**SIMULTANEOUS ELECTROSYNTHESIS OF ALKALINE HYDROGEN
PEROXIDE AND SODIUM CHLORATE**

by

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ABSTRACT

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 effects of superficial current density ($1.2 - 2.4 \text{ kA m}^{-2}$), sodium hydroxide concentration ($0.5 - 2.0 \text{ M}$) and catholyte flow ($0.1 \times 10^{-6} - 0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$) on the chlorate and peroxide current efficiencies were measured. The effect of peroxy to hydroxy mole ratio on the chlorate current efficiency was measured too.

The cell was operated at fixed anolyte flow of $2.0 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, inlet and outlet temperatures of $27/33^\circ\text{C}$ (anode side), $20/29^\circ\text{C}$ (cathode side), cell voltages of $3.0 - 4.2 \text{ V}$ (current density of $1.2 - 2.4 \text{ kA m}^{-2}$) and a fixed temperature of 70°C in the anolyte tank. Depending on the conditions, alkaline peroxide solution and sodium chlorate were cogenerated at peroxide current efficiency between 20% and 86%, chlorate current efficiency between 51.0% and 80.6% and peroxide concentration ranging from 0.069 M to 0.80 M. The cogeneration of the two chemicals was carried out at both concentrated ($2.4 - 2.8 \text{ M}$) and dilute ($0 - 0.5 \text{ M}$) chlorate solutions. A relative improvement on the current efficiencies at concentrated chlorate was observed. A chloride balance indicated negligible chloride loss to the catholyte.

The results are interpreted in terms of the electrochemical and chemical kinetics and the hydrodynamics of the cell.

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CHAPTER 1

INTRODUCTION

Sodium chlorate and hydrogen peroxide are strong oxidizing agents used in bleaching processes. While sodium chlorate is used in the pulp and paper mills for generating chlorine dioxide (a bleaching chemical), alkaline hydrogen peroxide is gaining popularity as both a brightening and extractive agent for wood pulp.

Although hydrogen peroxide was originally manufactured by an electrochemical route, it is today wholly produced by auto-oxidation of anthroquinone (a chemical route) and sold in stabilized water concentration of up to 90% by volume. For a complete account of its manufacture and detailed properties, reference is made to (1). On the other hand, sodium chlorate is commercially made by the electrolysis of relatively concentrated neutral sodium chloride solution in an undivided cell. For a complete description of chlorate process principle, see references (2, 3 and 60).

The use of alkaline hydrogen peroxide as a compliment of chlorine dioxide, chlorine and hypochlorite in the bleaching sequences is on the increase. The peroxide use is not limited to only mechanical pulps (as a brightening agent), its use in chemical pulp bleaching in one or more sequences is growing (4). When peroxide is used in an intermediate stage of chemical or semi-chemical pulping, the bleach liquor's combined extractive and oxidative effects contribute primarily to

delignification, although significant brightening may also occur. When applied in a final stage, the dominant action is oxidative and aimed at imparting a high and stable brightness to the pulp.

The use of oxidizing agents such as hydrogen peroxide and hypochlorite in the alkali treatment of the extraction stage of a multiple bleaching sequences is known to improve the effect of the alkali [5]. Also recent work [6], has shown that the combined use of peroxide and oxygen in the extraction stage results in greater delignification and higher brightness than with oxygen extraction stage alone. Hydrogen peroxide use in the extraction stage not only increases the delignification rate leading to a 55-60% effluent load elimination (7), it also allows a mill to decrease the amount of chlorine dioxide use, shorten the bleaching sequences, reduce the operating cost and improve the pulp out-put [6]. 1 kg H_2O_2 saves about 1.8 kg ClO_2 .

The hydrogen peroxide to alkali ratio required in the delignification or extraction stage is lower than that required for a bleaching stage. This work is aimed at generation of alkali peroxide to alkali ratio required for a delignification and extraction stages of pulp bleaching process. The demand and use of alkaline peroxide in the pulp mill industry is constrained by the high cost of hydrogen peroxide (\$1.0/kg, USA).

The disposal of chromate effluents (for pulp mills generating their $NaClO_3$ requirement or using purchased $NaClO_3$ solutions or unpurified solid $NaClO_3$) constitute a problem to the environment. The problems associated with sulphate disposal could be solved by the substitution of

hydrochloric acid for sulphuric acid. The resulting NaCl in such a substitution could be recycled for NaClO₃ generation if the chlorate is generated on site.

At 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 peroxy ions, there is also an increase in hydroxyl ion concentration (i.e., process is not net alkali consuming process).

When this is considered together with anodic oxidation of chloride, which requires hydroxyl ion for chlorate formation, a simultaneous production of alkaline peroxide on the cathode chamber and chlorate in the anode chamber of a divided cell seems an idea worthy of investigation.

There is little consideration in the literature regarding the simultaneous production of peroxide and chlorate in the same cell. Recently, Carlit company of Japan [8] obtained a patent using an organic compound in the cathode of a divided cell to make peroxide and alkali metal halogen acid salt in the anode chamber. The principle of a simultaneous production of alkaline peroxide and chlorate in the same cell could be extended and applied to other electrochemical systems

where one of the electrode reaction products is cheaper than the other electrode product.

The reason that little work has been previously done on the simultaneous peroxide and chlorate synthesis might have been the obvious problems of such a system. The problems to overcome 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 at the same time be stable in the anode side oxidative chlorate environment. The identification of a long lasting cathode for oxygen reduction is also required to be achieved. The opposing process factor requirements for the primary products of interest may be a reason too.

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 just an ordinary diaphragm separator. The use of oxygen depolarized cathode in chlorate synthesis could mean an energy reduction per ton of chlorate. The success and adaptation of the present process would eliminate the use of chromate in chlorate generation at pulp mill sites for those mills generating their chlorate requirements. Such a process would not only reduce the cost of production of chlorate that appears in form of chromate prices and environmental clean up exercises in the pulp mills, it could also mean lower energy per ton of chlorate produced.

The reaction stoichiometry on the cathode gives a product solution in which the minimum ratio by weight of sodium hydroxide to hydrogen peroxide is about 2:1. This is a constraint in the utilization of the

generated peroxide for bleaching purposes as the traditional bleaching sequence requires caustic to peroxide ratio of 1:1. Thus the alkaline peroxide generated in this sytem seems well suited for applications such as peroxide addition during caustic extraction and for some bleaching sequences where peroxide is used along with chlorine dioxide or oxygen.

CHAPTER 2

BACKGROUND

2.1 Previous Work

The simultaneous production of sodium chlorate and hydrogen peroxide in the same cell has not been commercialized. Recently (1986), a process of such a nature was documented (8). The idea of interest commonly expressed with regard to chlorate production and oxygen depolarized cathode is for energy reduction of the chlorate manufacturing process. In such a process, the peroxide formed is destroyed by the use of heavy metal catalysts (9). As pointed out earlier on, the lack of information on simultaneous production of alkaline peroxide and chlorate may be the result of the complex chemistry of the process and the belief in the impracticality of prevention of perhydroxyl ion from coming into contact with hypochlorite, the result of which could lead to not achieving a current efficiency of economic importance. The following is a review of the individual processes for electrosynthesis of sodium chlorate and alkaline peroxide solutions.

2.2 Sodium Chlorate

The preparation of sodium chlorate was first reported by Berzelius in 1808 (10) while in 1847 Kolbe (41) confirmed the electrochemical conversion of chloride to chlorate. The first commercial electrochemical production of chlorate was set up in France 19 years later (2). The chlorate cell used platinum anodes. In Sweden, Carlson

(2) reported in 1894 the use of graphite anodes instead of platinum. Muller suggested in 1898 that the use of a diaphragm was unnecessary in chlorate cells if chromate is added to the electrolyte (2). Wagner in 1954 (12) explained the role of dichromate in chlorate synthesis. The mechanism of electrochemical chlorate formation was postulated by Forester and his students in 1899 (13). According to this postulation (which has stood the test of time), discharge of chloride ions is followed by a series of chemical reactions. Oxygen evolution on the anode through hypochlorite discharge is responsible for losses in current efficiency.

Other principal contributors in the theory and practice of chlorate synthesis include Knibbs and Palfreeman (14), de Valera (15), Nagai and Takai (16), Beck (3), Jacksic et al (17, 18), Ibl and Landolt (19), Tilak (20) and a host of others. Ever since the commercialization of electrochemical production of chlorate, active studies and investigation into ways of improving chlorate cell performance have been the order of the day. Such studies include those aimed at reducing energy consumption per ton of chlorate, increasing current efficiency, achieving high chemical chlorate formation, etc. The design and use of chlorate electrolyzers with external or separate reactors came as a consequence of such research. Operating the electrolyzers at high temperatures reduces power consumption as the operating voltage is lower than at low temperatures. Materials capable of being used at high temperature and corrosive environment of the chlorate cell are relatively expensive.

Another direction of energy reduction in chlorate cell contemplated (that does not necessarily involve a very high temperature of operation) is the use of cathode voltage reduction. Suggestions have been made on the use of air or oxygen depolarized cathodes (9, 21) or coupling of a chlorate cell with a fuel cell in order to achieve a higher energy efficiency in the chlorate cell. Although none of these have been successfully commercialized, any break through in the use of air depolarized cathode could mean a decrease in the power consumption per ton of chlorate produced. The use of an oxygen depolarized cathode reduces the decomposition voltage of chloride (to chlorate) from 2.19 V to 0.96 V. This work is aimed at exploring the principle of the oxygen depolarized cathode for chlorate production using a divided cell.

2.3 Hydrogen Peroxide

The electroreduction of oxygen at a cathode, though recognized since 1882 as a source of hydrogen peroxide (22) has not been used on a commercial scale. A joint venture by Dow and Huron chemicals Ltd. led to a pilot plant (1000 kg/day) of peroxide solution in Ontario in 1986 (23).

Principal workers in the field of oxygen reduction on a cathode for peroxide production include Fischer and Priess in 1913 (24), Berl from 1935 - 1943 (25), Mizuno (1948-50) (26), Grangaard - between 1966 - 1970 (27), Oloman and Watkinson (28,29,30) between 1974-1979, and Brown et al [33].

Fischer and Priess (24) studied the electroreduction of oxygen in acid solution on a mercury cathode at oxygen pressures of up to 100 atm. A hydrogen peroxide of 2.3% wt concentration at a current density

of 0.023 kA m^{-2} with a power consumption of 2.8 kW per kg of hydrogen peroxide was produced. In 1939, E. Berl reported hydrogen peroxide formation by reduction of oxygen in alkali solution on a cathode of active carbon. The reaction was carried out at near atmospheric pressure using a diaphragm. A 2.5% wt hydrogen peroxide in 50% potassium hydroxide was obtained (25). Mizuno reinvestigated Berl's work again between 1948-1950 in Japan (26), while later studies of reduction of oxygen on active carbon led to a series of patents by Grangaard (27). The Grangaard's cell produced 0.5% solution of hydrogen peroxide in 2% sodium hydroxide with a power consumption of 13.82×10^3 kJ per kg of peroxide. Between 1971-1976, Oloman and Watkinson (29-32) reported methods of reduction of oxygen on carbon cathodes for peroxide production including the use of trickle beds and cell pressurization (30). In one of their earlier works, an alkaline peroxide solution of 3.7% wt hydrogen peroxide at 54% current efficiency and NaOH/H₂O₂ ratio of 3.2 kg/kg was reported made at a power consumption of 18.24×10^3 kJ/kg H₂O₂, a reactor inlet pressure of 9.2 atm. abs, and oxygen and electrolyte flow of $3.33 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ and $3.33 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$ respectively at a current density of 300 A m^{-2} (30). Brown et al (33) also reported producing a stream of 1.5% wt peroxide in 1.0 M sodium hydroxide at a current efficiency of 67%, cell voltage of 2V and current density of 300 A m^{-2} , at ambient temperature and pressure.

2.4 The Electrochemistry of Sodium Chlorate Production

Sodium chlorate is produced industrially by the electrolysis of a near neutral (pH = 6.5) concentrated solution of sodium chloride in an

Simple Chlorate Cell

Figure 1

undivided cell (see Fig.1). The overall chemical reaction in chlorate production is

The desirable reactions that lead to chlorate formation are:

After reaction (4), the following reactions subsequently occur in the vicinity of the anode (if the pH condition is satisfactory; pH = 6.5):

Thus 6 Faradays are required to produce 1 kg-mol of chlorate or 1512 Ah/kg of chlorate at 100% efficiency. The overall reaction of chlorate production (eqn. 3) is an endothermic reaction with an overall heat of reaction (ΔH) of 937.22 kJ/kg-mol. Thus the thermoneutral voltage of the reaction is calculated using Gibb's equation to be 2.189 V

$$-ZFE = \Delta G \quad (9)$$

$$E = -\Delta G/ZF \quad (10)$$

However in practice, chlorate cells operate at total cell voltages of between 3-4V at temperatures of greater or equal to 80°C. Under the

operating conditions, current efficiency of 93-96% is achieved with subsequent heat generation. The heat generated could be calculated from

$$Q_h = [(100/CE) (32.94)E] - \Delta H \text{ (J/kg-mol)} \quad (11)$$

This excess heat produced is normally removed using some cooling medium.

As stated in equations (4), (6), (7) and (8) - the reactions favour chlorate formation. After the discharge of chloride ions on the anode, the chlorine formed at anode dissolves in the boundary layer.

The aqueous or dissolved chlorine then hydrolyzes forming HOCl and OCl⁻ as in equation (6). An expression for the concentration of HOCl formed was given by Yokota (44) as:

$$C_{\text{HOCl}} = \text{Exp}[-13.8385 - 2.30259 \times 10^{-3}(T-273) + 5.92106 \times 10^{-5} C_{\text{NaCl}} + 2.30259 \times \text{pH}] \quad (12)$$

where T = temperature in Kelvin

C_i = Concentration of i in moles/m³

Some of HOCl formed dissociates into H⁺ and OCl⁻ and in the bulk solution, the HOCl combines with OCl⁻ to form chlorate. The equilibrium constants of the reactions at some given temperatures are:

(6.18 x 10⁻² mol./Kg solvent/atm at 25°C)

$$(2.4 \times 10^2 \text{ (mol/m}^3\text{)}^2 \text{ at } 25^\circ\text{C) (ref. 36)}$$

$$(2.7 \times 10^{-5} \text{ mol/m}^3) \text{ (36, 37)}$$

$$(76.0 \times 10^4 \text{ (mol/m}^3\text{)}^2 \text{ at } 70^\circ\text{C) (37)}$$

Reaction (8) is a slow reaction whose optimal rate occurs at a pH value equal to $\text{pK} - \log 2$ where $\text{pK} = -\log$ (equilibrium constant) for reaction (8).

2.4.1 Kinetics of Chlorate Formation

Two mechanisms are presented in the literature for purely chemical conversion of hypochlorite to chlorate:

- The reaction sequence first proposed by Foerster (13) and confirmed by many others (14, 37, 38, 39) as given in equations (4), (6), (7) and (8).
- The reaction mechanism proposed by Lister (40).

Whereas Foerster's mechanism is a third order reactions involving 2 moles of HOCl and 1 mole of OCl^- , Lister's proposal is bimolecular as shown in equations (13) and (14).

Reaction (14) is the rate controlling reaction in the mechanism proposed by Lister. Recently, Tilak et al. (20) showed that Foerster's mechanism correspond to chlorate cell conditions rather than Lister's. The rate for chemical chlorate formation using Foerster's mechanism is expressed

as:

$$\frac{dC_{ClO_3}}{dt} = K C_{ClO^-} C_{HClO}^2 \quad (15)$$

The dependence of K (apparent rate constant) on temperature was determined by Knibbs and Palfreeman (14) from 30°C to 80°C. The rate of formation of chlorate is obtained by multiplying the right hand side of eqn. (15) by the volume of the reactor, V. Thus a high yield of chlorate is obtained by an external reactor of large volume. A current efficiency of less than 100% is the norm in chlorate cells in industrial practice.

2.4.2 Secondary Reactions Affecting Chlorate Current Efficiency

Several side reactions occur simultaneously with the favourable reactions at the electrodes and in the bulk of the solution. These side reactions decrease the chlorate current efficiency. These side reactions could be considered as either anodic, cathodic or bulk parasitic reactions.

2.4.3 Anodic Side Reactions

On the introduction of DSA (Dimensionally Stable Anodes), the chlorate current efficiency was improved from the 80-85% range of carbon anodes to 93-96% range. The primary reactions that account for this efficiency loss in DSA operated chlorate cells are:

- (a) oxygen evolution
- (b) hypochlorite oxidation

The oxygen evolution in chlorate cell depends on the material of

the anode, the pH of the solution and the chloride concentration of the solution. The evolution of oxygen varies from 1.0% to 3% on noble metal based electrodes in the pH range 5.5 - 6.5. If chloride and chlorate ion concentrations are too low, the oxygen evolution will occur excessively. The oxygen evolution is represented by equation (16).

The oxidation of ClO^- at the anode has been a topic of much investigation for the past 80 years and it is still of interest today. The interest in the oxidation lies in it being an alternative route to chemical chlorate formation. The reaction is:

The hypochlorous acid formed in the immediate vicinity of the anode and the resulting hypochlorite ions are oxidized at the electrode to chlorate ions as soon as formed (eqn. 17). If all chlorate is formed by reaction (17), the maximum efficiency attainable in chlorate cell would be 66.7%. In order to avoid this route to chlorate formation, the use of an external chemical reactor was introduced (17,18). Reaction (17) is minimized because of reaction (8) which is favoured by the larger external reactor that reduces the concentration of ClO^- . The oxidation of chlorate can occur to a little extent in the cell.

2.4.4 Bulk Parasitic Reactions in Chlorate Electrosynthesis

Reactions (19) and (20) are two common bulk reactions whose occurrence lower the chlorate efficiency. These two reactions are pH dependent.

Reaction (19) occurs if an acid is added to the cell solution while the decomposition of OCl^- (reaction (20)) can occur in presence of heavy metals. The decomposition of chlorate to form chlorine dioxide (the bleaching agent in pulp mill industries) is favoured at pH less than 1.0.

Lister (40) studied reaction (21) carefully and found that at 40°C, the reaction proceeds at a rate of $1.0 \times 10^{-2} \text{ g-mol/m}^3\text{.sec}$ in pure acid solutions at pH less than 1.

2.4.5 Cathodic Side Reactions

The primary cathode reaction is hydrogen evolution

(E° at 25°C = 0.0 V)

However, the thermodynamic and kinetic considerations favor OCl^- and ClO_3^- reduction reactions (eqn. 23 and 24).

Sodium dichromate is added in the electrolyte (12) to suppress reactions (23) and (24). Some other functions attributed to dichromate include:

- (1) Suppressing the corrosion of Fe Cathode (41-43)
- (2) Buffering the electrolyte in the range 5-7 (38)
- (3) Inhibiting the O_2 evolution reaction at anode (21)

The role of dichromate as corrosion suppressor has been disputed by Viswanathan et al. (20). According to them, there is no difference between the open circuit voltage of a typical chlorate cell solution in the absence or presence of dichromate. The buffering action of chromate is traced to the equilibrium reaction.

The removal of the chromate from the final product constitute part of the separation steps that are carried out before shipping the chlorate.

2.4.6 Suppression of Cathodic Secondary Reactions

The cathode current losses due to chlorate and hypochlorite reduction are governed by diffusion of ions towards the electrode surface and could be suppressed by concentration polarization at high enough current density (44). To reach the cathode, these ions approach

the cathode by diffusion and convection against an adverse potential gradient. In the presence of excess of supporting electrolyte, the adverse potential gradient is small and the transport of anions is affected only slightly. In the absence of convection (e.g., passage across membrane), a material balance for any species i could be written as:

$$N_i = -Z_i U_i F C_i \nabla \phi - D_i \nabla C_i \quad (26)$$

where

N_i = flux of species i (moles/m² s)

Z_i = valence of species i

U_i = mobility of i (m² • mole/J.sec) = D_i/RT

C_i = concentrations of species i (mol/m³)

$\nabla \phi$ = potential gradient (V/m)

D_i = diffusivity of species i (m²/s)

By increasing the local current density, the potential gradient term is increased, thus suppressing the anion transportation to the cathode. Muller (45) first suggested the introduction of dichromate in the industrial chlorate process to suppress cathode hypochlorite reduction and to achieve a suitable pH buffering effect as well as inhibit iron corrosion. The chrome action was theoretically explained as consisting of the formation of a thin cathode surface layer. This provides hypochlorite ion concentration polarization and thus prevents its reduction.

Wagner (12) showed theoretically that there exists a critical

potential difference across the cathode diffusion boundary layer of the order of or greater than $KT/|Z_i|e = 0.025/|Z_i|$ (where k is Boltzman constant, T is temperature in Kelvin, Z_i is hypochlorite ion valency or that of any other reducible anion and e is the electron charge), providing the adverse potential gradient for negatively charged hypochlorite ion so that their reduction is effectively suppressed. With a relatively low current density or potential gradient, chromate reduction takes place and will cease after a sufficient cathode layer of chromium oxide is formed. Under such conditions, an anion approaching the cathode will be repulsed by an adverse potential gradient. Thus an effective diaphragm is formed on the cathode without excessive IR drop or electrode polarization.

2.4.7 Energy Consumption in Chlorate Cells

The chlorate synthesis is one of the most energy intensive electrochemical processes of commercial importance. The energy consumption of a chlorate cell is a function of current efficiency, CE, expressed as a fraction and cell voltage, E in volts:

$$P = 4.94 \times 10^6 \times E/CE \quad (\text{kJ/ton}) \quad (27)$$

The current efficiency is a function of operating characteristics and cell design. The cell voltage is made up of thermodynamic decomposition voltages of the anode and cathode, anodic and cathodic over voltages, ohmic drop between anode and cathode due to gas/electrolyte mixture and ohmic drop across the hardware.

