorate current efficiencies were investigated. The results show that increasing the superficial current density increases the peroxide concentration (at the expense of its current efficiency) and favours chlorate current efficiency. It was also found that increase in

the peroxy-hydroxy mole ratio in the catholyte lowers the chlorate current efficiency.

The best results for the two products at low chlorate run include 56.5 and 76.0% current efficiency for peroxide and chlorate respectively at 2.4 kA m^{-2}, 1.0 M caustic, 4.6 kg m^{-2} s^{-1} catholyte loading (peroxide concentration $= 0.117$ M) and 75.4% peroxide current efficiency (0.130 M HO$_2^-$) with 70.3% chlorate current efficiency at 1.2 kA m^{-2}, 4.6 kg m^{-2} s^{-1} catholyte loading and 2.0 M caustic. In strong chlorate solution runs, some improvement was observed in the current efficiencies of the two products. A peroxide current efficiency of 78.2% (0.81 M) at 2.0 M caustic and 0.92 kg m^{-2} s^{-1} catholyte loading was obtained with a 72.3% chlorate current efficiency.

A chloride balance over the system over a short time indicated a small loss of chloride from the anolyte to the catholyte and the addition of HCl to control the pH of the anolyte stream reflects the ability of the process to transfer OH$^-$ ions across the membrane at a rate equivalent to Cl$_2$ generation.

Other factors which can be expected to influence the process, but which were not investigated, include the temperature of the inlet electrolytes, the direction of flow of the two electrolytes into the cell and the anolyte flow rate.

This work demonstrates that sodium chlorate and hydrogen peroxide may be generated simultaneously in the same cell at reasonable current densities. The benefit obtained for the lower chlorate current efficiency (compared to traditional chlorate cells) is the peroxide generated. The process may be suited for a simultaneous on-site generation of alkaline peroxide and chlorate in a pulp mill.

Acknowledgements

References

[1] D. L. Camichael and E. B. Althouse, Tappi Journal 11 (1981) 90.
[2] Japan Carllite Co., Japanese patent 61 284 591 (1986).
[3] P. K. Norkus and A. Y. Prokopchik, Zhur. Anal. Khim. 16 (1961) 336.
[4] E. E. Kalu, M.A.Sc Thesis, University of B.C., Canada (1987).
[5] R. L. Plackett and J. P. Burman, Biometrika 33 (1946) 305.
[6] G. Brown, D. F. Dong, J. A. McIntye and R. F. Phillips, Tappi Proceedings 1983 Pulping Conferences (1983) 341.
[7] C. Oloman, J. Electrochem. Soc. 126 (1979) 1885.
[8] C. Oloman and A. P. Watkinson, J. Appl. Electrochem. 9 (1979) 117.
[9] J. H. B. George, A. R. Horne and C. R. Schlaikjer, J. Electrochem. Soc. 117 (1970) 892.
[10] J. E. Coleman in 'Tutorial Lectures in Electrochemical Engineering and Technology', A.I.Ch.E. Symposium Series No. 204 (1981) 244.
[11] D. Dong, Meeting of Electrochemical Society, Canadian Section, Toronto, (2 February, 1990).