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Electrolysis of weak black liquor Part II: Effect of process parameters on the energy efficiency of the electrolytic cell

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A laboratory study of the effects of process parameters on the performance of weak black liquor (WBL) electrolysis cells showed that anode material, current density and temperature are critical to the operation. The two latter variables showed an interaction effect upon the operation of the cell. In terms of energy efficiency, the IrO_2 anode performed better than the Pt anode. The addition of sodium sulfate to the WBL was beneficial to the energy efficiency. No chlorine gas was produced when electrolyzing WBL containing sodium chloride within the pH range 5.4 to 13.

1. Introduction

Electrolysis of weak black liquor (WBL) represents an attractive alternative for increasing the production capacity of an existing kraft mill [1]. The process has the potential to provide incremental capacity for an overloaded kraft recovery system, while simultaneously unloading the furnace, the lime kiln and the causticizing plant. In order to reduce the organic load to the furnace, we propose to remove lignin from WBL using an electrolytic process allowing the conversion of the sodium salts to caustic. In our initial study, we reported tests conducted to define the process parameters [2]. It was found that more than 75% of the lignin could be precipitated from the WBL and 80% of the sodium salts could be converted to caustic. We also performed a test for an extended period of time to demonstrate the technical feasibility of continuous operation [3].

The objective of this study was to investigate the effect of the following process parameters on the cell energy efficiency: type of WBL, type of membrane, addition of sodium sulphate to the WBL, concentration of caustic in the catholyte, anode material, current density, temperature, and presence of sodium chloride.

To develop a process suitable for most kraft mills, we considered testing the two main types of WBL encountered in kraft pulping. The liquors were classified according to the feedstock: hardwood weak black liquor (HWWBL) from the pulping of a feedstock containing mostly hardwoods and softwood weak black liquor (SWWBL) from a feedstock consisting mostly of softwoods. Samples of each type of liquor were obtained from Canadian pulp and paper operating plants and tests were performed under identical operating conditions.

The membrane part of the electrolytic cell plays an important role in the economics of the process. The membrane should have a good chemical resistance, a low electrical resistance, a high selectivity (or low back diffusion rate) for hydroxyl ions and a low cost. Based on these parameters, two membranes from two different manufacturers were selected for testing: a more expensive membrane from Dupont (Nafion® 324) and a low cost membrane from RAI Corporation (R-4010).

The addition of sodium sulphate to the feed of the electrolytic process was considered for various reasons. Adding the salt cake from the ClO_2 generator to the WBL fed to the cell may represent an attractive alternative for recycling this waste product into useful caustic. It could improve the energy efficiency of the cell by increasing the conductivity of the anolyte (WBL), thus reducing both the voltage drop and the energy consumption. This option of recycling salt cake offers the possibility to convert the Na_2SO_4 directly to caustic and to eliminate the operating problems in mixing that salt, containing residual sulphuric acid, with strong liquor. The production of NaOH from the Na_2SO_4 also helps to control the sulphide concentration in the pulping liquor. Recovery furnace catch (Na_2SO_4 with small amount of Na_2CO_3) can also be used with similar benefits.

A caustic solution of about 15–20% (NaOH, w/w) is a useful concentration for providing NaOH for various specific uses within the mill (e.g., white liquor). For the extraction step, in the bleaching area, a lower concentration (3–4% NaOH, w/w) is required. Thus, to cover the range of concentration used in a kraft mill, tests were run with initial sodium hydroxide concentrations of 4 and 17% (w/w) in the catholyte.

The anode material is of great importance to the technical viability of the process. The reaction, and the rate, of an electrolytic process depend strongly on the electrode material and its catalytic activity.

The anode material must have good electrocatalytic behaviour [4] and good corrosion resistance to caustic and acid. It has to be specific to promote the oxygen evolution reaction and prevent undesirable by-products such as chlorine or other gases. Therefore, the performance of graphite, nickel, platinum and iridium oxide coated-titanium anodes was investigated.