2.4.8 Energy Conservation in Chlorate Cells

The need for reducing the energy requirement in a chlorate cell is demonstrated by the fact that about 50% of the production costs is energy related while only 30% accounts for capital investments. Some ways of achieving this reduction in energy include a high temperature cell operation and thermodynamic voltage reduction.

The operation of a high temperature chlorate cell is constrained by the high cost of materials of construction that will withstand the high temperature and the oxidative environment of chlorate cell. The theoretical decomposition voltage for chlorate electrosynthesis at 25°C is 2.19 V(SHE). Most commercial operations run at 3-4 volts at current densities of 2-3 kA m⁻² per cell. The reduction in the thermodynamic decomposition voltage could be achieved by the use of an air (oxygen) depolarized cathode (9,21). However, to contemplate such reductions, one must evaluate the impact such a reduction will have on capital and operating costs of the cell.

Traditionally, the hydrogen obtained in a chlorate cell is used as a boiler fuel. The present work is aimed at depolarizing the cathode using oxygen or air and at the same time obtaining an alkaline peroxide by product from the cathode and chlorate from the anode. It is hoped that the alkaline peroxide may be useful to the pulp mills.

2.5 Electrochemistry of Hydrogen Peroxide

Hydrogen peroxide can be prepared electrochemically either through the electrolysis of persulphuric acid or through the reduction of oxygen in alkaline or acid solutions.

2.5.1 Electrochemical Reduction of Oxygen in Alkaline Solution

Dissolved oxygen in an electrolyte can be reduced at a cathode to hydrogen peroxide or to water. Various cells using O_2 electrodes have been contemplated and some are still being investigated. The voltage losses associated with some of such cells result in substantial energy losses and thus seriously compromise the applicability of many such cells. Limited cell life due to precipitation of sodium peroxides and high cost are further problems associated with oxygen consuming cathodes. The trickle bed electrochemical reactor developed by Oloman and Watkinson (31), does not seem to suffer from $NaHO_2$ precipitation deterioration.

Oxygen electrochemistry plays an important role in corrosion processes. In the presence of air, oxygen reduction is often the cathodic process which drives the potential of iron and ferrous alloys into the passivation range where corrosion is inhibited. It is thus important to understand the electrochemistry of O_2 .

Oxygen cathodes deviate from thermodynamic potential by 0.3 to 0.4 V in alkaline electrolytes at operating temperatures of 60 to 80°C. This polarisation is mainly associated with the irreversibility of the overall O_2 reduction reactions in alkali solution - the stoichiometry of which is given by Latimer (46) as follows:

2.5.2 Pathways for Oxygen Reduction

Two mechanistic considerations for O_2 reduction are considered in most works viz:

- (i) The direct 4 electron pathway and
- (ii) The peroxide pathway (the series processes)

(i) The Direct 4-Electron Pathway

The 4-electron pathway involves a series of steps in which O_2 is reduced to OH^- or water without hydrogen peroxide being produced in the solution phase (eqn. 28). The reduction process involves adsorbed peroxide intermediate which does not appear in the solution phase (i.e., does not desorb). The distinctions between this pathway and the peroxide pathway are dependent on the purity of the electrolyte, electrode potential and temperature. This pathway is predominant on clean platinum (47).

(ii) The Peroxide Pathway

In alkaline solution, the peroxide pathway of oxygen is believed to proceed as follows (47):

or

$$(E^0 = -0.076VSHE)$$

The peroxide is further electroreduced to OH^- or catalytically decomposed i.e.:

Peroxide reduction:

or

Peroxide catalytic decomposition

Net Reaction:

Thus the net reaction of peroxide pathway is same as the four electron pathway. The HO_2^- is the perhydroxyl ion which is formed in alkaline aqueous solution when hydrogen peroxide is dissolved.

The dissociation constant of this reaction is given by

$$K = [\text{H}^+][\text{HO}_2^-]/[\text{H}_2\text{O}_2] = 2.4 \times 10^{-9} \text{ mol m}^{-3} \text{ at } 25^\circ\text{C} \quad (34)$$

The mechanism of the oxygen electrode has been widely studied in the past. Mechanistic compilations (which depend on reaction conditions) have resulted to reported Tafel behaviour differences from one investigation to another. Appelby (48), reported three Tafel regions for oxygen reduction while many others reported two. There is always a low slope region of approximately 60 mv/decade and a high region ranging from 120 mv to over 200 mv/decade. The origin of these larger Tafel slopes is not well understood.

Davies et al. (49) however established that the reduction of O_2 to HO_2^- as well as the reverse anodic process do not involve actual split

of the O_2 bond but rather a modification of the bond occurs. The electrochemical reaction orders of reaction (29) are given as +1 for O_2 and 0 or +1 for H^+ in acid or alkaline solution respectively by Vetter (50). In reaction (30), the order is +1 for H_2O_2 (the neutral molecule) and 0 for H^+ over the whole pH range. The equilibrium constant of peroxide catalytic decomposition reaction (eqn. 31) is calculated using data for the free energies of formation (32) as:

$$K = [O_2] [OH^-]^2/[HO_2^-]^2 \approx 10^{16} \text{ atm. at } 25^\circ C \quad (35)$$

Using the above data for the thermodynamics of O_2 reduction with the Nernst equation, Oloman (32) predicted an equilibrium concentration of 10^{-16} M HO_2^- at $25^\circ C$, pH=14 and oxygen partial pressure of 1 atm. Under the same conditions, chemical equilibrium of 10^{-8} M was calculated. Thus the prediction from thermodynamics shows clearly that peroxide is not accumulated in this process.

The only possible means of knowing the feasibility of making H_2O_2 is to look into the kinetics of the reaction. The kinetics of oxygen reduction on a cathode are dependent on many factors. Such factors include:

- (a) Cathode surface composition
- (b) Electrolyte composition and purity
- (c) Mass transfer of active species between cathode and catholyte
- (d) Current density
- (e) Temperature of catholyte

a. Cathode surface composition

The nature of cathode surface determines to a large extent the kinetics of oxygen reduction. The work of Yeager (47) gives illustrations of catalysts (surfaces) on which the peroxide pathway is clearly predominant as including carbon, graphite and gold (in alkaline electrolytes), while the 4-electron pathway predominates on clean platinum and certain transition metal macrocyclics such as adsorbed iron tetrasulphonated phthalocyanine. In the presence of impurities, the series pathway can become predominant even on clean platinum.

Most effort in oxygen reduced cathode studies is geared towards developing an effective catalyst for the reduction. The 4-electron pathway is of importance to the fuel cell industry and chlor-alkali plants. However in the present studies, the objective is to allow the accumulation of peroxide i.e. peroxide pathway is the mechanism of importance in the present work. According to Yeager (47), transition metal oxides and macrocyclic complexes appear more likely candidate catalysts for the 4-electron pathway and today most oxygen electrode investigators are in the area of macrocyclic molecules.

b. Electrolyte composition

The peroxide pathway is the predominant process in O_2 reduction in porous carbon (graphite) electrodes. Under these conditions then, the electrode potential within the electrode responds to local O_2 , OH^- and H_2O concentrations through the Nernst equation i.e.,

$$E_1 = E_{0,1} - \frac{RT}{2F} \ln \frac{[OH^-] [HO_2^-]}{[H_2O] [O_2]} \quad (36)$$

$$E_2 = E_{0,2} - \frac{RT}{2F} \ln \frac{[\text{OH}^-]^3}{[\text{H}_2\text{O}_2^-][\text{H}_2\text{O}]} \quad (37)$$

where the quantities in brackets correspond to the activities of the indicated species. Equation (36) shows that an increase in oxygen pressure and a decrease in H_2O_2^- and OH^- ion concentration favours peroxide production. On the other hand, equation (37) shows that a decrease in OH^- concentrations favours peroxide reduction. Park et al. (54) using KOH (with platinum electrode) showed that the rate of hydrogen peroxide production and its decomposition appear to increase after passing through a maximum in 0.3 M KOH as the KOH concentration increases. It is suggested as perhaps due to the formation of an intermediate product of superoxide ion i.e.,

which is stabilized in nonprotic medium. Reaction (29) is decreased by an increase in pH because the rate of the reaction is determined by the concentration of the neutral hydrogen peroxide molecule but not by H_2O_2^- ion (32). Oloman (32) presented in graphical form the actual relationship between the concentration of neutral species of H_2O_2 and the pH of the solution.

c. Mass Transfer

Oxygen has a low solubility in concentrated caustic, for example 2×10^{-5} M in 9 M NaOH (30% by weight) at 85°C. At 20°C, the solubility of oxygen in dilute water solutions of electrolytes is approximately

1.3×10^{-3} mole per litre. Consequently, to achieve practical current densities in O_2 reduction, an effective mass transfer between the cathode and the catholyte is important. Various means of achieving high mass transfer rate (i.e., increase in mass transfer coefficient) have been employed - such as the use of porous electrodes, gas bubbling, electrode vibration, fast flow of electrolyte, eddy promoters, etc. The limiting current density, i_L , limits the productivity of the cell as it is dependent on the maximum oxygen transfer rate to the cathode. This limiting current density is given by

$$i_L = 2 F K_d C_b \quad (39)$$

where

i_L = oxygen transfer limited current density ($A\ m^{-2}$)

C_b = bulk oxygen concentration ($mol\ m^{-3}$)

F = Faradays number (96500 coulombs/gm equiv)

K_d = oxygen transfer coefficient ($m\ s^{-1}$)

The oxygen transfer coefficient depends on the hydrodynamic conditions (including particle size) in the reactor. The limiting current density is thus dependent on the hydrodynamic conditions in the reactor. When the operating current density exceeds the limiting current density, alternative reactions (e.g., reduction of peroxide or H_2 liberation) take place. It is also known that even below the limiting current density alternate reactions do occur. The extent of these reactions is a complex interaction of the reaction thermodynamics, interfacial concentration of the reactive species and the electrode

kinetics. Improvement in the value of K_d generally promotes O_2 dissolution and the suppression of peroxide reduction, while increase in current density on the electrode lowers the interfacial O_2 concentration thus raising the (cathodic) potential and enhancing the rate of peroxide reduction (see Oloman (32)).

(d) Current Density

The effect of current density on alkaline peroxide electrogeneration is very important as could be deduced from the two consecutive loss reactions of peroxide production, viz:

From the works of Oloman and Watkinson (31), McIntyre and Phillips [34] and Brown et al [33], it is known that increase in current density leads to loss of current efficiency in peroxide production. This was explained as due to the increase in the cathode overvoltage (with increase in current density) which results in a more negative cathode potential. As the cathode becomes more negative, the rate of reaction (40) increases. Because reaction (40) is kinetically slow, it is possible to isolate peroxide at even higher current densities. The effect of this loss mechanism can be reduced by operating at lower current densities or by increasing the specific surface area of the cathode.

(e) Temperature

The rate of oxygen reduction on a cathode is temperature dependent. However, there is relatively little data on the temperature dependency of this reduction. The solubility of oxygen in aqueous solution is temperature dependent, thus an increase in temperature reduces the amount of soluble oxygen and hence the amount of oxygen transferred to the electrode. The dissociation (chemical) of peroxide will also be affected by temperature - thus the rate of the electrochemical process will be affected by the temperature. In the documented electrochemical synthesis of peroxide (31, 33, 34), no attempt was made to investigate the influence of temperature on peroxide concentration or current efficiency.

2.5.3 Hydrogen Peroxide Production in Trickle Bed Electrochemical Reactors

Oloman and Watkinson (28) developed a trickle bed electrochemical reactor for the production of dilute alkaline peroxide solutions by reduction of oxygen. The trickle-bed electrochemical reactor consisted of a metal cathode plate, a thin bed of graphite particles, a porous non-conducting diaphragm (could be a cationic membrane) and a metal anode plate compressed in a sandwich as shown in Fig 2. The graphite beds were contained in asbestos/neoprene gaskets and the electrode plates held between bolted mild steel channels to hold internal pressures of up to 2000 kPa.

The Oloman-Watkinson trickle-bed cell could have a single electrolyte feed as shown in Fig 2 or with some minor modifications a

Fig. 2 Trickle bed electrochemical cell for generation of alkaline hydrogen peroxide.

(from ref. 28)

separate anolyte and catholyte feeds. The anode electrode and the cathode current feeder electrode were 316 stainless steel. Oxygen gas was generated on the anode.

2.6 Coupling of Cathode Reaction of Oloman-Watkinson Peroxide Cell with Anode Reaction of a Chlorate Cell

The motivation in this work is to explore the feasibility of making a cheap alkaline peroxide and sodium chlorate in the same electro-chemical cell. The incorporation of such a process in a pulp mill would not only make cheap peroxide available but would remove the problems associated with chromium effluent in ClO_2 generation in pulp mills.

The fixed-bed cell developed by Oloman and Watkinson [30] is a candidate cell for such a process. The Oloman-Watkinson cell is a divided cell with a cathode of fixed carbon bed for generating alkaline peroxide and an anode electrode of stainless steel at which O_2 is generated. The separator used could be a diaphragm or cation membrane.

In converting this cell into a peroxy-chlorate cell, the anode electrode should be a DSA and the separator could be a diaphragm or an anion specific membrane. An anion specific membrane is preferred.

2.6.1 Process Description

Figure 3 shows schematically the basic reactions in a membrane peroxy-chlorate cell. An explanation of the basic process principle requires an understanding of the ion transport across the separator. The anion exchange membrane which divides the cell into an anode and a cathode chamber is hydrodynamically impermeable but permits the passage

of negatively charged anions. All ions in the cell (when in operation) are under a combined influence of electric field (migrational), concentration potential (diffusion) and convection forces. These combined forces are responsible for ion transport in solution and across the membrane.

An analysis of the ion movement in the reactor could be given using the Nernst-Einstein equation:

$$N_i = -Z_i D_i C_i \frac{F}{RT} \frac{d\phi}{dx} - D_i \frac{dC_i}{dx} + C_i v \quad (42)$$

Fig. 3 Schematic diagram of a membrane peroxy-chlorate cell showing electrode reactions and transport processes.

The addition of a water flux term ($C_i v$) is according to Koh (51) and Kruissink (52).

On the application of this equation to the anolyte side anions (Cl^- , ClO_3^- , ClO^- and Cl_3^-), the electrical (or migrational) flux $[DC(\frac{F}{RT}) \frac{d\phi}{dx}]$ and water flux terms ($C_i v$) favour the transportation of these anions towards the anode while the diffusion term ($D \frac{dc}{dx}$) favour the movement of the anions towards the cathode. The consequence of these opposing fluxes is that the net flux of anolyte anions could be towards the anode instead of the catholyte. [The net flux depends on relative magnitude of DVC (toward the catholyte) and $ZFC D \nabla \phi$ (toward the anode) - hence depends on current density and concentration of ClO^- , ClO_3^- , Cl^- and Cl_3^-]. Therefore, the net flux of anolyte anions into the catholyte would be lower than the flux towards the anode side (if other conditions favour this). For instance, the net migrational flux for Cl^- ions in 3.0 M NaCl at 80°C is 4.75×10^{-4} moles/ m^2 s (assuming a potential drop of 0.8 V across a membrane of thickness 2.54×10^{-5} m). The Cl^- self diffusion coefficient in the membrane is assumed to be 15.3×10^{-11} m^2 s^{-1} (53). Under the same conditions, the concentration flux is -1.81×10^{-5} mol (m^2 s) $^{-1}$. Thus the net chloride flux towards the anode will be 4.57×10^{-4} mol (m^2 s) $^{-1}$.

On considering the anions in the catholyte, the electrical flux term, water flux term and the diffusion flux drive the anions towards

the anode. It is thus possible to have OH^- ions transport from the catholyte into the anolyte for neutralization of the H^+ ions that result from the Cl_2 gas hydrolysis. The cation transport across the membrane is prevented.

Equations (1) and (2) show the unequal balance in hydroxyl ion generation (by the cathode reactions) and hydroxyl ion consumption (by the chlorate formation). For successful synthesis of chlorate, the balance between the hydroxyl requirements in the anode and the hydroxyl ion generation in the cathode could be supplied by the caustic electrolyte used in the cathode.

The successful production of chlorate and peroxide in the same cell will depend on the selective transport of OH^- ions over the HO_2^- ions across the separator from the catholyte to the anolyte. As shown in equation (42), the selective transport of OH^- ions over HO_2^- ion would depend on both the differences between their diffusion coefficients and concentrations. According to Oloman [23], the hydroxyl ion has a diffusion coefficient that is about four times that of perhydroxyl ion in 1.0 M NaOH. With a low ratio of HO_2^- concentration to OH^- concentration (pulp mill requirement), the selective transport of OH^- over HO_2^- across the membrane is likely to be favoured.

Yeager et al [53] reported the self diffusion coefficients of Na^+ in cation membrane for concentrated sodium chloride (3.0 M). Their reported results show that the diffusion coefficient for Na^+ is less than its value in water (at 25°C) as compared to its value in perfluorinated sulphonate and carboxylate membrane. It is likely that

OH^- and HO_2^- ions would have lower diffusion coefficients in anionic membrane than in water. If such is true, OH^- ions will be the major current carrier in the process.

2.6.2 Problems Inherent in the Coupled Process

The success of a coupled synthesis of this nature depends on the overcoming of many economic and technical problems that are inherent in such a system.

The economic feasibility of this process would depend on the ratio of the products of interest. Thus the kg of H_2O_2 produced per kg of chlorate produced and the current efficiencies achieved at such ratios would determine the economic feasibility of the process.

In addition to this, the peroxide and chlorate concentrations must be of commercial interest to warrant the process to be considered as successful.

The major technical problems to overcome in the successful application of this process pertain to the performance of the separator used between the cathode and the anode chambers. The requirement of a good separator to use for this process include the following:

High Conductivity: Any good separator to use must be able to allow the passage of electric current. Thus such a separator must allow a voltage drop of less than 1 V across it at a current density of 2-3 kA m^{-2} . Since electric current is carried by ions in electrolytes, if an ion exchange membrane is the separator used, the molecular design of such a membrane would have to involve materials that will give the

membrane a high conductivity, i.e., a lower power consumption achievement or low membrane resistance.

Selectivity: The success of this process depends on the selective passage of OH^- ions over the HO_2^- ions into the anolyte. Peroxyhydroxyl ion (HO_2^-) reacts with OCl^- ions. This reaction is a chlorate efficient limiting process as hypochlorite (OCl^-) is an intermediate ion in chlorate synthesis. Thus, this process requires a separator that will selectively allow OH^- ions but will block the passage of any other ions - either anions or cation. However, the present technology on separator precludes a "one ion" specific separator - thus such requirement is too stringent to be met. The only way this problem is resolved is the lower mobility of HO_2^- ions and the relative concentration of HO_2^- compared to the OH^- ions.

For anion membranes, their permselectivities depend upon the various components such as polymer backbone compositions, charge densities, morphologies and crosslinking levels. Most anion-exchange polymeric membranes not only have transport selectivities between anions and cations, but also have selectivities towards various anions. This is an advantage in processes where certain anions are to be excluded from being transported across the membranes.

Dimension Stability: The separator must be able to maintain its size and flatness under extreme temperature conditions or pressure. For the present process, a cell temperature of 60°C may be required.

Chemical Stability: If the separator to be used contains atomic groups which can be attacked by Cl_2 , ClO^- or ClO_3^- ions even at high temperature, it cannot be utilized (e.g., C-H bonds). The chemical and thermal stability of ion exchange membranes were problems that contributed to the late entry of permselective membranes into the chlor-alkali industry. Until the use of perfluorinated chains were introduced, ion-exchange membranes tried in chlor-alkali industry tended to degrade in the presence of oxidizing agents such as chlorine. Anionic membranes normally use quaternary amines as the exchange sites. These species are quite unstable chemically under common industrial conditions. There is therefore limited application of anion membranes in electrosynthesis processes. Cross-linking of anion polymeric materials tend to strengthen them chemically.

In order to use an anion membrane in this process, a diaphragm (asbestos or polymeric material) could be used on the anode side of the anion membrane. The idea is to prevent a direct contact between generated chlorine and the membrane. The chemical stability of the membrane is the major problem in the success of this process.

Separator Life: The separator life span is an important factor worthy of consideration in choosing any membrane. In the chlor-alkali industry, where membrane cells are in commercial use, the average life span of a membrane is two years. Based on that, one can suggest same life span for any separator to be acceptable in this process.

Capital and Energy Costs: The economics of this process depend on both the capital costs and energy requirement. The capital costs for the process must be compared with the combined capital costs of a separate chlorate cell and peroxide cell. Similarly, the energy requirement of a peroxy-chlorate cell must be considered in contrast to the combined energy requirement of a chlorate cell and peroxide cell. If the coupled process production of chlorate and peroxide is cheaper relative to separate productions, one would consider the coupling an economically viable process. Of course other economic variables such as the operating costs must be included in any economic viability analysis of the process.

HO₂⁻ and OCl⁻ Reactions (Efficiency Loss Reactions): The reaction of HO₂⁻ with OCl⁻ as shown in equation (43) constitute current efficiency loss reactions in both the anode and cathode chambers.

The transport of either HO₂⁻ or OCl⁻ across the membrane leads to the reaction as shown in equation (43).

2.6.3 Direction of Flow of Anolyte and Catholyte

The use of a membrane as a separator in this process offers possibilities for process variations. One difference between the use of diaphragm and a membrane is the mass flow control in the electrochemical reactor. There are two possible flow directions for the anolyte and catholyte streams as shown in Figure 4 - Co-current and counter-current flows.

Fig. 4 Possible flow configurations for the anolyte and catholyte streams using membrane as cell separator (a) co-current flow (b) counter-current flow.

Since the reaction between OCl^- and HO_2^- ions constitute efficiency loss to both chlorate and peroxide current efficiencies and the HO_2^- transport into the anolyte depends on HO_2^- concentrations in the catholyte, the system current efficiencies would depend to some extent on the flow arrangement chosen. Simmrock (55) showed that in a chlor-alkali membrane electrolysis, the current efficiency increased by 5 to 6% by the replacement of a conventional flow arrangement with a counter-current series flow.

The counter-current arrangement (b) could have higher current efficiencies depending on the electrolyte concentration which affects electrolyte resistance, the membrane resistance and overvoltages. In this work, the co-current stream flow is used.

CHAPTER 3

OBJECT

The aim of this work is to investigate the possibility of making alkaline hydrogen peroxide and sodium chlorate in the same cell.

The work involves the design and construction of the equipment and its use in exploratory experiments involving the search for a suitable separator between the anode and cathode chambers. An examination of several variables that could affect the process will be undertaken.

Further examination of major effects is carried out in more detail. The variables whose effects on chlorate and peroxide current efficiencies are examined in more detail are;

1. catholyte flow
2. sodium hydroxide concentration
3. superficial current density.

CHAPTER 4

APPARATUS, METHODS AND ACCURACY

One electrochemical reactor was used in this work. It was a laboratory unit made to operate in a continuous manner with electrolyte feed rates from 83.33×10^{-9} to $33.33 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$. The reactor was built to operate at atmospheric pressure.

4.1 Apparatus

A line diagram of the equipment used is illustrated in Fig 5 and the photographs of the apparatus are shown in Figs 6 and 7. The electrochemical reactor consisted of a cathode bed sandwiched between a flat feeder electrode plate, an anion membrane and an anode chamber. The cell is fed from the top with separate anolyte and catholyte solutions (co-current flow in the cell). The reactor employs an anode monopole chlorine electrode $3 \times 10^{-3} \text{ m}$ thick (DSA, Electrode Corporation, U.S.A.). The anode chamber was contained in a $3 \times 10^{-3} \text{ m}$ thick neoprene gasket with PVC mesh membrane support (mesh size 10, Cole Parmer, U.S.A.). The anion membrane was protected on the anode side by an asbestos diaphragm of thickness $0.8 \times 10^{-3} \text{ m}$. (Albion Ind. Prod. Ltd., Vancouver). The anion membrane was 'RAIPORE' 1035 (R-1035, Electrosynthesis Co.Inc., N.Y. U.S.A.) and was $2.54 \times 10^{-5} \text{ m}$ (film) in thickness.

The cathode bed was a fixed bed of graphite felt (Graphite felt Grade GF, Carborundum Corp. N.Y., U.S.A.) of dimensions: length 23 x

APPARATUS FOR ELECTROCHEMICAL COGENERATION OF SODIUM CHLORATE AND ALKALINE PEROXIDE SOLUTIONS

Fig. 5

Fig. 6 Photographs of the apparatus for simultaneous electrosynthesis of alkaline peroxide and sodium chlorate.

10^{-2} m, width 36.2×10^{-3} m and 3×10^{-3} m thick (when compressed). The cathode bed was pretreated by soaking in 5 N nitric acid for 2 hours or more and then washed with distilled water. The cathode feeder plate was a 0.8×10^{-3} m thick 316 stainless steel. The cathode bed was contained in a 3×10^{-3} m thick neoprene rubber gasket. The cell was held together by plexi-glass compression plates of thickness, 25.4×10^{-3} m. Some important dimensions of the reactor are given in Table 1. Figure 8 shows the side and top elevations of the electrochemical reactor. Some relevant technical specifications of the graphite are listed in Table 2.

The equipment consists of an anolyte holding volume or external reactor, a catholyte feed tank, two circulation or March metering pumps (model 210-10R, Cole Parmer, U.S.A.), an anolyte pH controller (chemcadet pH meter/controller, model No. 5652-00, Cole Parmer Company, U.S.A.), two chemical feed pumps (Chemfeed, model C-1530SP, Cole Parmer), two tube coolers of titanium, an oxygen tank and a D.C. power supply (Soresen Power supplies, model DCR 40-25B).

The anolyte was pumped from a 2.2 litre reaction tank thermostated to a constant temperature, then passed through a pH probe connected to the pH meter/controller for the monitoring and control of the anolyte tank pH. The pH value of the outflow from the anolyte 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 from the automatic pH controller. The anolyte passed through the anode chamber of the cell and was recycled to the anolyte external reactor. The catholyte was delivered from a 20 litre tank and passed once through the cell and was sampled before disposal to the drains.

Front View

Side View

Fig. 7 Electrochemical reactor used for cogeneration of alkaline peroxide and sodium chlorate.

Fig. 8 Side and top elevations of a peroxy-chlorate cell

Top Elevation

Side Elevation

Table 1
Dimensions of peroxy-chlorate cell

Compression plates	43.2×10^{-2} m long $\times$ 12.7×10^{-2} m wide $\times$ 2.54×10^{-2} m thick
Chlorine or DSA electrode (anode) RuO ₂ /TiO ₂ coated platinized electrode (Electrode Corporation)	48.3×10^{-2} m long $\times$ 12.7×10^{-2} m wide $\times$ 3×10^{-3} m thick
Effective superficial area of membrane	83.3×10^{-4} m
Anode chamber dimensions	23×10^{-2} m long $\times$ 3.62×10^{-2} m wide $\times$ 3×10^{-3} m thick (in the direction of current flow)
Cathode bed dimensions (compressed)	23×10^{-2} m long $\times$ 3.62×10^{-2} m wide $\times$ 3×10^{-3} m thick
PVC mesh membrane support (mesh size - 10)	23×10^{-2} m $\times$ 3.6×10^{-2} m (2 used)

Both the anolyte and catholyte were pre-cooled before the cell by passing through water cooled titanium coolers each of which consisted of an outer copper tube (1.27×10^{-2} m diameter and 30.5×10^{-2} m length) and an inner 0.635×10^{-2} m. titanium tube. The water was fed countercurrently to the electrolyte in the inner tube. The cell was not cooled.

The flows of the anolyte and the catholyte to the reactor were measured by rotameters and controlled manually through needle valves. The oxygen gas was delivered from an oxygen gas cylinder. The oxygen flow was controlled by a needle valve and measured by a rotameter. The gas was mixed with the sodium hydroxide (catholyte) in a Tee before entering the cell.

Power for the cell was obtained from a direct current power supply with a maximum power output of 1.0 kVA and capable of either voltage or current controls up to 40.0 volts or 25 amperes.

All parts in contact with the anolyte are made of either polypropylene, polyethelene, teflon, glass or plexiglass while for the catholyte, polypropylene, stainless steel, glass or plexiglass were used. No corrosion was observed during the experimental program. The specifications of the parts of the apparatus are given in Appendix 1.

4.2 Methods

The anolyte solution was prepared from 99.0 percent pure sodium chloride (BDH company) and deionized water. The catholyte sodium hydroxide was of same purity and from the same source and was prepared in like manner.

Table 2
Properties of graphite felt (cathode bed)

Felt thickness (before compression) m	6.35×10^{-3} m
Surface area (B.E.T. adsorption) $\text{m}^2 \text{g}^{-1}$	0.23
Porosity	0.94
Carbon content (wt. fraction)	0.99
Fibre diam μm	10.0

After exploratory experiments (involving the identification of the separator and process conditions) indicated that sodium chlorate and alkaline hydrogen peroxide could be made simultaneously in the same cell, a series of experimental runs were carried out. The experimentation consisted of runs in which measurements were made on the catholyte feed rates, anolyte flow, the pH of the anolyte in the external reactor, the temperature of the anolyte tank, the temperature of feeds into and out of the cell, the oxygen flow, the current to the cell, the voltage drop across the cell, the concentration of peroxide in the catholyte exiting from the cell, the concentration of chlorate in the anolyte tank, the concentrations of active chlorine (hypochlorite and hypochlorous acid) in the anolyte leaving the cell (for some runs) and in the anolyte tank, the initial and final sodium chloride concentration in the anolyte tank, the sodium chloride concentration in the catholyte, the initial and final anolyte solution volume and the duration of run or operation.

To carry out an experimental run, the cathode and anode feed tanks were first charged respectively with a solution of sodium hydroxide and sodium chloride (in some runs a mixture of sodium chloride and chlorate was used as the anolyte solution) of known concentrations. The anolyte line was flushed with the anolyte solution into the drains to make sure that no chlorate left in the line (from previous experimentation) is recirculated. The anolyte tank was thermostated and heated to the operating temperature.

The anolyte rate through the cell was set at $2.0 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ and the oxygen gas flow was kept at $8.5 \times 10^{-6} \text{ m}^3$ per second (STP). The

oxygen was mixed with the sodium hydroxide before the catholyte flows into the cell. The current through the cell was then set with the power supply in the current control mode.

Samples of the catholyte product were taken at intervals of time for analysis of peroxide concentration. A conventional titration method using potassium permanganate (0.1N) as titrant and sulphuric acid for the acidification of sample before titration was used. The method is accurate enough for this purpose [32].

Samples of the anolyte product were taken and the concentrations of active chlorine (sum of concentrations of hypochlorite, hypochlorous acid and molecular chlorine) and chlorate were analyzed. A potentiometric titration method was used and the technique is based on a modified method due to Norkus and Prokopchik [56]. The detailed technique is given in Appendix 2.

A sample each of the anolyte and catholyte was obtained to serve for the determination of the chloride ion concentrations by using a conventional titration method of silver nitrate as titrant and potassium bichromate as indicator. The catholyte was first neutralized using 1.0 M nitric acid. A total of 51 runs were carried out. Eight of these runs were at high chlorate concentrations. A high chlorate concentration is meant any concentration greater than or equal to 1.0 M.

The ranges of operating variables covered* in this work are given in Table 3. Sample calculations, including the chloride balance in the system are shown in Appendix 2.

*All pressures are gauge pressures.

Table 3
Range of experimental variables

Variable	Units	Range
Catholyte flow	$\text{cm}^3 \text{ s}^{-1}$	0.10 - 0.50
NaOH Concentration	M	0.5 - 2.0
Superficial Current Density	kA m^{-2}	1.2 - 2.4
Current	A	10.0 - 20.0
Temperature	$^{\circ}\text{C}$	18.0 - 70.0
pH		6.0 - 7.0
Pressure	kPa	0 - 82.7

4.3 Accuracy

A list of the quantities measured, the method used and an estimate of the accuracy of each method is shown in Table 4. Measurements were made with the most convenient techniques. The maximum degree of uncertainty in the calculated quantities are as follows:

Peroxide concentration	$\pm 2\%$
Current efficiency (peroxide)	$\pm 7\%$
Separator current density	$\pm 3\%$
Chlorate concentration	$\pm 5\%$
Chlorate current efficiency	$\pm 10\%$
Active chlorine concentration	$\pm 3\%$
Sodium chloride concentration	$\pm 2\%$
Total moles of chlorate	$\pm 3\%$

Table 4
Estimates of experimental accuracy

Quantity	Range	Method	Accuracy
Current	10 - 25 amps	Ammeter	$\pm 3\%$
Sodium hydroxide Conc.	0.5 - 2.0 moles/litre	Titration	$\pm 1.5\%$
Catholyte flow	0.1 - 0.5 cm ³ /s	Rotameter	$\pm 10\%$
Oxygen flow	2.5 - 8.5 cm ³ /s	Rotameter	$\pm 3\%$
Sodium chloride Conc.	0.5 - 4.0 moles/litre	Titration	$\pm 2.3\%$
Anolyte flow	0.5 - 3.0 cm ³ /s	Rotameter	$\pm 4\%$
Anolyte tank temp.	40 - 70°C	Thermometer	$\pm 1^\circ\text{C}$
Anolyte tank pH	5 - 7.5	pH meter	± 0.05 pH
Pressure	0 - 82.7 kPa	Pressure gauge	± 1.4 kPa
Cell temperature	19 - 35°C	Temp.gauge	$\pm 1^\circ\text{C}$
Cell voltage	2.9 - 4.7 v	Thermometer Volmeter	$\pm 0.2\%$
Anolyte volume	1.5 - 2.5 litres	Graduated cylinder	$\pm 2.0\%$
Peroxide, chlorate and chloride titre	1 - 50 ml	50 ml burette	± 0.05 ml

CHAPTER 5

RESULTS AND DISCUSSION

5.1 General Considerations

In the simultaneous electrosynthesis of sodium chlorate and alkaline hydrogen peroxide, current efficiencies or rate of production of the products could be used as a measure of the system performance. In this work, current efficiency is used.

The current efficiency is defined here as

current efficiency = $100 \times \frac{\text{Rate of production of the desired species}}{\text{Rate of Production of the desired Species in stoichiometric equivalence to the total current in the process.}}$

$$\text{i.e.} \quad \text{CE} = 100 \frac{MZF}{I\tau} \quad (44)$$

where

M = moles of desired product

F = Faraday's number (coul/g-equiv)

I = current (A)

τ = total time of cell operation in seconds

Z = stoichiometric number of electrons transferred per mole of product

CE = current efficiency (%)

The basic anode process in this system is chloride ion oxidation, accompanied by intermediate hydrolysis of elemental chlorine which yields hypochlorous species (hypochlorite and hypochlorous acid) or available chlorine. The active chlorine as an intermediate product could be converted to chlorate in two parallel ways, viz--the chemical route in the external reactor and the electrochemical route in the cell.

In evaluating the sodium chlorate current efficiency, an assumption is made that all the chlorate produced is through the chemical route. The chemical route is the combination of equations (4), (6) and (7) or

The total moles of electrons required to produce one mole of chlorate through the chemical route as in equation (45) is 6 moles of electrons. Thus, the chlorate efficiency is expressed as

$$\eta_{\text{ClO}_3^-} = \frac{600 \text{ FN}}{I \tau} \quad (46)$$

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

$$\eta_{\text{H}_2\text{O}_2} = \frac{193 \text{ QC}}{I} \times 100 \quad (47)$$

where

Q = flow rate of catholyte in cm^3/s

C = concentration of peroxide in moles/cm^3

I = current in amperes

The current efficiency as a figure of merit of the process is determined by the chemistry of the process, operating conditions and the design of the cell.

5.1.1 Preliminary Experiments

Prior to screening of the process variables and main investigations, exploratory experiments were carried out to investigate whether alkaline peroxide and chlorate could be produced simultaneously in the same electrochemical cell. The search for suitable separator included the trial of:

- (i) Porous asbestos diaphragm — convective diffusion mitigated its usefulness
- (ii) Celgard microporous polypropylene (type 5511) (Celanese Corp. USA) — the polypropylene product could not stand high temperature and long operation in chlorine environment.
- (iii) Ionics MA-3475 anion membrane (Electrosynthesis Co., Inc. USA) — has fabric base but was not chemically suitable for use in the process.
- (iv) RAIPORE - R-1035 anion membrane (Electrosynthesis Co., Inc. USA) backed by asbestos diaphragm. This combination of anion membrane with an asbestos diaphragm was found suitable for this work.

In one of the exploratory experiments (using R-1035 - asbestos diaphragm), the concentrations of chlorate and peroxide and their current efficiencies were followed for 10 hours. The 10 hours run was divided into two--4 hours and 6 hours of different anolyte average

flows. In the first 4 hours, the average anolyte flow was kept at $0.6 \text{ cm}^3 \text{ s}^{-1}$ while in the next 6 hours the average anolyte flow was kept at $3.4 \text{ cm}^3 \text{ s}^{-1}$. The catholyte flow was kept constant at $0.2 \text{ cm}^3 \text{ s}^{-1}$.

Experimental conditions and results obtained in this preliminary experiment are recorded in Tables 5 and 6. Considering first the chlorate side, we find that

1. The chlorate concentration increases or rises with time of operation (see Fig. 9)
2. The chlorate efficiency at the average anolyte flow of $0.6 \text{ cm}^3 \text{ s}^{-1}$ (first 4 hours of the run) has an average value of 57.2% with the individual calculated values varying between 70% to 49%.
3. The average value when the average anolyte flow was $3.4 \text{ cm}^3 \text{ s}^{-1}$ was 57.4% with the individual values varying between 60% and 56%.

On the cathode side the following observations are made:

- (a) In the first 4 hours, the peroxide concentration was almost constant at 0.47 M with an average efficiency of 72.0% (Table 5).
- (b) The concentration of peroxide is seen to increase on increasing the anolyte flow--the average concentration between the 5th and 10th hours is 0.58 M with an average current efficiency of 84.0%.

The cell voltage has an average value of 5.96 V at a low anolyte flow of $0.6 \text{ cm}^3 \text{ s}^{-1}$ but falls to an average of 3.7 V when the anolyte flow was increased to $3.4 \text{ cm}^3 \text{ s}^{-1}$. The anolyte tank pH was manually controlled and lies between 5.3 and 5.75 pH. In these preliminary runs, the feeds were not cooled before entering into the cell--thus high

Table 5
Preliminary exploratory experimental results
(0th hour - 4th hour)

Time (mins)	Anolyte Flow (cm ³ s ⁻¹)	Chlorate Conc. x 10 ³ (M)	Chlorate Current Efficiency (%)	Catholyte Flow (cm ³ s ⁻¹)	Peroxide Conc. (M)	Peroxide Current Efficiency (%)
30	0.53	27.1	70.0	0.20	0.45	69.5
90	0.57	68.8	59.0	0.20	0.47	72.6
135	0.61	83.12	47.5	0.20	0.47	72.6
180	0.68	140.8	60.4	0.20	0.47	72.6
240	0.65	153.3	49.3	0.20	0.47	72.6

Conditions:

NaOH conc = 2.0 M
Oxygen flow = 8.5 cm³ s⁻¹ (STP)
Catholyte cell side temp (°C) = 18/48 (inlet/outlet)
Catholyte side pressure (kPa) = 0/0
Anolyte cell side temp (°C) = 30/62
Anolyte cell pressure (kPa) = 0/0
Anolyte tank pH = 5.5
Anolyte tank temp (°C) = 70
Cell voltage (V) = 5.9
Average anolyte tank vol = 2 litres
Current supply = 25A (CD = 3 kA m⁻²)

Table 6
Preliminary exploratory experimental results
(6th hour - 10th hour)

Time (mins)	Anolyte Flow (cm ³ s ⁻¹)	Chlorate Conc. x 10 ³ (M)	Chlorate Current Efficiency (%)	Catholyte Flow (cm ³ s ⁻¹)	Peroxide Conc. (M)	Peroxide Current Efficiency (%)
300	3.20	233.50	60.0	0.18	0.51	71.0
360	3.50	269.5	57.8	0.20	0.58	89.6
420	3.40	311.5	57.3	0.20	0.58	89.6
480	3.50	358.1	57.6	0.20	0.58	89.6
540	3.40	394.8	56.4	0.18	0.52	72.3
600	3.30	431.3	55.5	0.20	0.58	89.6

Conditions:

NaOH conc = 2.0 M
Oxygen flow = 8.5 cm³ s⁻¹ (STP)
Catholyte cell side temp (°C) = 20/46
Catholyte side pressure (kPa) = 0/0
Anolyte cell side temp (°C) = 56/59
Anolyte cell pressure (kPa) = 13.8/0
Anolyte tank pH = 5.6
Anolyte tank temp (°C) = 70
Cell voltage (V) = 3.7
Average anolyte tank vol = 2 litre
Current supply = 25A (3 kA m⁻²)

Preliminary exploratory experimental results

Figure 9

values of inlet and outlet temperatures (for the anolyte side) were observed while the catholyte exit temperature was between 46 and 48°C. A pressure drop of less than 6.9 kPa in the reactor on the anolyte side at low anolyte flow was observed while an average of 13.8 kPa drop in pressure was recorded when the anolyte flow was increased. There was a small pressure drop (less than 6.9 kPa) on the catholyte side of the cell.

This preliminary experiment demonstrates that alkaline hydrogen peroxide and chlorate can be made simultaneously in the same cell at reasonable current efficiencies.

5.1.2 Screening the Process Variables

In selecting the process variables or factors to be investigated for their relative importance, the knowledge of factors that affect chlorate and alkaline peroxide synthesis independently was taken into consideration. In view of the knowledge, the following factors were considered as possible experimental plan factors.

1. NaOH concentration
2. Catholyte flow
3. Oxygen flow
4. Temperature of the catholyte inlet into cell
5. Anolyte flow
6. NaCl concentration
7. NaClO₃ concentration
8. Anolyte tank temperature
9. Anolyte stream cell inlet temperature

10. Anolyte side pressure
11. Catholyte side pressure
12. Current or current density
13. Separator
14. pH of anolyte tank solution
15. Electrolyte flow directions (co-current or counter current flows)

In considering the above factors, there are bound to be some interactions and an efficient method of investigating the relative importance of each factor would be a complete factorial design. This would however involve 2^{15} (or 3278800) experiments for 15 factors at 2 levels of each!

Based on preliminary experiments and equipment limitations, the 15 factors were reduced to 9. The 9 factors chosen to investigate for possible effect on the efficiencies are:

1. Catholyte (NaOH) concentration
2. Oxygen flow
3. Catholyte flow
4. NaCl concentration
5. NaClO₃ concentration
6. Anolyte flow
7. Anolyte tank temperature
8. Current or current density
9. Anolyte tank pH

To carry out a factorial experiment for 9 factors at 2 levels of each requires 2^9 or 512 experiments. Although such would have been invaluable in obtaining information relating to interactions, a more

practical method of screening the variables would be sought.

In this work, the Plackett-Burman (P-B) (57) design is chosen at two levels of each factor. According to this design, N experiments could be used to study N-1 variables. For the present problem, N=12 is chosen. To choose a number that cannot be expressed in powers of 2 i.e., $N \neq 2^n$, where n is a whole number, we limit the power of this design. If N were a factor of 2^n , then possible factors interactions could be obtained.