High current density and temperature assures maximum sodium flux through the membrane and maximum production rate of caustic per unit membrane area. This combination should minimize the capital investment. The sodium fluxes and energy efficiency were evaluated (i) at medium (250 mA cm^{-2}) and (ii) maximum current density (400 mA cm^{-2}) as recommended by the membrane manufacturer, and temperatures varied from 55 to 80 °C.

The concentration of sodium chloride in some WBL may be high and may potentially affect the formation of chlorine gas at the anode. To simulate the WBL of a Canadian west coast mill, NaCl was added to a sample of SWWBL from an eastern mill. The liquor was electrolysed and the gas stream monitored for evolution of chlorine gas.

2. Experimental details

The tests were carried out in the batch mode with an experimental apparatus shown in Fig. 1. The experimental operating conditions were described in the previous study [2].

The effect of various parameters on the performance of the electrolytic cell were studied in relation to energy efficiency. The energy consumption is reported in kWh per kg of caustic produced as NaOH. The current efficiency of the electrolytic cell is defined as the ratio of the actual over the theoretical chemical production (NaOH), for the quantity of electricity passed through the cell. The sodium recovery was calculated from the quantity of caustic produced as sodium, in the catholyte, over the quantity of sodium initially present in the WBL.

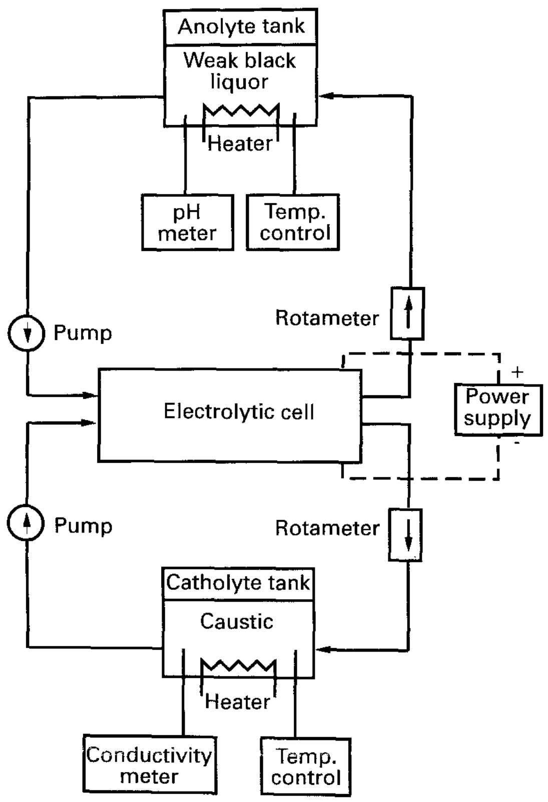

Fig. 1. Schematic diagram of the experimental apparatus – batch mode operation.

3. Results

3.1. *Effect of type of liquor*

Two types of liquor were tested: HWWBL from the pulping of a feedstock containing mostly maple (<10% softwoods) and SWWBL from a furnish consisting of 68% spruce, 20% pine and 12% hardwood. The typical composition of each liquor is shown in Table 1. The pH of HWWBL was higher due to a higher effective alkali. Even though the SWWBL contained less sodium, its conductivity was better.

The results of the tests comparing the energy efficiency for each liquor are presented in Figs 2 and 3. The experiment with SWWBL was terminated after 112 min because of an excessive electrical resistance caused by lignin precipitation. As electrolysis proceeded, the lignin concentration decreased through precipitation as a result of the decline in the pH of the WBL to a value of 3.5. With HWWBL, the experiment could be carried out for 160 min before encountering the same phenomenon.