Although in the original P-B paper (57), use of dummy variables was not suggested as binding, in the present work, 2 dummy variables were used to relate the uncertainty of our results with experimental errors, confounding or interactions.

The P-B design for 12 experiments is shown in Fig. 10. In the figure, the following letters are used to represent the factors of interest.

- A - NaOH concentration (M)
- B - Catholyte flow (cm^3/s)
- C - Dummy
- D - Oxygen flow (cm^3/s)
- E - NaCl concentration (M)
- F - Anolyte flow (cm^3/s)
- G - NaClO_3 concentration (M)
- H - Anolyte tank temp ($^{\circ}\text{C}$)
- I - Anolyte tank pH
- J - Dummy
- K - current (A)

In Fig 10, (+) plus sign stands for high level and (-) minus sign for low level of factor in question.

Magnitude of the Levels

Table 7 shows the magnitudes - both low and high - of the factor levels used. In choosing the levels, consideration was given to (i) reported experimental results of individual alkaline and chlorate synthesis (ii) preliminary results of work already carried out (iii) Industrial practices for the manufacture of the chlorate of sodium.

An instance of (i), Oloman and Watkinson (28), generated alkaline peroxide of 0.8 M concentration at 60%, current efficiency in 2.0 M caustic with pressurized cell while Brown et al [33] claimed a 1.5% wt peroxide in 1.0 M caustic at 67% current efficiency (no pressurization). Thus a low level of 0.5 M and a high level of 2.0 M caustic was used.

Design and Order of Experimentation

As shown in Fig 10, two levels of each factor were considered and twelve experiments carried out. Each experiment was carried out for a specific duration of time and the current efficiency of the product of interest calculated.

The experiments were completely randomized as shown in the last column of Fig 10. The efficiency calculation obtained from the experimental results are as shown in Table 8.

Table 7
Magnitudes of levels of factors

Factor	Low Level (-)	High Level (+)
A - NaOH Conc. (M)	0.5	2.0
B - Catholyte flow (cm ³ /s)	0.10	1.0
C - Dummy	-	-
D - O ₂ flow (cm ³ /s, STP)	2.0	10.0
E - NaCl Conc (M)	0.5	5.0
F - Anolyte flow (cm ³ /s)	0.5	3.0
G - NaClO ₃ conc (M)	0.0	0.2
H - Anolyte tank temp (°C)	40.	70.
I - Anolyte tank pH	5.0	7.5
J - Dummy	-	-
K - Current (A)	5.0	25.0

Table 8
Variable screening experimental results

Run #	A	B	C	D	E	F	G	H	I	J	K		% ClO ₃ ⁻ Current Efficiency	H ₂ O ₂ % Current Efficiency
3	+	+	-	+	+	+	-	-	-	+	-		8.50	73.3
12	+	-	+	+	+	-	-	-	+	-	+		62.08	48.28
4	-	+	+	+	-	-	-	+	-	+	+		5.43	19.30
11	+	+	+	-	-	-	+	-	+	+	-		67.76	72.27
1	+	+	-	-	-	+	-	+	+	-	+		74.31	10.13
6	+	-	-	-	+	-	+	+	-	+	+		41.77	54.04
7	-	-	-	+	-	+	+	-	+	+	+		60.40	20.50
8	-	-	+	-	+	+	-	+	+	+	-		40.9	82.0
9	-	+	-	+	+	-	+	+	+	-	-		49.84	82.4
10	+	-	+	+	-	+	+	+	-	-	-		56.57	50.18
5	-	+	+	-	+	+	+	-	-	-	+		50.21	3.0
2	-	-	-	-	-	-	-	-	-	-	-		6.75	36.67

Computation of Test Statistics

Each of the variables according to P-B design shown in Fig. 10, (during the 12 runs) appears at its high level six times and at its low level six times. The effect of a variable on the response (efficiency) is simply the difference between the average value of the response for the six runs at high level and the average value of the response for the six runs at the low level. i.e.,

$$E_A = \frac{R0 \text{ at } (+)}{6} - \frac{R0 \text{ at } (-)}{6} \quad (48)$$

where

E_A = Effect of A

R0 = response or result (efficiency)

The effects of the dummy variables are calculated in like manner as for real variables. In the absence of interactions and the levels are reproduced perfectly with no error in response measurement, the effect shown by a dummy variable will be zero. A deviation of a dummy effect from zero is assumed to be a measure of the lack of experimental precision plus any analytical error in response measurement.

The variance of an effect was estimated using the following P-B derived equation

$$V_{\text{eff}} = \frac{\sum (E_d)^2}{n} \quad (49)$$

where

V_{eff} = variance of an effect

E_d = effect shown by a dummy

n = number of dummy variables

The relationship between the variance of an effect and the standard error of an effect is given by:

$$S.E_{\text{eff}} = (V_{\text{eff}})^{1/2} \quad (50)$$

From the responses of the 12 runs, the effect of each of the variables was calculated and the standard error of the effects obtained. The results obtained are shown in Table 9 for ClO_3^- and Table 10 for peroxide. The significance of each effect was determined by a t-test:

$$t = \frac{\text{effect}}{S.E_{\text{eff}}} \quad (51)$$

The number of dummies provided the number of degrees of freedom for entering the tabular values of t.

The results in Table 9 shows that at 90% confidence level, the analyte tank pH is an important factor in the chlorate efficiency. It is also found that at lower confidence levels, the NaClO_3 concentration and NaOH concentration seem to be important in the chlorate efficiency. On the other hand Table 10 for the peroxide efficiency shows that the current is an important factor. At lower confidence levels, the NaCl concentration seem to be important. It is interesting to observe that no one factor was important for the two products up to the same confidence level.

That many of the factors seem not to be important up to the 90% confidence level may be a result of lack of experimental precision,

Table 9
Variables and effects for ClO_3

Variable Name	Level		Effect (-) to (+)	Relative Significance		
	Low	High		t-Test	Prob.	Conf. Level
NaOH concentration (M)	0.5	2.0	16.24	1.610	0.26	74%
Catholyte flow rate (cm^3/s)	0.1	1.0	-2.07	0.205		
Dummy	-	-	6.90	0.683		
Oxygen flow rate (cm^3/s)	2.0	10.0	-6.48	0.642		
NaCl concentration (M)	1.0	5.0	-2.99	0.296		55%
Anolyte flow rate (cm^3/s)	0.5	3.0	9.54	0.945	0.45	
NaClO_3 concentration (M)	0	0.2	21.43	2.123	0.18	
Anolyte tank temp ($^{\circ}\text{C}$)	40	70.0	2.19	0.217		
Anolyte tank pH	5.5	7.5	31.01	3.070	0.10	91%
Dummy	-	-	-12.50	1.240	0.35	
Current (A)	5.0	25.0	10.65	1.055	0.40	60%

Table 10
Variables and effects for peroxide

Variable Name	Level		Effect (-) to (+)	Relative Significance		
	Low	High		t-Test	Prob.	Conf. Level
NaOH concentration (M)	0.5	2.0	10.72	1.002	0.42	58%
Catholyte flow rate (cm ³ /s)	0.1	1.0	-5.21	0.487		
Dummy	-	-	-0.335	0.031		
Oxygen flow rate (cm ³ /s)	2.0	10.0	5.975	0.559		
NaCl concentration (M)	1.0	5.0	22.328	2.087	0.18	82%
Anolyte flow rate (cm ³ /s)	0.5	3.0	-12.308	1.150	0.37	63%
NaClO ₃ concentration (M)	0	0.2	2.118	0.198		
Anolyte tank temp (°C)	40	70.0	7.338	0.686		
Anolyte tank pH	5.5	7.5	13.182	1.232	0.35	65%
Dummy	-	-	15.125	1.414	0.29	
Current (A)	5	25.0	-40.262	3.764	0.07	93%

interactions or confounding amongst the factors. As pointed out earlier on, the aim of this variable screening is to reduce the number of factors to be investigated. From these results, it was decided to investigate further the effects of the following on the coupled process:

1. NaOH concentration - at a 74% confidence level of being important in ClO_3^- efficiency
2. Current - 93% confidence level of being important in peroxide synthesis
3. NaClO_3 concentration - 82% confidence level of being relevant in chlorate synthesis
4. Catholyte flow - It was not shown to be important to any appreciable degree in both peroxide and chlorate efficiency. However results from preliminary experiments showed that catholyte at rates lower than $1.0 \text{ cm}^3 \text{ s}^{-1}$ do affect the peroxide and chlorate current efficiencies.

5.2 Factorial Experiments

Further experiments were carried out to elucidate the effects of catholyte flow rate, sodium hydroxide concentration and current density on the coupled synthesis. The factorial experiments were divided into two groups of chlorate concentrations, viz:

- (a) low chlorate concentration run
- (b) strong chlorate solution run.

A low chlorate concentration is meant a chlorate concentration less than 1.0 M while a high or strong chlorate solution refers to any chlorate concentration greater than 1.0 M.

Table 11 shows the list of independent and dependent variables and the levels at which the factorial experiments were performed. The results of the factorial experiments at three levels for the low chlorate runs are presented in Tables 12 and 13 while those of two level runs for the strong chlorate solutions are shown in Tables 14 and 15. Some of the useful results obtained from the factorial experimental runs (three and two levels inclusive) are contained in Tables A-C in Appendix 2. The principal features of these results are discussed below.

5.3 Low Chlorate Concentration Runs

5.3.1 Superficial Current Density Effects

The results in Tables 12 and 13 illustrate the effect of current density (i.e., current density based on the active area of metal current feeder plates or the separator). The principal features of these results are:

- i. At any given caustic concentration and flow, the chlorate efficiency increases with increase in current density (see Fig. 11 for typical result).
- ii. The chlorate efficiency increases with increase in catholyte flow rate at any given current density.
- iii. The peroxide efficiency, at any given caustic concentration and catholyte flow falls with increase in current density (see Fig. 12 for typical results).
- iv. The peroxide efficiency also rises with rise in catholyte flow at any given current density.

Table 11
List of independent and dependent variables

Independent	Levels	
	Low ClO_3^- runs	High ClO_3^- runs
Catholyte concentration (M)	0.5, 1.0 and 2.0	1.0 and 2.0
Current density (A)	1.2, 1.8 and 2.4	1.2 and 2.4
Catholyte flow ($\text{cm}^3 \text{ s}^{-1}$)	0.1, 0.3 and 0.5	0.1 and 0.5
<u>Dependent Variable</u>		
Chlorate current efficiency		
Peroxide current efficiency		
Chlorate concentration		
Peroxide concentration		

Table 12

Chlorate current efficiency and concentration at low chlorate concentration runs

Current Density kA/m ²	Catholyte Flow Rate cm ³ /s	Catholyte (NaOH Concentration (M))					
		0.5		1.0		2.0	
		ClO ₃ ⁻ current Efficiency (%)	ClO ₃ ⁻ Conc. Initial/final (M)	ClO ₃ ⁻ current Efficiency (%)	ClO ₃ ⁻ Conc. Initial/final (M)	ClO ₃ ⁻ current Efficiency (%)	ClO ₃ ⁻ Conc. Initial/final (M)
1.2 (10A)	0.1	53.0	0.0/0.049	52.7	0.376/0.425	53.2	0.0/0.033
	0.3	57.4	0.209/0.263	62.6	0.0/0.058	59.7	0.289/0.327
	0.5	68.5	0.258/0.322	70.3	0.0/0.066	70.3	0.0/0.044
1.8 (15A)	0.1	60.2	0.0/0.084	61.5	0.382/0.477	65.0	0.032/0.046
	0.3	68.0	0.029/0.124	67.5	0.058/0.152	70.0	0.235/0.327
	0.5	73.5	0.376/0.479	72.0	0.0/0.067	74.0	0.042/0.090
2.4 (20A)	0.1	69.1	0.0/0.129	69.0	0.475/0.604	62.6	0.099/0.190
	0.3	72.1	0.110/0.244	72.5	0.200/0.335	67.0	0.158/0.241
	0.5	78.0	0.225/0.370	76.0	0.055/0.153	72.9	0.102/0.193

*All the concentrations are normalized to 2.0 litres solution.

Conditions: Average cell voltages: 1.2 kA m⁻² - 3.00 V; 1.8 kA m⁻² - 3.46 V; 2.4 kA m⁻² - 4.1 V

	Anolyte Side	Catholyte Side
Cell temp (°C)	27/33	22/30
Cell press. (kPa) range	0.0-58.6/0.0	0.0-44.8/0.0
Oxygen flow (cm ³ s ⁻¹ , STP)	-	8.5
Anolyte tank pH	6.5 ± 0.2	-
Anolyte flow (cm ³ s ⁻¹)	2.0	-
Anolyte tank temp (°C)	70.0	-
NaCl conc. (M)	3.5 - 4.2	0.1 - 3 × 10 ⁻³
NaClO ₃ conc. (M)	0.0 - 0.5	-

Table 13

Peroxide current efficiency and concentration at low chlorate concentration runs

Current Density kA/m ²	Catholyte Flow Rate cm ³ /s	Catholyte (NaOH Concentration (m))					
		0.5		1.0		2.0	
		Peroxide Current Eff. (%)	Peroxide Conc. (M)	Peroxide Current Eff. (%)	Peroxide Conc. (M)	Peroxide Current Eff. (%)	Peroxide Conc. (M)
1.2 (10A)	0.1	29.5	0.153	51.8	0.268	86.1	0.446
	0.3	50.4	0.087	67.6	0.115	75.4	0.130
	0.5	62.0	0.064	66.6	0.069	66.2	0.069
1.8 (15A)	0.1	20.0	0.155	32.0	0.249	57.7	0.449
	0.3	34.7	0.09	44.4	0.115	54.0	0.140
	0.5	48.3	0.075	60.8	0.097	44.0	0.068
2.4 (20A)	0.1	15.9	0.145	28.4	0.275	52.7	0.52
	0.3	25.4	0.087	41.3	0.143	45.2	0.156
	0.5	39.5	0.082	56.5	0.117	37.7	0.077

Conditions: Average cell voltages: 1.2 kA m⁻² - 3.00 V; 1.8 kA m⁻² - 3.46 V; 2.4 kA m⁻² - 4.1 V

	Anolyte Side	Catholyte Side
Cell temp (°C)	27/33	22/30
Cell press. (kPa) range	0.0-58.6/0.0	0.0-44.8/0.0
Oxygen flow (cm ³ s ⁻¹ , STP)	-	8.5
Anolyte tank pH	6.5 ± 0.2	-
Anolyte flow (cm ³ s ⁻¹)	2.0	-
Anolyte tank temp (°C)	70.0	-
NaCl conc. (M)	3.5 - 4.2	0.1 - 3 × 10 ⁻³
NaClO ₃ conc. (M)	0 - 0.5	-

Table 14

Chlorate current efficiency and concentration at high chlorate concentration runs

Current Density kA/m ²	Catholyte Flow Rate cm ³ 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 (10A)	0.1	61.1	2.700/2.738	77.3	2.890/2.942*
	0.5	69.0	2.700/2.744	67.0	2.723/2.788
2.4 (20A)	0.1	66.4	2.523/2.589	72.8	2.890/3.021
	0.5	80.6	2.903/3.015	51.0	2.836/2.883

*All the concentrations are normalized to 2.0 litres solution.

Conditions: Average cell voltages: 1.2 kA m⁻² - 3.1 V; 2.4 kA m⁻² - 4.2 V

	Anolyte Side	Catholyte Side
Cell temp (°C)	26/31	20/27
Cell press. (kPa)	0.0-44.8/0.0	0.0-48.3/0.0
Oxygen flow (cm ³ s ⁻¹ , STP)	-	8.5
Anolyte flow (cm ³ s ⁻¹)	2.0	-
Anolyte tank pH	6.5 ± 0.2	-
NaCl conc. (M)	2.5 - 3.2	0-4 × 10 ⁻³
NaClO ₃ conc. (M)	2.4-2.89	-

Table 15

Peroxide current efficiency and concentration at high chlorate concentration runs

Current Density kA/m ²	Catholyte Flow Rate cm ³ s ⁻¹	Catholyte (NaOH Concentration) (M)			
		1.0		2.0	
		Peroxide Current Efficiency (%)	Peroxide Conc. (M)	Peroxide Current Efficiency (%)	Peroxide Conc. (M)
1.2 (10A)	0.1	60.0	0.311	73.0	0.378
	0.5	77.2	0.080	96.5	0.100
2.4 (20A)	0.1	36.2	0.375	78.2	0.810
	0.5	63.7	0.132	61.4	0.127

Conditions: Average cell voltages: 1.2 kA m⁻² - 3.1 V
2.4 kA m⁻² - 4.2 V

	<u>Anolyte Side</u>	<u>Catholyte Side</u>
Cell temp (°C)	26/31	20/27
Cell press. (kPa)	0.0-44.8/0.0	0.0-48.3/0.0
Oxygen flow (cm ³ s ⁻¹ STP)	-	8.5
Anolyte flow (cm ³ s ⁻¹)	2.0	-
Anolyte tank pH	6.5 ± 0.2	-
NaCl conc. (M)	2.5 - 3.2	0-4 × 10 ⁻³
NaClO ₃ conc. (M)	2.4-2.89	-

Effect of superficial current density on chlorate current efficiency

Figure. 11

Effect of superficial current density on peroxide current efficiency

Figure 12

The effect of current density on chlorate current efficiency can be explained in part as due to change in moles of hypochlorite. An increase of current density tends to increase the number of moles of hypochlorite to be converted to chlorate in the chemical reactor. An increase in current density also increases the rate of gas evolution and thus accelerates the mass transfer. The result of this is an increase in the rate of the electrochemical chlorate formation which may decrease the overall current efficiency. Also an increase in current density increases the electrical transference flux of the OH^- and HO_2^- anions into the anolyte. The increase in HO_2^- flux into the anolyte decreases hypochlorite concentration. The results of Table 12 indicate that at any given catholyte flow and NaOH concentration, the chlorate current efficiency loss due to peroxide transport into the anolyte is overcompensated by efficiency increase due to generation of hypochlorite.

The effects of superficial current density on peroxide current efficiency and concentration are illustrated in Table 13. The table shows that an increase in current density results in a decrease in peroxide current efficiency and an increase in peroxide concentration at any given catholyte flow and NaOH concentration. Increase in the current density results in a more negative cathode potential. This negative cathode potential increases the rate of peroxide reduction, i.e.,

An increase in current density does not only result to higher peroxide

concentration but also results in HO_2^- migration to the anolyte. These result in loss in peroxide current efficiency. At 2.0 M NaOH, current efficiency decreases from 86% (HO_2^- concentration of 0.446 M) at 1.2 kA m^{-2} to 53.0% (peroxide concentration of 0.520 M) at 2.4 kA m^{-2} for a catholyte flow of $0.1 \text{ x cm}^3 \text{ s}^{-1}$. This is an improvement in efficiency over the results of Oloman and Watkinson [28]. They obtained an 84.0% efficiency at 0.5 kA m^{-2} (peroxide concentration = 0.30 M) and 60% at 1.5 kA m^{-2} (peroxide concentration = 0.70 M) under a pressure of 930 kPa, oxygen flow of $32.0 \text{ cm}^3 \text{ s}^{-1}$ and catholyte flow of $0.17 \text{ cm}^3 \text{ s}^{-1}$.

5.3.2 Effect of Catholyte Flow

The influence of catholyte flow on the process is shown in Table 12 for the chlorate side and in Table 13 for the peroxide side. Table 12 indicates that the chlorate current efficiency increases with rise in catholyte flow at fixed current density. This could be explained as due to lower peroxide concentration that results with higher catholyte flow. A lower peroxide concentration (at a constant current density) means a lower peroxide migrational flux and diffusional flux into the anolyte thus leading to a lower hypochlorite loss in the anolyte. With such lower loss in hypochlorite, more chlorate is formed giving rise to a higher chlorate current efficiency with a rise in catholyte flow.

It is also seen in Table 12 that for the 0.5 M and 1.0 M NaOH conditions, the chlorate current efficiency relationship with the catholyte flow is in the order: values of chlorate efficiency at $2.4 \text{ kA m}^{-2} > 1.8 \text{ kA m}^{-2} > 1.2 \text{ kA m}^{-2}$ i.e., the chlorate current efficiency

increases with current density at any given catholyte flow. However, this trend is broken at 2.0 M NaOH. Table 12 and Fig. 13 indicate that the values of chlorate current efficiency at 2.4 kA m⁻² at any given catholyte flow lies between the values of the efficiency at 1.8 kA m⁻² and 1.2 kA m⁻². Thus, the maximum current efficiency for the chlorate side is obtained at 1.8 kA m⁻². This behaviour could be attributed to the combined influence of peroxide concentration and current density effects. Table 12 shows that the peroxide concentration at 2.0 M NaOH and 2.40 kA m⁻² is higher than the values obtained at 1.8 kA m⁻². It is likely that the increase in chlorate current efficiency due to increase in current density (at 2.0 M NaOH) is undercompensated by the loss of efficiency due to higher peroxide concentration.

The effects of catholyte rate on the peroxide current efficiency and concentration are demonstrated in Table 13. At 0.5 M and 1.0 M NaOH, it is seen that the peroxide efficiency increases with increasing catholyte flow while the peroxide concentration falls. However, at 2.0 M NaOH, the trend in current efficiency found for the lower caustic concentration is reversed. Thus, increasing the catholyte flow lowers the current efficiency. Further, it is observed that in the region of operation, the peroxide current efficiency decreases with increase in current density at any given catholyte flow rate.

Oloman and Watkinson [31] operated a peroxide cell of the type used here (with a cationic membrane and oxygen generation at the anode at a caustic concentration of 2.0 M) and observed a rise in peroxide current efficiency with increasing catholyte flow. Although they operated the

Effect of catholyte flow on chlorate current efficiency

Figure 13

trickle bed cell at a current density range of $0.4 - 1.6 \text{ kA m}^{-2}$, the observation made here contrasts with their results at 2.0 M NaOH concentration. This observation underlies the interacting effect of the anolyte side reactions to the catholyte reactions.

The flow of the catholyte affects the peroxide loss mechanisms hence its importance in the peroxide current efficiency. At lower flow of the catholyte, there is a higher peroxide concentration. Peroxide loss through migration and diffusion into the anolyte and loss due to reduction at the catholyte are favoured by higher peroxide concentration. Thus the lower current efficiency obtained at lower catholyte flow may be a consequence of the above losses. The other loss reaction that occurs include the decomposition of peroxide.

Trace metal ions act as catalyst for reaction (52). It is likely that the decrease in peroxide current efficiency with higher catholyte flow at 2.0 M caustic may be due to peroxide concentration effect on efficiency as already pointed out. At 2.0 M NaOH , the peroxide concentration is higher than the concentration obtained at any lower NaOH concentration under the same operating conditions.

5.3.3 Effect of NaOH Concentration

The effects of NaOH concentration on the chlorate current efficiency are shown in Table 13. The following features are observed:

- a. At current density of 1.2 kA m^{-2} , the chlorate current efficiency seems to remain constant with increase in NaOH concentration.

- b. At 1.8 kA m^{-2} , a slow increase in chlorate current efficiency is observed with rise in NaOH concentration.
- c. At 2.4 kA m^{-2} , the chlorate current efficiency is observed to fall with NaOH concentration (Fig 14). This contrasts with the observations made in (a) and (b) above.

The observation made in (a) above could be explained in part by electrical transference flux term at 1.2 kA m^{-2} and diffusion flux. The loss of chlorate intermediates by the transport of peroxide into the anolyte from the catholyte seems to remain constant with increase in NaOH concentration. Although Table 13 shows that the peroxide concentration increases with NaOH concentration, the observation indicates that the higher diffusion coefficient of OH^- ions and concentration affect the anolyte side more than the peroxide effect. The chlorate current efficiency then remains indifferent to the NaOH concentration at 1.2 kA m^{-2} .

At 1.8 kA m^{-2} , there is an increase in ClO^- moles generated as well as increase in migration of HO_2^- and OH^- ions into the anolyte. The increase in chlorate efficiency due to ClO^- moles generated and OH^- migrations is lowered by HO_2^- migration into the anolyte. This explains the observations made in (b).

The observation made in (c) is accounted for by the increased importance of migration and concentrations of peroxide at 2.4 kA m^{-2} .

The effect of NaOH concentration on the peroxide current efficiency and concentration are shown in Table 13.

The results indicate the following:

Effect of NaOH concentration on chlorate current efficiency

Figure 14

- (i) The peroxide concentration and current efficiency increase with increase in NaOH concentration.
- (ii) The observation in (i) above with respect to efficiency seems to be consistent with low catholyte flow. As the catholyte rate increases, the efficiency does not rise as rapidly as it does at lower rate. In fact, it is observed that at a flow of $0.5 \text{ cm}^3 \text{ s}^{-1}$, the current efficiency falls with increase in caustic concentration. The same trend is observed for the peroxide concentration.

An examination of Table 13 and Figure 15 indicates that a critical caustic concentration could be defined. According to Figure 15, below a NaOH concentration of 1.5 M, the peroxide current efficiency increases with catholyte flow. However, at NaOH concentrations greater than 1.5 M, the efficiency of peroxide falls with increase in catholyte flow.

These effects are observed at all current densities experimented with. However, the effects are not well understood. This behaviour might well be a result of many other parameter interactions. As observed by Oloman and Watkinson [28] for a peroxide cell, (current density $0.2 - 0.8 \text{ kA m}^{-2}$) peroxide concentration and current efficiency increase with increase in NaOH concentration. It is suggested that high initial NaOH concentration could protect the peroxide from subsequent cathode reactions. It might well be that at high catholyte flow (at high NaOH concentration) the effects of flow and NaOH concentration on peroxide loss to the anolyte become more pronounced than the influence of other factors that favour the peroxide current efficiency.

Effect of NaOH concentration on peroxide current efficiency

Figure 15

5.3.4 Effect of Peroxy-Hydroxy Mole Ratio

Alkaline peroxide reacts with hypochlorite or dissolved elemental chlorine - important intermediates in the chlorate synthesis.

Hydrolysis of chlorine and even the formation of OCl^- require an alkaline environment (OH^- ions). Thus in a coupled process of this nature, it is possible to see the effect of the mole ratio of the two opposing substances on the chlorate current efficiency. These effects are illustrated in Table 16 and Figures 16, 17 and 18.

It is important to point out that peroxide molar concentration is not an independent variable (in this process) thus it could be argued that Figures 16 to 18 are simply the inverse of the effect of hydroxide concentration on chlorate current efficiency. However, comparison of these two does not seem to agree with the later argument. The hydroxyl ion molar concentration used in computing the mole ratio is the initial NaOH feed concentration into the cell.

The following observations could be made from the peroxy-hydroxy mole ratio plots:

- a. The chlorate current efficiency falls with rise in peroxy-hydroxy mole ratio
- b. For the 0.5 M and 1.0 M NaOH, the graphs show the following trends for the average chlorate current efficiency
 $2.4 > 1.8 > 1.2 \text{ kA m}^{-2}$, (Fig 16 and 17)
- c. At 2.0 M NaOH, the chlorate current efficiency for the 2.4 kA m^{-2} lies between those at 1.8 kA m^{-2} and 1.2 kA m^{-2} (Fig. 18).

Figures (16-18) show that the fitted values are linear while the actual experimental points are non linear. The non-linearity of the

Table 16

Chlorate current efficiency as a function of peroxy-hydroxy mole ratio
(low chlorate run)

Current Density kA/m ²	Catholyte Flow Rate cm ³ /s	Catholyte (NaOH Concentration (M))					
		0.5		1.0		2.0	
		HO ₂ ⁻ /OH ⁻ Ratio	Chlorate Current Eff. (%)	HO ₂ ⁻ /OH ⁻ Ratio	Chlorate Current Eff. (%)	HO ₂ ⁻ /OH ⁻ Ratio	Chlorate Current Eff. (%)
1.2 (10A)	0.1	0.306	53.0	0.215	52.7	0.215	53.2
	0.3	0.170	57.4	0.115	62.6	0.065	59.7
	0.5	0.064	68.5	0.070	70.3	0.034	70.3
1.8 (15A)	0.1	0.310	60.2	0.249	61.50	0.2245	65.0
	0.3	0.180	68.0	0.115	67.5	0.07	70.0
	0.5	0.150	73.5	0.097	72.0	0.0335	74.0
2.4 (20A)	0.1	0.290	69.1	0.275	69.0	0.265	62.6
	0.3	0.174	72.1	0.143	72.5	0.078	67.0
	0.5	0.082	78.0	0.117	76.0	0.039	72.9

Conditions: Average cell voltages: 1.2 kA m⁻² - 3.00 V; 1.8 kA m⁻² - 3.46 V; 2.4 kA m⁻² - 4.10 V

	Anolyte Side	Catholyte Side
Cell temp (°C)	27/33	22/30
Cell press. (kPa) range	0.0-58.6/0.0	0.0-44.8/0.0
Oxygen flow (cm ³ s ⁻¹)	-	8.5
Anolyte tank pH	6.5 ± 0.2	-
Anolyte flow (cm ³ s ⁻¹)	2.0	-
Anolyte tank temp (°C)	70.0	-
NaCl conc. (M)	0.0 - 0.5	-
NaClO ₃ conc. (M)	0 - 0.5	-

Effect of $\text{HO}_2^-/\text{OH}^-$ mole ratio on chlorate current efficiency at 0.5 (M) NaOH

Figure 16

Effect of $\text{HO}_2^-/\text{OH}^-$ mole ratio on chlorate current efficiency at 2.0 (M) NaOH

Figure 18

actual experimental points could be a result of the relative fluxes of HO_2^- and OH^- .

5.4 High or Strong Chlorate Concentration Runs

Tables 14 and 15 show the experimental results at strong chlorate concentration. The investigation of the effects of NaOH, current density and catholyte flow on the current efficiencies of interest at high chlorate concentration was undertaken in order to assess the industrial possibilities of the process.

5.4.1 Chlorate Current Efficiency

Comparing Tables 12 and 14 (low and high chlorate runs respectively) for the chlorate current efficiency, the following observations could be made:

- (i) At 1.2 kA m^{-2} , the chlorate current efficiencies at $0.1 \text{ cm}^3 \text{ s}^{-1}$ catholyte rate (for both 1.0 and 2.0 M NaOH) in Table 14 are higher than the values obtained at low chlorate runs in Table 12. But at $0.5 \text{ cm}^3 \text{ s}^{-1}$ catholyte flow, the two tables give similar values.
- (ii) At 2.4 kA m^{-2} , the trend observed at 1.2 kA m^{-2} is not repeated. This may be a consequence of not replicating exactly all the necessary conditions of the low chlorate run for the high chlorate run.

5.4.2 Peroxide Concentration and Current Efficiency

Comparing the peroxide results for the low and high chlorate runs (c.f. Tables 13 and 15), the following could be inferred:

- (i) 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 and concentration is not well understood and it might well be due to membrane condition.

5.5 Cell Voltage

The economic optimum of an electrochemical process is governed by the current efficiency and the necessary electrolysis voltage. In a peroxy-chlorate cell, the peroxide concentration must be included additionally as a third factor.

To discuss the cell voltage, it must be borne in mind that the cell voltage depends on the characteristic elements of the electrolysis system. Thus the following elements are known to account for the voltage of a cell, viz: electrode materials (catalysts), separator (membrane or diaphragm), electrolyte concentrations, current density, operating temperature, operating pressure and electrolyte flows. No attempt is made here in discussing in details the relative contributions of each of the above factors to the cell voltage.

A survey of Appendix 2 (Tables A-C) however, shows that at a fixed anolyte flow, the current density and catholyte flow seem to be the most important factors affecting the cell voltage at the given conditions.

Typical relations between the cell voltage and separator current density are demonstrated in Figures 19 and 20 at given catholyte flows. The two figures indicate that the cell voltage increases linearly with current density. The observed increase in cell voltage with catholyte flow could be due to membrane bulging with higher catholyte flow.

The temperature effect on the conductivity of electrolytes and hence on cell voltages is well known. In this work, a lower cell voltage could be achieved by increasing the operating cell temperature.

Other ways of reducing the cell voltage are by increasing the working pressure in membrane electrolysis or working at a higher anolyte flow. Increase in working cell pressure would not only decrease the volumetric amount of gas, but an increase of the electrolysis temperature without increasing the evaporation rate of water is also achieved. In this work, the effect of pressure on the cell voltage is not explored.

The effect of anolyte flow on the cell voltage is illustrated in Table 17. The table indicates that operating at a lower anolyte flow increases the cell voltage. However, a high electrolyte flow gives rise to a higher pressure loss in the cell and membrane bulging. Thus a choice of electrolyte flow must be chosen that would not be detrimental to the membrane.

5.6 Length of Time of Use and Stability of Membrane

The membrane stability affects both current efficiencies of peroxide and chlorate and the cell voltage. The success of this work depends on the membrane performance. The use of an asbestos diaphragm

Effect of superficial current density on the cell voltage at 0.5 (M) NaOH

Figure 19

Effect of superficial current density on the cell voltage at 2. (M) NaOH

Figure 20

Table 17

Variation of cell voltage with anolyte flow

Anolyte Flow (cm ³ /s)	Cell Voltage (V)
0.57	6.0
0.68	5.8
3.2	3.7
3.5	3.7

Conditions:

NaOH conc	= 2.0 M
Oxygen flow	= 8.5 cm ³ s ⁻¹ (STP)
Catholyte flow	= 0.20 cm ³ s ⁻¹
Catholyte cell side temp (°C)	= 18/48
Catholyte side pressure (kPa)	= 0/0
Anolyte side temp (°C)	= 30/62
Anolyte cell side pressure (kPa)	= 0/0.0 (for flow < 1.0 cm ³ /s)
Anolyte cell side pressure (kPa)	= 13.8/0.0 (for flow > 3.0 cm ³ /s)
Anolyte tank pH	= 5.6
Anolyte tank temp (°C)	= 70.0
Average anolyte tank vol	= 2.0 L
Current supply	= 25A (3 kA m ⁻²)
Peroxide conc (M)	= 0.47 (at lower anolyte flow)
Peroxide conc (M)	= 0.58 (at higher anolyte flow)

on the anode side of the anionic membrane was to protect the membrane and prolong its life. Since no physical or chemical tests were carried out on the membrane in order to evaluate its deterioration, the reproducibility of product current efficiencies and the cell voltage changes with time were used as a yardstick for measuring the membrane stability.

5.6.1 Typical Cell Voltage with Time

The cell voltage variation with time for an ion specific permeable membrane could be used as a qualitative measure of resistance changes of the membrane. If the fixed group of a specific membrane is degraded due to usage, there are bound to be changes in resistance of the cell, hence the cell voltage will vary with time. 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 used for over 20 hours is as shown in Table 18. From these results, a conclusion could be made that the variation in cell voltage with time does not indicate a serious membrane damage - at least in the first 20 hours of its use.

5.6.2 Product Current Efficiency with Membrane Usage

Some experimental runs were repeated. The repetition involves keeping all the process variables within the same values - except that the time the membrane has been in use was not kept constant i.e., the age of the membrane. The observations made in the experimental runs include an anolyte pink coloration of each initial 'new membrane' run.

Table 18
Cell voltage variation with time

	AA	BB
Time (min)	Cell Voltage (V)	Cell Voltage (V)
1	3.13	4.19
15	3.13	4.25
30	3.12	4.24
45	3.16	-
60	3.14	4.17
90	3.17	4.18
105	-	4.20
120	3.14	4.18
180	-	4.10

Conditions:

	<u>AA</u>	<u>BB</u>
Current density (kA/m^2)	1.2	2.4
NaOH conc (M)	2.0	2.0
Catholyte flow ($\text{cm}^3 \text{s}^{-1}$)	0.10	0.5
Oxygen flow ($\text{cm}^3 \text{s}^{-1}$ STP)	4.50	4.5
Anolyte flow ($\text{cm}^3 \text{s}^{-1}$)	2.0	2.0
Anolyte tank temp ($^{\circ}\text{C}$)	70.0	70.0
Anolyte tank pH	6.6	6.5
Anolyte side cell temp ($^{\circ}\text{C}$) in/out	24/27	23/30
Catholyte side cell temp ($^{\circ}\text{C}$) in/out	19/21	18/23
Anolyte side cell pressure (kPa)	17.2/0.0	58.6/0.0
Catholyte side cell pressure (kPa)	55.2/0.0	41.4/0.0
Chlorate current efficiency (%)	77.3	51.0
Peroxide current efficiency (%)	73.0	61.0

However, the pink coloration observed in the use of a new membrane was not pronounced nor was such observed in subsequent runs. This slight coloration may be due to a wearing away of the membrane - most probably as a result of reaction between the generated chlorate intermediates and membrane backbone materials. This wearing did not manifest itself in the cell voltage results neither did it show in subsequent runs using the same membrane.

A typical replicated result is shown in Table 19. Run A₂ is a repeat of A₁ while B₂ is a repeat of B₁. The results of A₁ and A₂ do not vary so much as to be attributed to membrane degradation, while those of B₁ and B₂ differ. The difference between B₁ and B₂ could be due to inability to replicate all experimental conditions precisely or due to experimental errors. The most probable conditions not replicated according to Table 19 are temperature and pressure. A temperature difference of 2°C however can't account for the difference in B₁ and B₂ chlorate current efficiency. The pressure difference is also low and the pressure effects are not well understood. It could otherwise be deduced that the membrane loses part of its stability after 26 hours of use.

5.7 HCl Addition

According to equations (1) and (2), the amount of

OH⁻ furnished by the peroxide formation reaction (rxn 1) would not be enough to make a mole of chlorate for a passage of 6 moles of

Table 19

The effect of length of time of use of membrane on product current efficiencies

	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
H ₂ O 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 (hrs)	3.0	25.0	12.0	28.0

Conditions	A ₁	A ₂	B ₁	B ₂
NaOH conc (M)	2.0	2.0	1.0	1.0
Catholyte flow (cm ³ s ⁻¹)	0.10	0.10	0.50	0.50
Oxygen flow (cm ³ s ⁻¹ , STP)	.5	.5	8.5	8.5
Anolyte flow (cm ³ /s)	2.0	2.0	2.0	2.0
Anolyte tank temp (°C)	70.0	70.0	68.0	70.0
Anolyte tank pH	6.65	6.6	6.7	6.50
Anolyte side cell press (kPa)	20.7/0	55.2/0	46.2/0	55.2/0
catholyte side cell press (kPa)	13.8/0	17.2/0	46.2/0	48.3/0
Anolyte side cell temp (°C)	26/30	24/27	26/32	26/33
Catholyte side cell temp (°C)	22/24	19/21	20/25	19/23
Cell voltage	3.0	3.14	4.2	4.20
Time of run (min)	180	128	130	175

electricity. Thus the two reactions above give a stoichiometry that could be interpreted to mean that a simultaneous synthesis of alkaline peroxide and chlorate in the same cell would require alkaline addition from an external source into the anolyte. In the present work, such was not the case. The reason for this could be (a) reaction (1) is carried out in alkaline media, hence enough OH^- ions would be available to make up the OH^- production in reaction (1); (b) other side reactions producing OH^- ions occur as well as reaction (1).

In this work, HCl addition into the anolyte was used to keep and control the anolyte tank pH. The HCl requirement varied from run to run. The reasons for this variation were:

- (i) The length of operation of the cell for each run was not often the same for all runs.
- (ii) In some runs, because of time lag of the controller, the required pH is overshoot and thus small amount of NaOH had to be added to bring the pH to the range of operation. The overshooting of pH could occur in either side of the set point thus leading to addition of extra HCl that might not have been necessary had the addition relied solely on the amount of OH^- from the cathode (fine control). Some typical results are illustrated in Table C in Appendix 1.

The pH overshooting didn't occur in all the runs. The addition of HCl into the anolyte tank accounts for some chlorate losses due to the reaction of H^+ ions with ClO^- and ClO_3^- .

From the results, it is likely that the amount of HCl requirement in this process would be less than that required to produce the same

amount of chlorate in an undivided chlorate cell. This deduction could be made intuitively based on the fact that in this process, limited transfer of OH^- into the anolyte is allowed while in the traditional chlorate cell, there is no control in the amount of OH^- moving into the anode side of the cell. The use of HCl to control the anolyte pH shows that major current carrier in the process is OH^- ion as predicted by theory.

5.7.1 Chloride Balance

The membrane serves to separate and thereby prevent the mixing of the anolyte and catholyte. Ideally, only negative ions migrate and diffuse through the anion exchange membrane while the two parts of the cell are sealed from each other.

Although the anions in the anolyte are under the influence of negative electric potential to migrate into the catholyte chamber, they are still 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 would 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 in accounting for chloride loss in form of undissolved chlorine gas (vented out) and chlorate in the catholyte.

A typical chloride balance result is shown in Table 20. The results in Table 20 indicate that not much of the chloride is lost to the catholyte. Using a porous diaphragm as a separator in this system,

Table 20

A typical chloride balance result

	Input	Output
Moles of Cl^- in NaCl	6.46	6.29
Moles of Cl^- in NaClO_3	5.84	5.95
Moles of Cl^- in OCl^-	-	0.02
Moles of Cl^- in $10 \text{ cm}^3 \text{ HCl}$ (HCl conc = 1.0 M)	0.01	-
Moles of Cl^- in catholyte	-	0.01
Total moles of Cl^-	12.31	12.27

Conditions: (Run # D1R)

Duration of run (mins)	= 128
NaOH conc (M)	= 2.0
Oxygen flow ($\text{cm}^3 \text{ s}^{-1}$, STP)	= 8.5
NaCl conc (initial/final) (M)	= 3.2/3.0
Anolyte flow ($\text{cm}^3 \text{ s}^{-1}$)	= 2.0
Catholyte flow ($\text{cm}^3 \text{ s}^{-1}$)	= 0.10
Anolyte tank temp ($^{\circ}\text{C}$)	= 70
Anolyte tank pH	= 6.60
Vol of 1 M HCl added (cm^3)	= 10.0
Catholyte Cl^- conc (M)	= 9×10^{-3}
Current density kA/m^2	= 1.2
Anolyte side cell temp ($^{\circ}\text{C}$)	= 24/27
Catholyte side cell temp ($^{\circ}\text{C}$)	= 19/25
Anolyte tank vol (initial/final) (l)	= 2.020/2.095
NaClO_3 conc (M) (initial/final)	= 2.89/2.84
Peroxide conc (M)	= 0.378
Chlorate current efficiency (%)	= 77.3
Peroxide current efficiency (%)	= 73.0
Superficial membrane area (cm^2)	= 83.3

more chloride and chlorate would be expected to be lost to the catholyte due to convection transfer between anode and cathode chamber. Some useful data are provided in Table C of Appendix 2 for Cl^- material balance in some of the experimental runs.

5.7.2 Water transport across the membrane

In almost all the experimental runs, an increase in volume of anolyte solution volume was noticed. This increase in anolyte volume was as a result of 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 density, hydration number of ions and membrane structure. George et al [58] observed that water transport across an ion exchange membrane is markedly higher at low current densities than at higher current densities. This was explained as due to the fact that at high current densities, some ions are forced through the smaller pores thereby preventing any free water molecule from passing through such pores. Other ions with their accompanying H_2O pass through the larger pores. Under a low current density all or most water passes through the smaller pores with little or no ions being forced through these pores.