Over the duration of the test, the energy required per kg of caustic produced (Fig. 2) was higher for the SWWBL, approximately 12.5 kWh kg^{-1} as compared

Table 1. Composition of softwood (SWWBL) and hardwood (HWWBL) weak black liquors tested

Component	*Type of liquor*	
	SWWBL	*HWWBL*
pH	11.4	12.8
Conductivity (mmho)	69.0	61.9
Sodium (g dm^{-3})	22.0	34.4
U.V. Lignin (g dm^{-3})	39.4	43.6
Total dissolved solids (g dm^{-3})	115.4	165.6
Alkalinity (g dm^{-3})	15.4	35.0
Effective alkali (g dm^{-3})	7.8	12.6
Active alkali (g dm^{-3})	8.6	1.9
Carbonate (g dm^{-3})	9.2	12.9
Sulphide (g dm^{-3})	0.8	0.8
Thiosulphate (g dm^{-3})	3.1	4.7
Chloride (g dm^{-3})	0.7	0.4
Sulphate (g dm^{-3})	3.7	3.9
Metal impurities (mg dm^{-3})		
Al	30	20
Mg	56.2	15.2
Ca	16.8	30.6
Fe	3	8
Cr	<1	<1
Ni	<1	<1

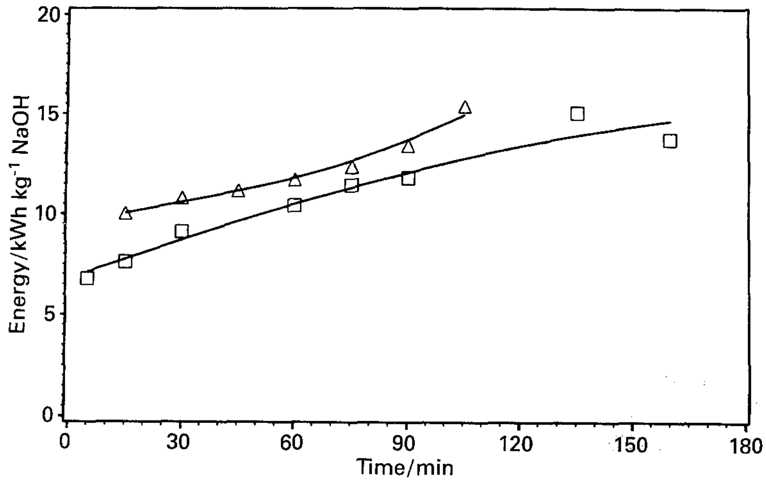

Fig. 2. Effect of the type of liquor on the energy required for producing caustic during electrolysis of weak black liquor at 55 °C. Key: (□) hardwood liquor and (△) softwood liquor.

to 10 kWh kg^{-1} for the HWWBL. This is mainly due to a lower current efficiency (Fig. 3) for SWWBL (60%) than HWWBL (85%). This may be related to the liquor composition, particularly the much lower sodium concentration in that liquor (see Table 1).

Through these experiments, it was also observed that the cell voltage drop (V) with SWWBL was increasing faster than with HWWBL. This may be partly attributed to the lower conductivity of the liquor and/or the different chemical composition, particularly with respect to the concentrations of extractants. These components, potential fouling agents, are often present in SWWBL at elevated concentration and this may result in a higher voltage drop at the anode and the membrane. The energy requirement of the process can be minimized for both liquors, however, by an appropriate washing cycle in the anolyte compartment. Based on our results, the anode and membrane washing is expected to be more frequent when processing SWWBL.

Due to the buffering effect of Na_2CO_3, the pH remained high until the solution was almost depleted of this salt. This helps reduce back-diffusion of hydroxide to the anolyte and maintain a higher current efficiency at a given sodium recovery. Higher Na_2CO_3 content in the WBL may increase the energy efficiency of the process assuming that the CO_2 generated near the anode escapes freely. Foaming was observed in the WBL when pH decreased from 7 to 5.5 due to carbon dioxide produced from the decomposition of sodium bicarbonate.

3.2. *Effect of membrane type*

The two membranes tested were both cation-selective. The Nafion® 324 membrane is made by Dupont. It is a perfluorosulfonic acid cation exchange membrane and is mainly used in the chlor–alkali industry. Its thickness is approximately 0.2–0.3 mm and its resistance is 4.5 Ω cm^{-2}. Nafion® membranes are employed at a kraft mill of a member company to produce 12% sodium hydroxide from a brine solution. This plant has been in operation since 1976 [5]. The R-4010 membrane is a sulfonated styrene graft on a preformed two mil fluorinated polymer film. This membrane is approximately 0.1 mm thick and has a resistance that varies from 0.2 to 1.0 Ω cm^{-2}. It is manufactured by RAI Corporation. It is mainly used in electrodialysis systems for the desalination of water.