In the present work, no attempt was made at rationalizing or studying any relationship between the amount of water transported across the membrane and the experimental conditions. The only observation made is that, the increase in solution volume in the anolyte leads to a lower chlorate concentrations than would have obtained had the anolyte volume remain constant.

CHAPTER 6

CONCLUSIONS

Alkaline hydrogen peroxide and sodium chlorate were synthesized simultaneously in the same electrochemical cell, using a combination of an anion membrane and an asbestos diaphragm as the separator. The hydrogen peroxide was obtained by the electroreduction of oxygen in caustic on a fixed carbon bed cathode while the chlorate was obtained by the reaction of anodic electro-generated hypochlorite and hypochlorous acid in an external reactor.

In the operation of a continuous electrochemical reactor, the effects of current density, catholyte flow and sodium hydroxide concentration on the peroxide and chlorate current efficiencies were investigated. The effects of these variables on peroxide concentration were also studied.

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 the peroxy/hydroxy mole ratio in the catholyte affects the chlorate current efficiency--the higher this ratio, the lower the chlorate current efficiency.

An increase in catholyte flow favours the current efficiencies of the two products of interest, but results in a lower peroxide concentration. The NaOH concentration was shown to affect the peroxide concentration positively (i.e., increasing the NaOH concentration

results to an increase in peroxide concentration) for NaOH concentration lower than 1.5 M. A critical NaOH concentration at 1.5 M was defined as the optimum NaOH concentration above which other interacting factors appear to reverse the catholyte rate effects on alkaline hydrogen peroxide production.

The simultaneous synthesis was carried out at both a low or weak chlorate solutions (0-0.5 M) and at strong chlorate solutions (2.4 - 2.8 M) and was found that the two products could simultaneously be made under these chlorate conditions.

The cell was operated at average temperature of 27/33°C for the anode side and 20/30°C for the cathode side with operating cell voltages of 3-4.2V at superficial current densities of 1.20-2.40 kA m⁻².

A chloride balance over the system indicated a negligible loss of chloride to the catholyte and the addition of HCl make up to control pH of the anolyte side of the system reflects the ability of the process to transfer OH-ions across the membrane at a rate equivalent to Cl₂ generation.

At weak chlorate solutions, the range of chlorate current efficiencies obtained are 53 - 78% at the current density range of 1.2 - 2.4 kA m⁻², an anolyte flow of $2 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, anolyte tank temperature of 70°C with a catholyte flow between $0.1 \times 10^{-6} \text{ m}^3/\text{s}$ - $0.5 \times 10^{-6} \text{ m}^3/\text{s}$. The best results for the peroxide current efficiency under the same conditions were obtained at 1.2 kA m⁻² and these are:

62% (at 0.5 M NaOH, $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ catholyte flow and 0.064 M peroxide), 67% (at 1.5 M NaOH, $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ catholyte flow and

0.069 M peroxide), and 86% (at 2.0 M NaOH, $0.1 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ catholyte flow and 0.446 M peroxide).

The best results for the two products include 56.5% and 76% current efficiency for peroxide and chlorate respectively at 2.4 kA m^{-2} , 1.0 M caustic, $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ catholyte flow with other operating conditions same (the peroxide concentration = 0.117 M) and 75.4% peroxide current efficiency (0.130 M HO_2^-) and 70.3% chlorate current efficiency at 1.2 kA m^{-2} , $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ catholyte flow and 2.0 M caustic.

In strong solution of chlorate, some improved peroxide efficiency and chlorate efficiency results are observed. At 1.0 M caustic, 2.4 kA m^{-2} and catholyte flow of $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, the chlorate current efficiency and peroxide efficiency are 80.6% and 63.7% respectively (0.13 M peroxide). A peroxide current efficiency of 78.2% (0.81 M) at 2M caustic and $0.1 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ catholyte flow is obtained with a 72.3% chlorate efficiency.

Other factors which can be expected to influence the process, but which were not investigated are: Temperature of the electrolytes at cell entrances, pressure effects, pH effects, oxygen flow, direction of flow of the two electrolytes into the cell, anolyte flow etc.

This work shows that sodium chlorate could be generated simultaneously with alkaline hydrogen peroxide in the same cell at reasonable current efficiencies.

CHAPTER 7

RECOMMENDATIONS

Further work on this process should be directed towards studying the effects of some of the process variables that were kept constant in this work. Such factors include the pH of the anolyte, cell pressure, cell temperature, anolyte rate, oxygen rate, the electrolyte flow directions etc.

A more detailed study is required to find the effect of the peroxide/alkali mole ratio on the chlorate efficiency. Such studies should be carried out at both lower and higher ratios than are reported in this work. It is also suggested to use actual (final) caustic concentration instead of the initial or feed concentration used here. With such data, it could be possible to extrapolate the chlorate efficiency--peroxy-hydroxy ratio curve to the axis and thus be able to make reliable inferences concerning optimum peroxy-alkali ratio and chlorate current efficiency. Also such data could be used to design a cell for a specific alkali-peroxide/chlorate requirement.

The following are also suggested for future work.

1. Different diaphragm and membrane materials should be tested.
2. Experiments at higher reactor inlet temperatures should be done.
3. A mathematical model of the system should be developed. Such a model would be able to elucidate and account for the effects of many of the process variables.

4. The principle outlined here (coupling of two processes) should be applied to other systems.
5. A simultaneous operation of the cathode side under a low current density and the anode side under a high current density should be done. This could be achieved by using a perforated anode electrode. The perforations lead to a smaller active surface area than would be obtainable using the whole anode plate surface area. High current density on the anode favours chlorate formation while low current density on the cathode favours peroxide efficiency. The recommendation of (5) above could satisfy the current density requirements of chlorate and peroxide at reasonable current efficiencies.
6. A long term run to examine membrane stability should be done.

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NOMENCLATURE

C_i	concentration of species i	mol/m^3
C_b	oxygen bulk concentration	mol m^{-3}
CE	current efficiency	%
D_i	diffusivity of species i	$\text{m}^2 \text{s}^{-1}$
E	cell voltage	V
E^0	standard electrode potential	V (SHE)
E_d	effect shown by a dummy	
F	Faraday's number = 96,500	$\text{coul (gm equiv)}^{-1}$
I	current	Amperes
i_L	limiting current density	A m^{-2}
k	Boltzman constant	
K	rate constant	$(\text{mol/m}^3)^{-2} \text{sec}^{-1}$
K_d	mass transfer coefficient	m s^{-1}
M	number of moles of desired product	
n	number of dummy variables	
N_i	flux of species i	$\text{moles (m}^2 \text{s)}^{-1}$
P	energy consumed per ton	kJ/ton
q	electrolyte flow	$\text{m}^3 \text{s}^{-1}$
R	universal gas constant	kJ/kg-mol K
RO	response or result	
t	test statistic (t-test)	
T	temperature	Kelvin
U_i	mobility of species i	$\text{m}^2 \text{mol J}^{-1} \text{s}^{-1}$
v	electrolyte flow velocity	m s^{-1}
V_{eff}	variance of an effect	
Z_i	valence of species i	-
$\nabla\phi$	potential gradient	V m^{-1}
ΔH	heat of rxn	kJ/kg-mol
η_i	current efficiency of i	%
τ	time	sec

APPENDIX 1

AUXILLIARY EQUIPMENT SPECIFICATIONS

AUXILIARY EQUIPMENT SPECIFICATIONS

Power Supply

- Sorensen power supplies

Model DCR 40-25B

Volmeter range 0-40V

Ammeter range 0-30A (smallest division = 1A)

Voltmeter

- Data Technology Corp.

Digital voltmeter No. 345 0-10 volt

pH Meter/Controller

- Cole Parmer Inst. Co.

Model 5986-00 Combined Electrode

Pressure Gauge/Gauge Guards

- Chemplex Gauge Guards

GG MV 160 - pp

Range 0 - 160 psig

Valves

- Anolyte side - CHEMPLEX SYGEF 1/4" PP

Catholyte side - Swagelock 1/4" SS

Fittings

Anolyte side - Cole Parmer PP fittings

- Fabco PVC fittings

Catholyte side - Swagelock 316 SS

- Fabco PVC fittings

- Cole Parmer PP

Rotameters

Anolyte - Cole Parmer, Shielded Type (Gilmot)

Type: R-3232-22 Size 10

Float: glass

Tube O.D.: 3/16" (0.48 mm)

Catholyte - Brooks, tube size R-2-15-D

Float SS and glass

Thermometers

Anolyte side - Cole Parmer, Teflon coated

R-8177-19

Range 0-100°C

Catholyte side - Fisher Scientific Co. USA

Dial type SS

Range 0-120°C

Pumps

Feed Pumps - Cole Parmer, March Metering Pumps

Model 210-10R

Ceramic and Teflon material

Dosing Pumps - Chemfeed, supplied by Cole Parmer

Model C - 1530SP

Max Psi - 120

Max feed - 0.6 GPH

Tubing

FABCO 1/4" PP-43-0500

Cooler or Heat Exchanger

5 ft of 1/4" titanium contained in 1/2" copper tubing

Water Bath

Labline Instruments

Model 18100

Reagents

Oxygen - Canadian Liquid Air Ltd., commercial grade 99.5% O₂

Sodium hydroxide, BDH - 50% analytical grade

Sodium chloride, BDH - analytical grade

Sodium chlorate - Erco Chemical Co., Vancouver

Water - Laboratory, single distilled water

APPENDIX 2

TABULATED EXPERIMENTAL RESULTS

ANALYTICAL TECHNIQUE

AND

SAMPLE CALCULATION

Table A
Some Tabulated Experimental Results

Run #	Time (mins)	NaOH conc (M)	Oxygen Flow cm ³ /s (STP)	NaCl conc Initial/Final (M)	Electrolyte Flow Rate cm ³ /s		Anolyte Tank Temp (°C)	Anolyte Tank pH	Cath. Cl ⁻ Conc (M)	Current Density (kA/m ²)	Cell Press (kPa) inlet/out		Cell Temp (°C) Inlet/Out		Anolyte Volume (litres) Initial/Final	Anolyte Side Cell Sample pH	Product conc (M)		Cell Volt (V)	% Current Efficiency	
					Anode Side	Cath Side					Anode Side	Cath Side	Anode Side	Cath Side			ClO ₃ ⁻	HO ₂ ⁻		ClO ₃ ⁻	HO ₂ ⁻
C ₄	180	0.5	8.5	4.3/4.05	2.0	0.30	70	6.5	3.0	1.2	0/0	0/0	25/26	20/25	2.0/2.14	7.2	0.209/ 0.245	0.087	3.0	57.4	50.4
C ₆	180	0.5	8.5	3.625/ 3.575	2.0	0.30	70	6.6	3.0	2.4	13.8/ 0.0	0/0	26/33	21/33	2.0/2.2	7.3	0.11/ 0.223	0.087	4.2	72.1	25.4
C ₈	180	0.5	8.5	2.735/ 2.43	2.0	0.50	70	6.6	2.0	1.8	13.8/ 0.0	13.8/ 0.0	31/35	22/31	2.110/ 2.181	7.15	0.376/ 0.463	0.075	3.75	73.5	48.3
C ₁₀	180	1.0	8.5	3.5/3.3	2.0	0.10	70	6.7	42.0	1.2	44.8/ 0.0	0/0	27/31	18/36	1.90/ 1.955	7.1	0.423/ 0.475	0.225	3.1	67.	52
C ₁₂	180	1.0	8.5	3.3/-	2.0	0.10	71	6.6	2.0	2.4	55.2/ 0.0	0/0	27/37	18/30	1.90/ 2.085	7.2	0.075/ 0.579	0.275	4.1	69	28.4
C ₁₄	180	1.0	8.5	4.6/4.3	2.0	0.1	71	6.8	3.0	1.8	55.2/ 0.0	0/0	30/35	23/33	2.0/2.085	7.2	0.058/ 0.146	0.115	3.47	67.3	44.4
C ₁₈	125	1.0	8.5	4.3/4.0	2.0	0.5	73	6.6	2.0	2.4	144.8/ 0.0	41.4/ 0.0	27/34	19/30	2.0/2.025	7.0	0.055/ 0.155	0.117	4.4	76.0	56.5
C ₂₂	120	2.0	8.5	-	2.0	0.10	70	6.7	7.0	1.2	43.4/ 0.0	13.8/ 0.0	28/30	20/23	2.0/2.06	7.1	0.0/ 0.032	0.446	3.0	53.2	86.1

Table A cont'd

Run #	Time (mins)	NaOH conc (M)	Oxygen Flow cm ³ /s (STP)	NaCl conc Initial/Final (M)	Electrolyte Flow Rate cm ³ /s		Anolyte Tank Temp (°C)	Anolyte Tank pH	Cath. Cl ⁻ Conc (M)	Current Density (kA/m ²)	Cell Press (kPa) inlet/out		Cell Temp (°C) inlet/out		Anolyte Volume (litres) Initial/Final	Anolyte Side Cell Sample pH	Product conc (M)		Cell Volt (V)	± Current Efficiency	
					Anode Side	Cath Side					Anode Side	Cath Side	Anode Side	Cath Side			ClO ₃ ⁻	HO ₂ ⁻		ClO ₃ ⁻	HO ₂ ⁻
C ₂₃	120	2.0	8.5	-	2.0	0.10	71.0	6.7	3.0	1.8	55.2/0	0/0	27/33	20/23	2.0/2.065	7.1	0.032/0.099	0.449	3.45	75.0	58.0
C ₂₄	140	2.0	8.5	3.9/3.6	2.0	0.10	74	6.6	3.0	2.4	86.2/0	13.8/0.0	28/36	20/25	2/2.03	7.2	0.099/0.187	0.53	3.9	63.0	53
C ₂₅	120	2.0	8.5	3.5/3.0	2.0	0.30	70	6.8	5.0	2.4	34.5/0	41.4/0.0	25/31	20/23	2.0/2.02	7.0	0.158/0.230	0.107	4.0	67	31.0
C ₂₆	120	2.0	8.5	3.0/2.8	2.0	0.3	70	6.75	-	1.8	69.0/0	41.4/0.0	28/33	20/23	2.0/2.025	7.1	0.235/0.343	0.140	3.5	70	54
C ₂₇	123	2.0	8.5	3.1/2.85	2.0	0.3	70	6.6	7.0	1.2	43.4/0	43.4/0.0	26/29	18/21	3.1/2.85	7.0	0.289/0.327	0.130	2.97	60	75.0
C ₁₉	120	2.0	8.5	4.5/4.0	2.0	0.5	72	6.6	6.0	1.2	55.2/0	41.4/0.0	29/31	19/26	2/2.096	6.9	0/0.042	0.068	3.1	70.3	66.0
C ₁₇	120	2.0	8.5	3.8/3.3	2.0	0.5	70	6.6	6.0	1.8	41.4/0	24.1/0.0	29/33	20/29	1.84/1.925	7.1	0.133/0.204	0.075	3.8	79.0	51.0
C ₁₈	125	1.0	8.5	4.3/4.0	2.0	0.5	73	6.6	2.0	2.4	144.8/0.0	41.4/0.0	27/34	19/30	2.0/2.025	7.0	0.055/0.155	0.117	4.4	78.7	57.0

Table B
Some repeated runs

Run #	Time (mins)	NaOH conc (M)	Oxygen Flow cm ³ /s (STP)	NaCl conc Initial/Final (M)	Electrolyte Flow Rate cm ³ /s		Anolyte Tank Temp (°C)	Anolyte Tank pH	Cath. Cl ⁻ Conc (M)	Current Density (kA/m ²)	Cell Press (kPa) Inlet/out		Cell Temp (°C) Inlet/Out		Anolyte Volume (litres) Initial/Final	Anolyte Side Cell Sample pH	Product conc (M)		Cell Volt (V)	% Current Efficiency	
					Anode Side	Cath Side					Anode Side	Cath Side	Anode Side	Cath Side			ClO ₃ ⁻	HO ₂ ⁻		ClO ₃ ⁻	HO ₂ ⁻
C ₄	180	0.5	8.5	4.5/4.3	2.00	0.30	80	6.5	3.0	1.2	124/0	17.2/0.0	29/31	23/29	2.0/2.10	7.0	0.191/0.214	0.083	3.0	36.2	51.3
C ₄ R	180	0.5	8.5	4.3/4.05	2.0	0.30	70	6.6	3.0	1.2	0/0	0/0	25/26	20/25	2.0/2.14	7.2	0.209/0.245	0.087	3.0	57.4	50.4
C ₁₀	180	1.0	8.5	4.52/4.2	2.0	0.10	70	6.5	2.5	1.2	13.8/0.0	0/0	21/24	21/24	2.0/2.12	6.01	0.376/0.401	0.225	3.0	53.0	52.0
C ₁₀ R	180	1.0	8.5	3.5/3.3	2.0	0.10	70	6.7	42.0	1.2	44.8/0.0	0/0	27/31	18/36	1.90/1.955	7.1	0.475/0.579	0.275	3.1	67.0	52.0
C ₁₇	120	1.0	8.5	4.7/4.3	2.0	0.50	70	6.8	3.0	1.8	124/0	55.2/0.0	27/31	19/27	2.0/2.075	7.2	0/0.055	0.097	3.8	61.0	61.0
C ₁₇ R	120	1.0	8.5	3.8/3.3	2.0	0.5	70	6.6	6.0	1.8	41.4/0.0	24.0/0.0	29/33	20/29	1.84/1.925	7.1	0.132/0.204	0.075	3.8	79.0	51.0
C ₂₆	120	2.0	8.5	3.2/3.1	2.0	0.3	70	6.6	4.0	1.8	41.4/0.0	41.4/0.0	26/31	18/21	2.0/2.0	7.0	0.242/0.289	0.145	3.5	51.0	42.0
C ₂₆ R	170	2.0	8.5	3.0/2.8	2.0	0.3	70	6.75	-	1.8	69.0/0.0	41.4/0.0	28/33	20/23	2.0/2.025	7.1	0.235/0.323	0.140	3.5	70.0	54

Table B Cont'd

Run #	Time (mins)	NaOH conc (M)	Oxygen Flow cm ³ /s (STP)	NaCl conc Initial/Final (M)	Electrolyte Flow Rate cm ³ /s		Anolyte Tank Temp (°C)	Anolyte Tank pH	Cath. Cl ⁻ Conc (M)	Current Density (kA/m ²)	Cell Press (kPa) Inlet/out		Cell Temp (°C) Inlet/Out		Anolyte Volume (litres) Initial/Final	Anolyte Side Cell Sample pH	Product conc (M)		Cell Volt (V)	% Current Efficiency	
					Anode Side	Cath Side					Anode Side	Cath Side	Anode Side	Cath Side			ClO ₃ ⁻	HO ₂ ⁻		ClO ₃ ⁻	HO ₂ ⁻
D ₁	180	2.0	8.5	3.0/2.7	2.0	0.10	70	6.65	3.0	1.2	20.7/0.0	13.8/0.0	26/30	22/24	2.02/2.125	7.10	2.86/2.78	0.404	3.0	73.0	78
D ₁ R	128	2.0	8.5	3.23.0	2.0	0.10	70	6.6	9.0	1.2	55.2/0.0	17.2/0.0	24/27	19/25	2.020/2.095	-	2.89/2.84	0.378	3.14	7.3	73
D ₃	120	2.0	8.5	2.9/2.5	2.0	0.50	70	6.7	-	2.4	20.7/0.0	48.3/0.0	26/32	21/25	2.0/2.148	7.3	2.714/2.588	0.166	4.0	53.0	80
D ₃ R ₁	180	2.0	8.5	3.0/2.7	2.0	0.50	70	6.5	3.0	2.4	58.6/0.0	41.4/0.0	23/30	18/23	2.0/2.030	-	2.836/2.887	0.127	4.0	51.0	61.4
D ₅	130	1.0	8.5	2.9/2.4	2.0	0.50	68	6.7	1.0	2.4	46.2/0.0	46.2/0.0	26/32	20/25	1.50/1.70	7.4	2.66/2.669	0.146	4.2	60	70
D ₅ R	175	1.0	8.5	2.9/2.4	2.0	0.50	68	6.7	1.0	2.4	55.2/0.0	48.3/0.0	26/33	19/23	2.025/2.20	-	2.882/2.772	0.146	4.2	73	70

Appendix 2

Some useful data for Cl^- material balance

Run #	Anolyte Vol (L) Initial/Final	NaCl Conc Initial/Final (M)	NaClO_3 Conc. Initial/Final (M)	OCl^- Conc. Initial/Final 10^3 (M)	Conc of HCl Used (M)	Vol of HCl Added (cm^3)	Catholyte Flow (cm^3/s)	$10^3 \times \text{Cl}^-$ Conc. in Catholyte (M)	Duration of Run (min)
D ₁ R	2.02/2.095	3.2/3.0	2.89/2.84	0.0/8.75	1.0	10.0	0.10	9.0	128
D ₃ R ₁	2.0/2.030	3.0/2.7	2.84/2.89	8.75/9.58	1.0	0.0	0.50	3.0	180
D ₅ R	2.025/2.20	3.2/2.8	2.88/2.77	0.0/10.42	1.0	30.0	0.50	3.0	175
D ₈	1.50/1.60	2.8/2.6	2.70/2.5785	0.0/8.75	1.0	20.0	0.10	10.50	120
D ₄	2.0/2.136	2.8/2.6	2.723/2.610	0.0/9.50	2.12	80.0	0.50	1.50	155

SAMPLING AND ANALYSIS

On leaving the reactor, the catholyte product solution was sampled. A ml or more of the sample was pipetted from the measuring cylinder into an excess of 2 M sulphuric acid. The acid solution of peroxide was then titrated with 0.1 N (0.02 M) solution of potassium permanganate, which had been standardized against a solution of sodium oxalate.

The equation for the reaction between peroxide and permanganate under acid condition is:

Thus peroxide concentration in the product solution is given by

$$\text{Peroxide conc} = \frac{(\text{Volume of KMnO}_4 \text{ used}) \times (\text{Molarity of KMnO}_4)}{(\text{Volume of Sample}) \times 2}$$

For the anolyte, just before the power is switched off, a sample of 2 ml (for low chlorate runs) or two samples of 1 ml and 2 ml (for high chlorate runs) are taken from the anolyte tank. [For cell sample analysis, a sample is taken just after exiting from the cell.]

In the high chlorate run, the 1 ml sample is diluted to 100 ml and 5 ml of this dilute solution taken for chlorate analysis. The 2 ml sample of the high chlorate run is used for hypochlorite (active chlorine) analysis. For the low chlorate run, the 2 ml sample is used for both chlorate and hypochlorite analysis.

The following procedure was used for the hypochlorite and chlorate analysis. After the addition of 0.1 M (20 ml) sodium hydrogen carbonate

solution to the sample, hypochlorite was titrated potentiometrically with a solution of 0.025 M (0.1 N) As_2O_3 . A 250 ml beaker containing platinum and calomel electrodes was used. The platinum electrode was immersed briefly in conc. sulfuric acid containing chromate before each run.

When a large potential change occurs at the end point of the hypochlorite, an excess arsenic (III) oxide was added followed by about 40 mg potassium bromide and a volume of chemically pure concentrated hydrochloric acid to achieve at least 20% HCl in the solution. The solution was allowed to stand for 5 minutes. After that time, the excess As_2O_3 was titrated potentiometrically with 0.0167 M (0.1 N) KBrO_3 . The change in potential was followed. A typical potentiometric curve for low chlorate run is illustrated in Figure A1.

For the chloride analysis, 1 ml sample is diluted to 100 ml and 5 ml sample of dilute solution titrated against silver nitrate using dichromate as indicator. For the catholyte chloride analysis, the sample is first neutralized using nitric acid before titrating with silver nitrate.

The equations of the reactions are as follows:

- (a) Reaction of hypochlorite (ClO^-) with As_2O_3

- (b) Reaction of chlorate with Arsenic (III) oxide in acid environment

- (c) Reaction of As_2O_3 with bromate in acid solution

At the end point of KBrO_3 titration, bromine is generated as follows:

Typical potentiometric titration curve

Figure A1

(d) Reaction of silver nitrate and chloride

Calculation of Concentration of ClO^- and ClO_3^-

Let the first end-point (hypochlorite end point) = V_{A1} (cm^3).

This is the volume of As_2O_3 used in titrating the amount of ClO^- contained in the sample.

Let the sample volume be = V_S (cm^3).

Let the total volume of As_2O_3 used (including excess) be = V_{TA} (cm^3).

Let the end-point in Bromate titration = V_B (cm^3).

Let the molarity of Arsenic be = M_A (moles/litre).

Let the molarity of Bromate be = M_B (moles/litre).

Molarity of ClO^- = M_{ClO^-} (moles/litre).

Molarity of ClO_3^- = $M_{\text{ClO}_3^-}$ (moles/litre).

Then for

(i) ClO^- concentration

$$M_{\text{ClO}^-} = \frac{2 \times M_A \times V_{A1}}{3 \times V_S}$$

(ii) ClO_3^- concentration

(a) Volume of excess As_2O_3 used for Bromate titrating, V_{AE}

$$V_{AE} = \frac{3 \times M_B \times V_B}{2 \times M_A}$$

(b) Volume of As_2O_3 used for ClO_3^- reaction is given by

$$V_{\text{ClO}_3^-} = V_{\text{TA}} - V_{\text{A1}} - V_{\text{AE}}$$

Therefore Molarity of ClO_3^- in sample

$$M_{\text{ClO}_3^-} = \frac{2 \times M_A \times V_{\text{ClO}_3^-}}{3 \times V_S}$$

Substituting for $V_{\text{ClO}_3^-}$ we obtain

$$M_{\text{ClO}_3^-} = \frac{2 \times M_A}{3 \times V_S} \left[V_{\text{TA}} - V_{\text{A1}} - \frac{3 \times M_B \times V_V}{2 \times M_A} \right]$$

Sample Calculation

Run D5R (Appendix 2, Table B)

Duration of Run = 175 min

Catholyte flow rate = $0.50 \text{ cm}^3/\text{s}$

Current = 20A

Initial anolyte tank volume = 2.025 litres

Final anolyte tank volume = 2.20 litres

Total volume of HCl added = 30 cm^3

Conc of HCl added = 1.0 M

I. Catholyte Sample Analysis

Catholyte sample volume = 5.0 ml

Permanganate conc. = 0.02 M

Permanganate titre = 14.6 ml

$$\text{Product peroxide conc} = \frac{14.60}{5.0} \times 0.02 \times \frac{5}{2}$$

$$= 0.146 \text{ M}$$

$$\text{Peroxide current efficiency} = \frac{0.146 \times 0.5 \times 10^{-3} \times 2 \times 96500}{20} \times 100$$
$$= 70.5\%$$

II. Initial ClO_3^- , Cl^- and ClO^-

No ClO^- present in the sample, i.e., $V_{A1} = 0$. 1 ml initial sample was diluted to 100 ml and 5 ml of this dilute sample used for potentiometric titration for ClO_3^- and 10 ml dilute solution used for Cl^- titration. From the potentiometric titration curve we obtained the end points:

For initial ClO_3^-

$$\text{Total As}_2\text{O}_3 \text{ added} = 10.0 \text{ ml } (V_{TA})$$

$$\text{Equivalent volume of KBrO}_3 = 1.395 \text{ ml } (V_B)$$

$$\text{As}_2\text{O}_3 \text{ concentration} = 0.025 \text{ M } (M_A)$$

$$\text{KBrO}_3 \text{ concentration} = 0.0167 \text{ M } (M_B)$$

$$\text{ClO}_3^- \text{ conc} = \frac{2 \times 0.025}{3 \times 5} [10.0 - 0 - \frac{3 \times 0.0167 \times 1.395}{2 \times 0.025}]$$
$$= 2.87 \times 10^{-2} \text{ M}$$

This is the dilute solution concentration

$$\text{Therefore actual analyte tank } \text{ClO}_3^- \text{ conc} = 2.87 \times 10^{-2} \times 100$$
$$= 2.87 \text{ M}$$

Initial Cl^- conc

$$\text{Sample vol} = 10 \text{ ml dil solution}$$

$$\text{AgNO}_3 \text{ conc} = 0.1 \text{ M}$$

$$\text{AgNO}_3 \text{ titre} = 3.2 \text{ ml}$$

$$\begin{aligned}\text{Cl}^- \text{ conc in dil solution} &= \frac{3.2 \times 0.1}{10.0} \\ &= 3.2 \times 10^{-2} \text{ M}\end{aligned}$$

$$\begin{aligned}\text{Therefore initial anolyte Cl}^- \text{ conc} &= 3.2 \times 10^{-2} \times 100 \\ &= 3.2 \text{ M}\end{aligned}$$

III. Final Anolyte Tank ClO⁻ Conc

$$\text{Sample volume} = 2.0 \text{ ml}$$

Equivalent As₂O₃ volume = 1.31 ml (from the potentiometric titration curve)

$$\text{As}_2\text{O}_3 \text{ conc} = 0.025 \text{ M}$$

$$\begin{aligned}\text{Hypochlorite conc} &= \frac{2 \times 0.025 \times 1.31}{3 \times 2.0} \\ &= 10.92 \times 10^{-3} \text{ M}\end{aligned}$$

IV. Final ClO₃⁻ and Cl⁻ Conc

1 ml final anolyte sample was diluted to 100 ml, 5 ml and 10 ml samples were taken for ClO₃⁻ and Cl⁻ analysis respectively.

From the potentiometric titration curve, the equivalent points or endpoints were obtained.

For final ClO₃⁻:

$$\text{Total As}_2\text{O}_3 \text{ added} = 10.0 \text{ ml}$$

$$\text{Equivalent volume of KBrO}_3 = 1.68 \text{ ml}$$

$$\text{As}_2\text{O}_3 \text{ conc} = 0.025 \text{ M}$$

$$\text{KBrO}_3 \text{ conc} = 0.0167 \text{ M}$$

The amount of ClO^- in 5 ml dil solution is assumed negligible

$$\begin{aligned}\text{ClO}_3^- \text{ conc} &= \frac{2 \times 0.025}{3 \times 5.0} \left[10.0 - 0 - \frac{3 \times 0.0167 \times 1.68}{2 \times 0.025} \right] \\ &= 2.77 \times 10^{-2} \text{ M (dil solution)}\end{aligned}$$

$$\begin{aligned}\text{Therefore actual final anolyte } \text{ClO}_3^- \text{ conc} &= 2.77 \times 10^{-2} \times 100 \\ &= 2.77 \text{ M}\end{aligned}$$

Final Anolyte Chloride Conc.

Sample vol = 10 ml dil solution

AgNO_3 conc = 0.10 M

AgNO_3 titre = 2.80 ml

$$\begin{aligned}\text{Cl}^- \text{ conc in dil solution} &= \frac{2.80 \times 0.10}{10} \\ &= 2.8 \times 10^{-2} \text{ M}\end{aligned}$$

$$\begin{aligned}\text{Therefore final anolyte } \text{Cl}^- \text{ conc} &= 2.8 \times 10^{-2} \times 100 \\ &= 2.80 \text{ M}\end{aligned}$$

V. Catholyte Chloride Conc

Catholyte sample volume = 10.0 ml

AgNO_3 conc = 0.10 M

AgNO_3 titre = 0.30 ml

$$\begin{aligned}\text{Cl}^- \text{ conc in catholyte} &= \frac{0.3 \times 0.1}{10} \\ &= 3 \times 10^{-3} \text{ M}\end{aligned}$$

Chlorate current efficiency

Initial total moles of chlorate in anolyte tank

$$= 2.025 \times 2.87$$

$$= 5.81 \text{ moles}$$

Final total moles of ClO_3^- in anolyte tank

$$= 2.20 \times 2.77$$

$$(\text{litres}) \times \left(\frac{\text{moles}}{\text{litre}}\right)$$

$$= 6.09 \text{ moles}$$

Therefore total moles of chlorate produced during the duration of run

$$= 6.09 - 5.81$$

$$= 0.28 \text{ moles}$$

Theoretical moles of ClO_3^- produced in 175 min at 20A

$$= \frac{175(\text{min}) \times 60\left(\frac{\text{S}}{\text{min}}\right) \times 20\left(\frac{\text{C}}{\text{S}}\right)}{6 \times 96500 \left(\frac{\text{C}}{\text{moles}}\right)}$$

$$= 0.36 \text{ moles}$$

Therefore chlorate current efficiency = $\frac{0.28}{0.36} \times 100\%$

$$= 77.8\%$$

Cl^- Balance

(i) Input Chloride

Initial anolyte volume = 2.025 litres

Initial NaCl conc = 3.2 M

$$\begin{aligned}\text{Therefore moles of Cl}^- \text{ in NaCl input} &= 3.2 \times 2.025 \\ &= 6.48 \text{ moles}\end{aligned}$$

$$\text{Input NaClO}_3 \text{ conc} = 2.87 \text{ M}$$

$$\begin{aligned}\text{Total moles of Cl}^- \text{ in NaClO}_3 &= 2.87 \times 2.025 \\ &= 5.81 \text{ moles}\end{aligned}$$

$$\text{Volume of HCl added} = 30 \text{ cm}^3$$

$$\text{Molarity of HCl used} = 1.0 \text{ M}$$

$$\begin{aligned}\text{Therefore moles of Cl}^- \text{ in HCl} &= 30 \times \frac{1}{1000} \text{ moles} \\ &= 0.03 \text{ moles}\end{aligned}$$

(ii) Output Chloride

$$\text{Final anolyte volume} = 2.20 \text{ litres}$$

$$\text{Final NaCl conc} = 2.8 \text{ M}$$

$$\begin{aligned}\text{Total moles of Cl}^- \text{ in outlet NaCl} &= 2.20 \times 2.8 \\ &= 6.16 \text{ moles}\end{aligned}$$

$$\text{Output NaClO}_3 \text{ conc} = 2.772 \text{ moles/litre}$$

$$\begin{aligned}\text{Moles of Cl}^- \text{ in NaClO}_3 &= 2.77 \times 2.20 \\ &= 6.09 \text{ moles}\end{aligned}$$

$$\text{Conc of OCl}^- = 10.92 \times 10^{-3} \text{ moles}$$

$$\begin{aligned}\text{Total moles of Cl}^- \text{ in OCl}^- &= 10.92 \times 10^{-3} \times 2.2 \\ &= 0.02 \text{ moles}\end{aligned}$$

Duration of run = 175 min

Catholyte flow rate = $0.50 \text{ cm}^3/\text{s}$

Catholyte Cl^- conc = $3 \times 10^{-3} \text{ M}$

Total volume of catholyte = $0.50 \times 175 \times 60 \times \frac{1}{1000}$

$$\left(\frac{\text{cm}^3}{\text{s}}\right)\left(\frac{\text{min}}{1}\right)\left(\frac{\text{s}}{\text{min}}\right) \times \left(\frac{\text{cm}^3}{\text{L}}\right)$$

= 5.25 litres

Total moles of Cl^- in catholyte = $3 \times 10^{-3} \times 5.25$

= 0.02 moles

Summary of Chloride Balance

Table D

	Inlet	Outlet
Moles of Cl^- in NaCl	6.48	6.16
Moles of Cl^- in NaClO_3	5.81	6.09
Moles of Cl^- in OCl^-	-	0.02
Moles of Cl^- in $30 \text{ cm}^3 \text{ HCl}$	0.03	-
Moles of Cl^- in catholyte	-	0.02
Total moles of Cl^-	12.32	12.29

$$\% \text{ amount of } \text{Cl}^- \text{ accounted for} = \frac{12.29}{12.32} \times 100\%$$

$$= 99.76\%$$

i.e., % amount of Cl^- unaccounted for = 0.24%

APPENDIX 3

SYSTEM MODELS

ELEMENTARY SYSTEM MODEL

An elementary process model is suggested. The model is only good for obtaining the chlorate current efficiency knowing peroxide concentration and other important factors of the model. This model is a modification of the chlorate system model suggested by Jacksic et al. [18]. The peroxide current efficiency is obtained using the electrochemical equivalent of peroxide reaction.

The Process Model

Process flow diagram showing electrochemical reactor for co-generation of sodium chlorate and alkaline peroxide solution

Figure C1

The cell is described in the body of the thesis (see Chapter 4) and as shown in Figure C1, a separate anolyte and separate feed is used. The major electrochemical reaction of interest are: on the cathode side is peroxide generation and on the anode side are Cl_2 gas generation and ClO^- oxidation. The membrane hydrodynamically separates the anolyte and the catholyte but allows migration and diffusion of anions across it.

Assumptions and Constraints

The following assumptions and constraints were used in derivation of the model:

- (1) Each of the two chambers of the electrolyzer is considered as a back mixed flow reactor with the membrane boundary acting as a mass exchange surface between them. The assumption is justified for the anode side which is an open channel. For the cathode side, it is not a justifiable assumption but would be used for the sake of simplicity.
- (2) The analysis is confined to the major reactions that lead to chlorate formation and loss and the HO_2^- species transport across the membrane.
- (3) All reactions between HO_2^- and ClO^- occur at the anolyte/membrane interface.
- (4) Isothermal operation of the cell at steady state is assumed.
- (5) The external reactor is considered as a back-mixed flow reactor.
- (6) The spatial dimension in the direction parallel to the current is the only important dimension for material balances. This follows from (1).

- (7) The relationship between the potential gradient and the current density through the membrane is given by

$$i = - \frac{\delta}{r} \frac{d\phi}{dx} \quad (C-1)$$

where

i is the current density based in the membrane surface area, $A\ m^{-2}$

r = membrane electrical resistance, Ωm^2

δ = membrane thickness, m

$\frac{d\phi}{dx}$ = potential gradient, $V\ m^{-1}$

- (8) The total available chlorine is the sum of the hypochlorous acid and hypochlorite.
- (9) In deriving the Faradaic stoichiometry and mass balance equations, hypochlorous acid and hypochlorite are able to take part in both Foerster's reactions of the chemical conversion and the anode oxidation for chlorate formation.
- (10) Linear concentration gradient in the membrane is assumed.

At quasi steady state, the material balance of available chlorine with respect to the cell is given by:

$$V_C \left(\frac{dC_C}{d\tau} \right) = 0 \quad (C-2)$$

where V_C = volume of the anode chamber, m^3

C_C = concentration of available chlorine, $moles/m^3$

τ = time in seconds

The partial contributors to the material balance will include the following:

- i. Available chlorine generated for chlorate formation - both for homogeneous (chemical) chlorate and heterogeneous (electrochemical) chlorate.
- ii. Generated available chlorine which is lost by reaction with peroxide that is transferred across the membrane.
- iii. Chlorine generated which is vented (unhydrolyzed chlorine).
- iv. Available chlorine generated which does not take part in any of the above mentioned reaction processes.

The equations of reactions for the above processes are given as follows:

Using t_i as the fraction of current for process i , the necessary equations could be stated as follows:

For a quasi steady state material balance:

- i. Anodic generation of available chlorine which is converted to chlorate by the two possible routes - homogenous and heterogenous routes

$$V_c \left(\frac{dC}{d\tau} \right)_1 = \frac{t_1 I}{2F} \quad (C-3)$$

where

I = current, Amps

F = Faraday constant, Coulombs/mole

τ = time in seconds

t_1 = fraction of current (current efficiency) for reaction (a) with subsequent hydrolysis and further conversion (homogeneous or oxidation (heterogeneous)) to chlorate.

- ii. Anodic generation of available chlorine, which is lost subsequently by reaction with perhydroxyl ions that are transferred across the membrane (see reaction f).

$$V_c \left(\frac{dC}{d\tau} \right)_2 = \frac{t_2 I}{2F} \quad (C-4)$$

where

t_2 is fraction of current used for chlorine that reacted with HO_2^- .

iii. Anodic generation of chlorine which is vented out as chlorine gas

$$V_c \left(\frac{dC}{d\tau} \right)_3 = \frac{t_3 I}{2F} \quad (C-5)$$

where t_3 is fraction of current used for vented chlorine.

iv. Anodic generation of available chlorine, which did not take part in either of reactions (i), (ii) or (iii), i.e., hydrolyzed but no chlorate formation.

$$V_c \left(\frac{dC}{d\tau} \right)_4 = \frac{t_4 I}{2F} \quad (C-6)$$

where t_4 is fraction of current used for chlorine that did not participate in any further reaction except to be hydrolyzed.

v. Anodic oxidation of available chlorine to chlorate (is a loss reaction) see reaction (e)

$$V_c \left(\frac{dC}{d\tau} \right)_{ox} = - \frac{t_5 I}{F} \quad (C-7)$$

where t_5 is the fraction of the current for the anodic chlorate formation.

- (f) Current losses due to available chlorine reaction with perhydroxyl ions

$$V_c \left(\frac{dC_c}{d\tau} \right)_{HO_2^-} = \frac{t_2 I}{2F} \quad (C-8)$$

- (g) Current losses due to vented out chlorine

$$V_c \left(\frac{dC_c}{d\tau} \right) = \frac{t_3 I}{2F} \quad (C-9)$$

- (h) Available chlorine conversion inside the anode chamber of the cell, into chlorate, assuming (a) back-mix flow reactor (b) Foerster mechanism then

$$V_c \left(\frac{dC_c}{d\tau} \right)_{RXnc} = - 3f_c^2 K_{rc} V_c [HClO]_c^2 [ClO^-]_c \quad (C-10)$$

where

f = hypochlorite or hypochlorous activity coefficient

K_{rc} = rate constant $((m^3/mole)^2 \text{ sec})$ for reaction

The right hand side of equation (C-10) is obtained based on assumption

(9) as follows:

For Eqn. (d), the rate equation could be written as

$$- \frac{d[ClO^-]}{d\tau} = - \frac{1}{2} \cdot \frac{d[HClO]}{d\tau} = \frac{d[ClO_3^-]}{d\tau} \quad (C-11)$$

or, otherwise

$$-\frac{dC_s}{d\tau} = -\frac{d([HClO] + [ClO^-])}{d\tau} = -3 \frac{d[ClO^-]}{d\tau} \quad (C-12)$$

where C_s = concentration of total available chlorine.

Introducing Foerster's kinetic law for the chemical conversion in concentrated solutions, eqn. (C-12) could be written

$$-\frac{dC_s}{d\tau} = 3 f^2 K_r [HClO]^2 [ClO^-] \quad (C-13)$$

Multiplying eqn. (C-13) by the volume of the reactor we obtain equation (C-10).