The energy performance of the R-4010 membrane was significantly affected by its low selectivity for OH^- ions. Its current efficiency dropped dramatically due to back-diffusion of OH^- to the anolyte. The voltage drop between the electrodes was also higher. Consequently, the energy consumption per kg of caustic produced was greater with the R-4010 membrane as compared to the Nafion® 324 (Fig. 4).

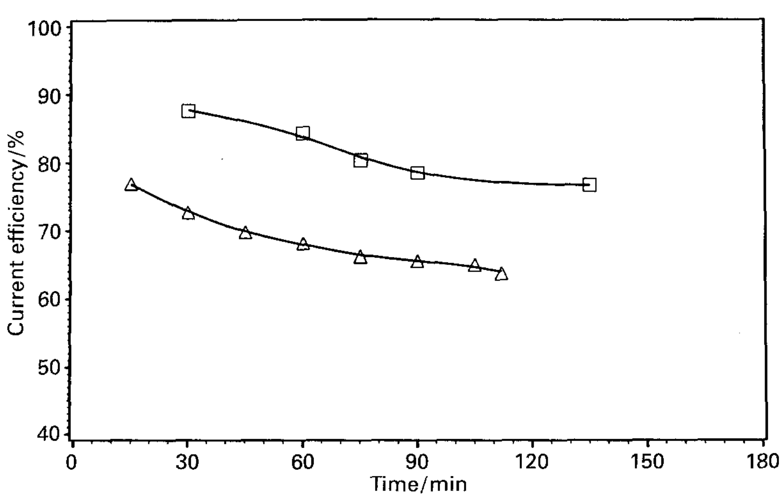

Fig. 3. Effect of the type of liquor on the current efficiency during electrolysis of weak black liquor at 55 °C. Key: (□) hardwood liquor and (△) softwood liquor.

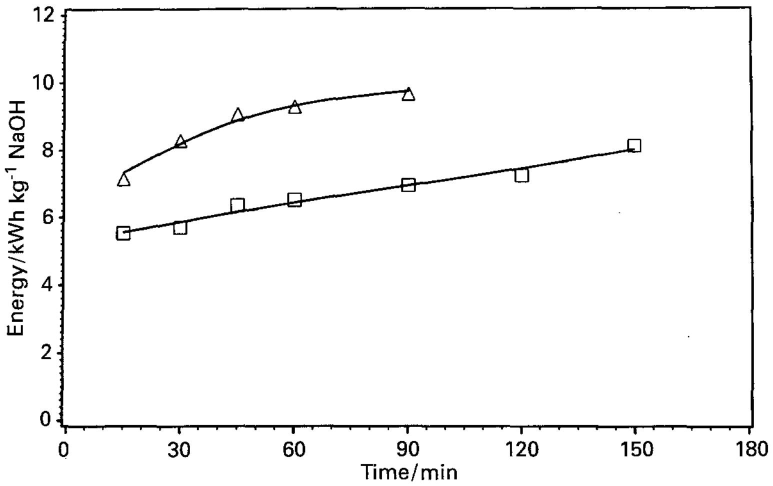

Fig. 4. Effect of the membrane type on the energy consumption during electrolysis of softwood weak black liquor at 55 °C and 250 mA cm^{-2}. Membrane: (□) Nafion®-324 and (△) R-4010.

3.3. *Effect of addition of Na_2SO_4 to WBL*

Given the numerous benefits anticipated with the option of recycling salt cake through the electrolytic process, the effect of adding sodium sulphate to WBL on the energy efficiency of the cell was studied.

Technical grade sodium sulphate was initially added to the liquor (HWWBL) to increase the sodium concentration from 31 to 64 g dm^{-3}. Experiments were carried out and the cell voltage drop (V) was compared to that obtained with regular liquor (HWWBL) with no salt added.

The addition of salt increased the conductivity of the solution of the anolyte (HWWBL). Consequently, the voltage drop between the electrodes (Fig. 5) was reduced, improving the energy efficiency. Moreover, addition of Na_2SO_4 to the feed liquor before electrolysis may help prevent the formation of an adherent organic coating on the membrane and anode as reported by Milton [6].

The addition of the waste salt from the ClO_2 generator to the WBL should be considered for improving the energy efficiency of the electrolytic process. The quantity of salt added should be carefully controlled by monitoring the pH of the WBL in order to avoid precipitation of the lignin from the residual acid content.

3.4. *Effect of caustic*

Electrolysis of WBL was tested using two different initial concentrations of circulating caustic in the catholyte: 1 M (4% NaOH, w/w) and 5 M (17% NaOH, w/w). The major effect of the caustic strength on the energy performance is a reduction in the voltage drop between the electrodes. Higher caustic levels are favourable within a certain range. The conductivity of a caustic solution increases with concentration and at 55 °C, reaches a maximum at about the 20% level before it starts to decrease. The NaOH level also affects the voltage drop across the membrane which could represent a significant fraction of the overall cell voltage drop. At higher caustic concentration (>25%), the voltage drop across the membrane is expected to be greater [7].

In the present study an increase in caustic concentration in the catholyte was beneficial to the performance of the cell, for the range tested (4–17% NaOH, w/w). The voltage drop across the electrodes was approximately 15 to 20% lower at the higher caustic level (Fig. 6). Based on manufacturer specifications, for a maximum current efficiency, the concentration of the caustic produced should be maintained below 20% when using the Nafion® 324 cation-selective membrane.

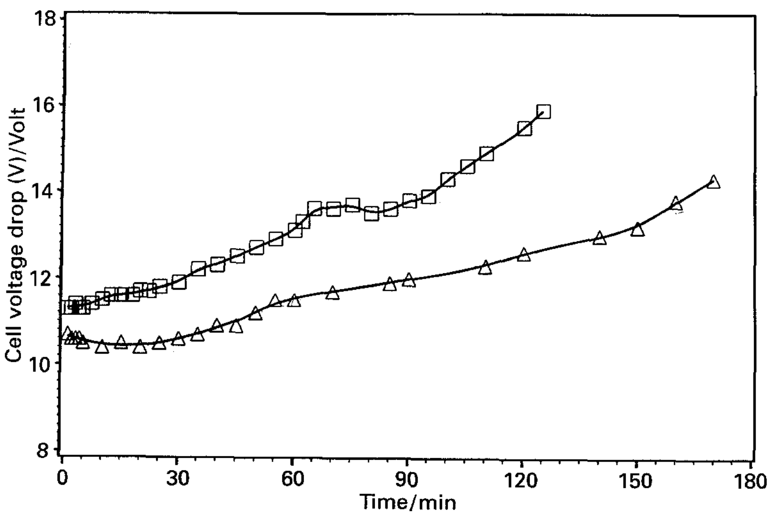

Fig. 5. Effect of sodium sulphate addition on cell voltage during electrolysis of hardwood weak black liquor at 55 °C and 400 mA cm^{-2}. Key: (□) no added Na_2SO_4 and (△) Na_2SO_4 added.