- (i) The available chlorine conversion to chlorate inside the holding volume (external reactor) is equal to the difference in quantities of available chlorine leaving the cell and entering the cell from the holding volume

$$V_c \left(\frac{dC_c}{d\tau} \right)_{RxnH} = -q(C_c - C_h) \quad (C-14)$$

where

q = electrolyte flow rate, m^3/s

C_c = concentration of available chlorine in cell, moles/ m^3

C_h = concentration of available chlorine in external reactor,
moles/ m^3

Doing a material balance over the anode part of the cell we have:

$$\begin{aligned} & \frac{t_1 I}{2F} + \frac{t_2 I}{2F} + \frac{t_3 I}{2F} + \frac{t_4 I}{2F} - \frac{t_5 I}{F} - \frac{t_2 I}{2F} - \frac{t_3 I}{2F} - q(C_c - C_h) \\ & - 3 f_c^2 K_{rc} V_c [HC10]_c^2 [C10^-]_c = 0 \end{aligned} \quad (C-15)$$

$$\text{Also } t_1 + t_2 + t_3 + t_4 + t_5 = 1 \quad (C-16)$$

from (C-16)

$$t_5 = 1 - t_1 - t_2 - t_3 - t_4 \quad (C-17)$$

Putting (C-17) into (C-15), we have

$$\begin{aligned} & \frac{t_1 I}{2F} + \frac{t_4 I}{2F} - \frac{I}{F} + \frac{t_1 I}{F} + \frac{t_2 I}{F} + \frac{t_3 I}{F} + \frac{t_4 I}{F} - 3 f_c^2 K_{rc} V_c [C10][HC10]^2 \\ & - q(C_c - C_h) = 0 \end{aligned}$$

solving for t_1 we obtain

$$\begin{aligned} t_1 = & \frac{2}{3} + 2\left(\frac{F}{I}\right) f_c^2 K_{rc} V_c [HC10]^2 [C10^-] + \frac{2(F)}{3(I)} q(C_c - C_h) \\ & - \frac{2}{3} (t_2 + t_3 + t_4) \end{aligned} \quad (C-18)$$

Simplifications

Replacing the concentration of hypochlorous acid and hypochlorite (total available chlorine) by

$$C_s = [HC10^-] + [C10^-] \quad (C-19)$$

and defining thermodynamic dissociation constant of hypochlorous acid by

$$K_a = \frac{a_{H_3O^+} f_{ClO^-} [ClO^-]}{f[HCIO] a_{H_2O}} \quad (C-20)$$

Rearranging equation (C-20), we define K^* as

$$K^* = \frac{a_{H_3O^+} [ClO^-]}{[HCIO]} = \frac{K_a f a_{H_2O}}{f_{ClO^-}} \quad (C-21)$$

From equation (C-19)

$$[HCIO] = C_s - [ClO^-] \quad (C-22)$$

Putting (C-22) into (C-21) we obtain,

$$\begin{aligned} K^* \{C_s - [ClO^-]\} &= a_{H_3O^+} [ClO^-] \\ \Rightarrow [K^* + a_{H_3O^+}] [ClO^-] &= K^* C_s \\ \Rightarrow [ClO^-] &= \frac{K^* C_s}{a_{H_3O^+} + K^*} \text{ or } \frac{K^* a_{H_3O^+} + C_s}{1 + \frac{K^*}{a_{H_3O^+}}} \end{aligned} \quad (C-23)$$

Putting (C-23) into (C-22) obtain

$$[HCIO] = C_s - \frac{K^* C_s}{a_{H_3O^+} + K^*} \quad (C-24)$$

Substituting into (C-18) using (C-23) and (C-24), obtain

$$t_1 = \frac{2}{3} + 2\left(\frac{F}{I}\right) f_c^2 K_{rc} V_c \left\{ \frac{C_c a_{H_3O^+}}{a_{H_3O^+} + K^*} \right\}_c^2 \left\{ \frac{K^* C_c}{K^* + a_{H_3O^+}} \right\} +$$

$$\frac{2}{3} \left(\frac{F}{I}\right) q(C_c - C_h) - \frac{2}{3}(t_2 + t_3 + t_4)$$

i.e.,

$$t_1 = \frac{2}{3} + 2\left(\frac{F}{I}\right) f_c K_{rc} V_c C_c^3 K^* a_{H_3O^+}^2 / (a_{H_3O^+} + K^*)^3$$

$$+ 2/3 \left(\frac{F}{I}\right) q(C_c - C_h) - \frac{2}{3}(t_2 + t_3 + t_4) \quad (C-25)$$

Assuming a back-mix flow reactor and doing a material balance over the holding volume (anolyte tank reactor), it could be shown that:

$$q(C_c - C_h) = 3f_h^2 K_{rh} V_h [HClO]_h^2 [ClO^-]_h \quad (C-26)$$

where

V_h = anolyte tank volume, m^3

K_{rh} = homogenous chlorate rate constant, $(m^3/mol)^2 \text{ sec}^{-1}$

From equations (C-19), (C-23), (C-24) and (C-26), equation (C-25) becomes

$$t_1 = \frac{2}{3} + 2f_c^2 K_{rc} V_c \left(\frac{F}{I}\right) \frac{K_c^* (a_{H_3O^+})_c^2 C_c^3}{[K_c^* + a_{H_3O^+}]_c^3} + 2f_h^2 K_{rh} V_h \left(\frac{F}{I}\right) \cdot$$

$$\frac{K_h^* (a_{H_3O^+})_h^2 C_h^3}{[K_h^* + (a_{H_3O^+})_h]^3} - \frac{2}{3}(t_2 + t_3 + t_4) \quad (C-27)$$

Approximating experimental values for K_a , Vogt [59] expressed K_a in the form:

$$- \log K_a = 7.744 - 0.0075 T/^{\circ}\text{C} \quad (\text{C-28})$$

Further he showed that experimental data of Jaksic et al (18) could be approximated as

$$\frac{K^*}{K_a} \approx 14 \quad (\text{C-29})$$

Hence from (C-28) and (C-29),

$$K^* = 14K_a = 14 \times 10^{-(7.744 - 0.0075 T/^{\circ}\text{C})} \quad (\text{C-30})$$

Using data from several authors collated by Kokoulina and Krishtalik

[37], we can fit an equation to express Kf^2 as

$$Kf^2 = 3.09 \times 10^4 \exp\left(-\frac{8.125 \times 10^3}{T}\right) \quad (\text{C-31})$$

where T is in Kelvin

Kf^2 is in $(\text{moles}/\text{m}^3)^{-2} \text{ sec}^{-1}$

For hydrogen ion concentration, $a_{\text{H}_3\text{O}^+}$, the pH of the solution is used,

i.e., $a_{\text{H}_3\text{O}^+} = 10^{-\text{pH}}$.

To simplify equation (C-27) further, assume values of t_3 and t_4 are negligible.

Obtain t_2 by equating flux of HO_2^- passing across the membrane with amount of active chlorine lost by reaction of perhydroxyl ions.

The flux or net flux of HO_2^- ions through the membrane from the catholyte to the anolyte can be written as

$$N_{\text{HO}_2^-} = U_{\text{HO}_2^-} F C_{\text{HO}_2^-} \left(\frac{d\phi}{dx} \right) - D_{\text{HO}_2^-} \left(\frac{dC_{\text{HO}_2^-}}{dx} \right) - v C_{\text{HO}_2^-} \quad (\text{C-32})$$

where

$N_{\text{HO}_2^-}$ = flux of perhydroxyl ions per unit area of membrane,
moles/m² · s

$U_{\text{HO}_2^-}$ = perhydroxyl ion mobility, m² mol J⁻¹ s⁻¹

$C_{\text{HO}_2^-}$ = peroxide concentration, mol/m³

$\frac{d\phi}{dx}$ = potential gradient across the membrane, V/m

$D_{\text{HO}_2^-}$ = diffusion coefficient of the perhydroxyl ion in the
membrane (m² s⁻¹)

v = electrolyte velocity along the x-direction inside the
membrane, m/s

Equation (C-32) can be simplified by assuming: that the electrolyte velocity in the membrane, $v = 0$.

The ion mobility is expressed as $U_{\text{HO}_2^-} = \frac{D_{\text{HO}_2^-}}{RT}$, using Plank-Einstein relation

$$\text{Express } \frac{dC_{\text{HO}_2^-}}{dx} = \frac{C^0 - C^a}{\delta} \quad (\text{C-33})$$

where

C^0 = bulk peroxide concentration in the catholyte

C^a = peroxide concentration in the anolyte = 0

i.e., assume all peroxide reacted immediately it enters into
the anolyte (assumption (3))

δ = membrane thickness in m

Thus (C-33) becomes

$$\frac{dC_{\text{HO}_2^-}}{dx} = \frac{C^0}{\delta} \quad (\text{C-34})$$

Assume the potential gradient through the membrane is given by

$$\frac{d\phi}{dx} = \frac{ir}{\delta} \quad (\text{C-35})$$

where

i is the current density based on the membrane surface area, kA m^{-2}

r = membrane electrical resistance, ohm m^2

Combining all these, equation (C-32) is rewritten as:

$$N_{\text{HO}_2^-} = \frac{D_{\text{HO}_2^-} F C_{\text{HO}_2^-}^0}{RT} - \frac{ir}{\delta} - \frac{D_{\text{HO}_2^-} C_{\text{HO}_2^-}^0}{\delta} \quad (\text{C-36})$$

If the total membrane surface area = A_c , then total moles of HO_2^- passing through the membrane from catholyte to the anolyte is given by

$$[\text{HO}_2^-] = A_c N_{\text{HO}_2^-} \quad (\text{moles/s}) \quad (\text{C-37})$$

By assuming moles of ClO^- lost through reaction with HO_2^- is equal to moles of HO_2^- passing through membrane we obtain

$$\frac{t_2 I}{2F} = A_c N_{\text{HO}_2^-}$$

$$t_2 = \frac{2F A_c N_{\text{HO}_2^-}}{I} \quad (\text{C-38})$$

Substituting for $N_{\text{HO}_2^-}$ in (C-38) using (C-36)

$$t_2 = \frac{2F^2 A_c D_{HO_2^-} C_{HO_2^-}^0 - i r}{I R T \delta} - \frac{2F A_c D_{HO_2^-} C_{HO_2^-}^0}{I \delta}$$

$$t_2 = \frac{2F A_c D_{HO_2^-} C_{HO_2^-}^0}{I \delta} \left[\frac{F i r}{R T} - 1 \right] \quad (C-39)$$

Substituting $t_3 = 0$, $t_4 = 0$ and using (C-39) for t_2 then equation (C-27) becomes:

$$t_1 = \frac{2}{3} + 2f_c^2 K_{rc} V_c \left(\frac{F}{I} \right) \frac{K_c^* (a_{H_3O^+})_c^2 C_c^3}{(K_c^* + a_{H_3O^+})_c^3} +$$

$$2 f_h^2 K_{rh} V_h \left(\frac{F}{I} \right) \frac{K_h^* (a_{H_3O^+})_h^2 C_h^3}{(K_h^* + (a_{H_3O^+})_h)^3} - \frac{2}{3} \left\{ \frac{2F A_c}{I \delta} D_{HO_2^-} C_{HO_2^-}^0 \left[\frac{F i r}{R T} - 1 \right] \right\}$$

(C-40)

The model equation (C-40) stands for the following:

t_1 = Total chlorate current efficiency of the process.

$2/3$ = Maximum chlorate efficiency achievable if all chlorate is formed through the electrochemical route

$$2 f_h^2 K_{rh} V_h \left(\frac{F}{I} \right) \frac{K_h^* (a_{H_3O^+})_h^2 C_h^3}{(K_h^* + (a_{H_3O^+})_h)^3} = \text{Chlorate formed in the cell volume, } V_c \text{ through the chemical route.}$$

$$2 f_h^2 K_{rh} V_h \left(\frac{F}{I} \right) \frac{K_h^* (a_{H_3O^+})_h^2 C_h^3}{(K_h^* + (a_{H_3O^+})_h)^3} = \text{Chlorate formed in the external reactor of volume } V_h, \text{ through the chemical route.}$$

$$\frac{2}{3} \left\{ \frac{2F A_c}{I \delta} D_{HO_2^-} C_{HO_2^-}^0 \left[\frac{F i r}{R T} - 1 \right] \right\} = \text{Chlorate lost due to reaction of } HO_2^- \text{ with chlorate intermediates.}$$

Example Use of the Model Equation

In using the model, some assumptions are made.

1. The diffusion coefficient of HO_2^- is assumed to be 1/4 of the value of OH^- ion diffusion coefficient in aqueous solution. In a recent work by Herrera and Yeager [53], the self diffusion coefficients of Na^+ , Cl^- , I^- , and SO_4^{2-} ions in sulfonate and carboxylate Nafion (cation) membranes were measured. The magnitude of the reported diffusion coefficient for the Na^+ cation (main current carrier in cation electrolysis of this type) in the membrane is lower than the value in solution ($15.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ in 3 M NaCl cf $1.334 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at infinite dilution). A value of $D_{\text{HO}_2^-} = 1.75 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ is assumed $D_{\text{OH}^-} = 7.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 25°C .

2. A constant HO_2^- concentration in the cell is assumed.

3. The average cell temperature used is the average of the inlet and outlet temperature on the anode side. The following are also known quantities.

Membrane thickness, $\delta = 5.08 \times 10^{-5} \text{ m}$

Effective superficial membrane surface area; $A_c = 83.33 \times 10^{-4} \text{ m}^2$

Anolyte cell volume, $V_c = 25 \times 10^{-6} \text{ m}^3$

Anolyte tank final volume, $V_h = 2.02 \times 10^{-3} \text{ m}^3$

Example: Consider run C₂₅ (table C2 in Appendix 3).

Cell temperature = 28°C

Anolyte tank reactor temperature = 70°C

Current density, $i = 2.4 \text{ kA m}^{-2}$

Current, $I = 20\text{A}$

Peroxide concentration, $C_{HO_2^-}^0 = 107.0 \text{ moles m}^{-3}$

$$t_1 = \frac{2}{3} + 2 K_{rc} f_c^2 V_c \left(\frac{F}{I}\right) \frac{K_c^* (pH)_c^2 C_c^3}{[K_c^* + (pH)_c]^3} + 2K_{rh} V_h \left(\frac{F}{I}\right) \times$$

$$\frac{K_h^* (pH)_h^2 C_h^3}{[K_h^* + (pH)_h]^3} - \frac{4F A_c D_{HO_2^-} C_{HO_2^-}^0}{3 I \delta} \left[\frac{F_{ir}}{RT} - 1\right] \quad (C-41)$$

If negligible conversion of available chlorine inside the cell is assumed, i.e., second term in eqn. (C-41) is assumed zero then t_1 may be expressed as

$$t_1 = \frac{2}{3} + 2 K_{rh} f_h^2 V_h \left(\frac{F}{I}\right) \frac{K_h^* (pH)_h^2 C_h^3}{[K_h^* + (pH)_h]^3} - \frac{4F A_c D_{HO_2^-} C_{HO_2^-}^0}{3 I \delta}$$

$$\left[\frac{F_{ir}}{RT} - 1\right] \quad (C-42)$$

the second term in equation (C-42) defines the yield of chlorate inside the holding volume to the overall current efficiency of the system. It can be expressed as

$$\text{i.e., second term} = \frac{2}{3} F \left(\frac{q}{I}\right) (C_c - C_h) \quad (C-43)$$

where C_c and C_h are the total available chlorine concentrations (moles/m³) of inflow and outflow of the holding volume, respectively.

The third term in equation (C-42) is the loss of chlorate current efficiency due to peroxide migration. The first term is the maximum chlorate efficiency that can be achieved if all the chlorate is formed

by available chlorine concentration in cell, $C_c = 30.6 \text{ moles m}^{-3}$

available chlorine concentration in anolyte reactor, $C_h = 12.6 \text{ moles}$

m^{-3} membrane resistance, $r = 1.85 \times 10^{-4} \text{ Ohm m}^2$.

Cell sample pH = 7.0

Anolyte tank sample pH = 6.8

At 28°C, the reaction rate constant for the chlorate formed in the cell,

$$\begin{aligned} K_{rc} f^2 &= 3.09 \times 10^4 \exp\left(-\frac{8.125 \times 10^3}{301}\right) \\ &= 5.85 \times 10^{-8} (\text{moles/m}^3)^{-2} \text{ sec}^{-1} \end{aligned}$$

for the rate constant in the external reactor, $K_{rh} f_h^2$ (at 70°C)

$$\begin{aligned} K_{rh} f^2 &= 3.09 \times 10^4 \exp\left(-\frac{8.125 \times 10^3}{343}\right) \\ &= 1.59 \times 10^{-6} (\text{moles/m}^3)^{-2} \text{ sec}^{-1} \end{aligned}$$

The equilibrium constant expression, k^*

- for the cell term, $K_c^* = 14 \times 10^{-(7.744-0.0075 \times 28)}$

$$= 4.094 \times 10^{-7}$$

- for the anolyte tank term, (T = 70°C)

$$K_h^* = 14 \times 10^{-(7.744-0.0075 \times 70)}$$

$$= 8.455 \times 10^{-7}$$

Cell $a_{\text{H}_3\text{O}^+} = 10^{-\text{pH}_c}$ and anolyte tank $a_{\text{H}_3\text{O}^+} = 10^{-\text{pH}_c}$

Using the model equation:

$$t_1 = \frac{2}{3} + 2 K_{rc} f_c^2 V_c \left(\frac{F}{I}\right) \frac{K_c^* (pH)_c^2 C_c^3}{[K_c^* + (pH)_c]^3} + 2 K_{rh} f_h^2 V_h (F/I) \times$$

$$\frac{K_h^* (pH)_h^2 C_h^3}{[K_h^* + (pH)_h]^3} - \frac{4F A_c D_{HO_2^-} C_{HO_2^-}^0}{3 I \delta} \left[\frac{F i_r}{RT_c} - 1 \right]$$

Substituting all the relevant values,

$$t_1 = \frac{2}{3} + 2 \times 5.85 \times 10^{-8} \times 25 \times 10^{-6} \left(\frac{96500}{20}\right) 4.094 \times 10^{-7} \times (10^{-4})^2$$

$$\left(\frac{m^3}{mol}\right)^2 \left(\frac{1}{sec}\right) \left(\frac{m^3}{l}\right) \left(\frac{coul}{g-equiv}\right) \left(\frac{sec}{coul}\right) \left(\frac{mol}{m^3}\right)^2$$

$$\frac{(30.6)^3}{[4.094 \times 10^{-7} + 10^{-4}]^3} + 2 \times 1.59 \times 10^{-6} \times 2.02 \times 10^{-3} \left(\frac{96500}{20}\right) \times$$

$$\left(\frac{mol}{m^3}\right)^3 \left(\frac{m^3}{mol}\right)^3$$

$$\frac{8.455 \times 10^{-7} \times (10^{-3.8})^2 \times (12.6)^3}{(8.455 \times 10^{-7} + 10^{-3.8})^3} - \frac{4 \times 96500 \times 83.33 \times 10^{-4}}{20 \times 5.08 \times 10^{-5} \times 3}$$

$$\times 107 \left(\frac{96500 \times 2400 \times 1.85 \times 10^{-4}}{8.314 \times 301} - 1 \right)$$

$$t_1 = 63.5\% \text{ (experimental value = 67\%)}$$

Using expression in (C-43) in (C-42) to replace the second term and assuming negligible contribution by second term of eqn (C-41), then,

$$t_1 = \frac{2}{3} + \frac{2}{3} F\left(\frac{q}{I}\right) (C_c - C_h) - \frac{4F A_c D_{HO_2^-} - C_{HO_2^-}^0}{3 I \delta} \left(\frac{F_{ir}}{RT} - 1\right) \quad (C-44)$$

Instead of equation (C-41) used for t_1 above, we can use eqn (C-44), with the following:

$$q = 2.0 \times 10^{-6} \text{ m}^3/\text{s}$$

Other factors remain same. Using (C-44)

$$t_1 = 75.1\%.$$

Some comparisons are made in Table C1 between the calculated t_1 values (using (C-44) of the model) and those obtained from the experimental results.

The only suggestion for the deviation of model equation (C-41) results from the experimental calculations might be the use of the approximations of Vogt (59) as in equations (C-29) and (C-30). Those approximations may be good for undivided chlorate cells. With respect to the peroxy-chlorate system, the approximations Vogt used did not take into consideration the interacting effects of the cathode chamber.

Table C1
Comparison of experimental and calculated ClO_3^-
current efficiencies

Run #	Calculated t_1 (C-44)	Experimental
C ₂₇	76.7	60.0
C ₈	71.2	73.5
C ₂₂	67.6	53.2
C ₁₈	74.8	78.7
C ₆	76.5	72.1
C ₁₇	79.8	79.0
C ₂₅	75.1	67.0

From the above table, it doesn't seem the model equation (C-44) describes the system well. It is likely that the calculated values owed their deviations (from the experimental results) to the assumed diffusion coefficient of HO_2^- ion. Some experimental results useful for the model equations are presented in Table C2 and Table A of Appendix II.

Table C2

Some experimental results for model equation

Run #	pH		ClO ⁻ Conc. (M) x 10 ³		Temp (°C)		ClO ₃ ⁻ Efficiency
	Cell Sample	Reactor Sample	Cell Sample	Reactor Sample	Cell Sample	Reactor Sample	% (6 moles e ⁻)
C ₄	7.2	6.5	18.75	5.45	25.5	70.0	57.4
C ₆	7.3	6.6	30.73	12.0	29.5	70	72.1
C ₈	7.15	6.6	22.50	15.0	33.0	70	73.5
C ₁₀	7.1	6.7	18.60	14.1	29.0	70	67.0
C ₁₂	7.2	6.6	29.20	15.93	34.0	71	69.0
C ₁₄	7.2	6.8	18.5	11.5	32.5	71	67.0
C ₁₈	7.0	6.6	31.9	14.8	30.5	73	76.0
C ₂₂	7.1	6.7	20.2	11.2	29.0	70	53.2
C ₂₃	7.1	6.7	27.2	13.7	30.0	71	75.0
C ₂₄	7.0	6.6	30.3	15.9	32.0	74	63.0
C ₂₅	7.0	6.8	30.6	12.6	28.0	70	67.0
C ₂₆	7.1	6.75	26.25	14.3	30.5	70	70.0
C ₂₇	7.0	6.6	22.8	12.6	27.5	70	60.0
C ₁₉	7.1	6.6	20.6	12.1	30.0	72.0	70.3
C ₁₇	7.1	6.6	24.0	6.5	31.0	70.0	79.0
C ₁₈	7.0	6.6	32.0	14.8	30.5	73.0	78.7