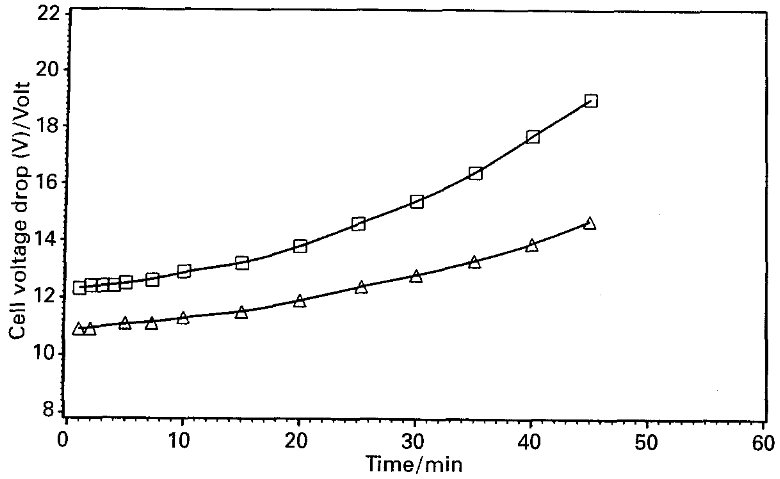

Fig. 6. Effect of caustic concentration in the catholyte on the cell voltage during electrolysis of softwood weak black liquor at 55 °C and 400 mA cm^{-2}. Key: (□) NaOH (4%) and (△) NaOH (17%).

3.5. *Effect of the anode material*

The performance of anode materials, graphite, nickel, platinum and iridium oxide-coated titanium were tested. The tests were performed with WBL from a softwood furnish which is more common in Canadian kraft mills.

The graphite and nickel anodes did not show good corrosion resistance. The carbon anode disintegrated into fine carbon particles within the first few hours of testing. With nickel, which is commonly used as an anode in the electrolysis of water in alkaline solution, a thick coating of black carbon-like material deposited on the anode after a few minutes of operation, causing the voltage drop to rise to the maximum available from the power supply. Chemical analyses revealed that the deposit contained sulphur and nickel indicating that the sulphur in the liquor reacted with the anode.

Platinum and iridium oxide-coated titanium were found to be successful candidates as anode materials. These electrodes favour the evolution of oxygen over chlorine. The average energy requirements when using IrO_2 and Pt anodes were 6.8 and 8.5 kWh kg^{-1} of caustic produced, respectively (Fig. 7). The IrO_2 anode thus required about 20% less energy per kg of caustic than the platinum anode. This could probably be explained in terms of the higher specific catalytic area of the IrO_2 electrode, which reduces the resistance at the anode and increases the reaction rate, both contributing to a lower energy consumption.

3.6. *Effect of the current density*

The higher the current density, the higher the flux of sodium across the cation-selective membrane and thus the caustic production rate in the catholyte. This means that less membrane area (or cell units) and lower capital investment will be required for a given production capacity. On the other hand, the higher current density will result in higher energy consumption per kg of caustic. High current densities might also shorten the life of the membrane.

The effect of current density on the performance of the cell was tested at 250 and 400 mA cm^{-2}. The results of the test are presented in Figs 8 and 9. As expected, the energy requirement increased with current density from about 8.5 to 12.5 kWh kg^{-1} of NaOH, when the current density increased from 250 to 400 mA cm^{-2} (Fig. 8). On the other hand, the flux of sodium through the membrane increased from about 1750 to 2500 g h^{-1} m^{-2} (Fig. 9). Increase in current density by 60% thus increased the energy requirement as well as the flux of sodium by 50% and 40%, respectively. Assuming that the life of the membrane and the anode are not considerably

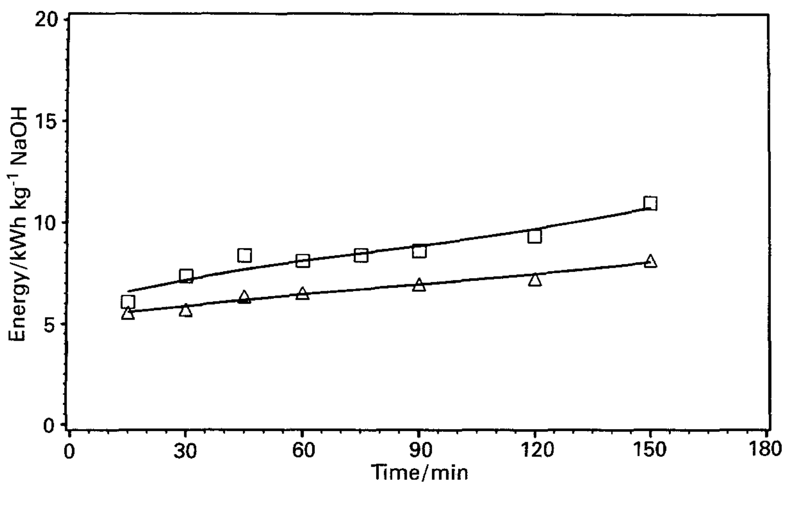

Fig. 7. Effect of anode material on the energy consumption during electrolysis of softwood weak black liquor at 55 °C and 250 mA cm^{-2}. Key: (□) platinum on titanium and (△) iridium oxide on titanium.

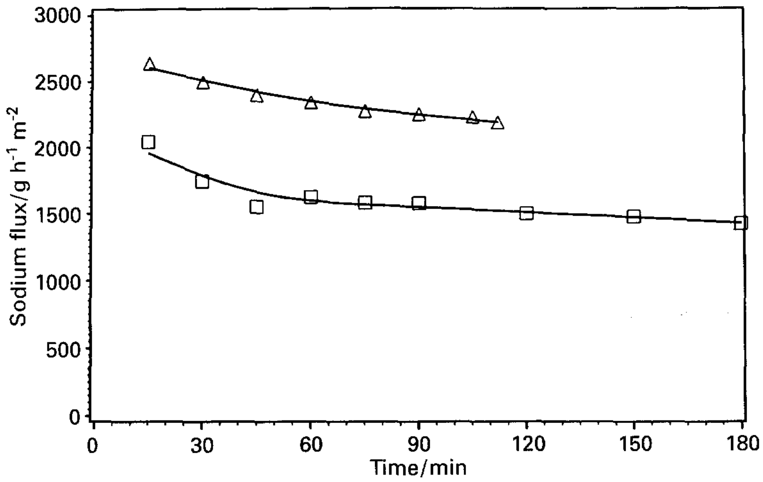

Fig. 8. Effect of current density on the sodium flux during electrolysis of softwood weak black liquor at 55 °C. Current densities: (□) 250 and (△) 400 mA cm^{-2}.

affected, operating at higher current density may be beneficial to the economics of the process.

3.7. *Effect of the temperature*

Based on preliminary tests to operate the cell at the highest current density and temperature, we observed a relationship between these two variables limiting the operable range. At current density of 400 mA cm^{-2} and temperature of 90 °C, fouling of the anode was very severe and irreversible. An increase in temperature above about 80 °C was reported to increase the stickiness of the precipitated lignin [8, 9]. Washing of the anode with fresh liquor did not restore the performance of the cell. For this reason, we suggest that temperature should not exceed 80 °C with a current density of 250–300 mA cm^{-2}. To increase the current density when operating at higher temperatures, increased turbulence in the anode compartment (by increasing the flow) might be necessary.

To compare energy efficiencies of the cell at two temperatures, experiments were performed at 55 and 80 °C and a moderate current density (250 mA cm^{-2}). The lignin precipitation occurred sooner during electrolysis at 80 °C, causing the interruption of the experiment at an early stage.

The performance of the cell was improved with an increase in temperature. The current efficiency increased and the energy consumption was reduced at the higher temperature as shown in Fig. 10.

3.8. *Effect of the addition of NaCl*

Sodium chloride was added to WBL to study its effect on the possible formation of chlorine gas. Although the IrO_2-coated titanium anode is especially designed for the evolution of oxygen, chlorine gas might be formed at the anode along with the oxygen when sodium chloride is present in the WBL.

To simulate a WBL of a Canadian west coast mill, 4.3 g dm^{-3} of NaCl, as sodium, was added to the SWWBL from an eastern mill. After addition, the fraction of sodium in the WBL, as NaCl, was calculated to be 12.5%.

Analysis of gas produced at the anode during electrolysis of NaCl containing WBL revealed no detectable amounts of chlorine. Moreover, the concentration of chloride ions in the anolyte, over the duration of the experiment, was relatively stable with a slight increase due to the reduction of anolyte volume. The concentration of chloride ions in the catholyte was negligible (<1 ppm). A mass balance also showed no detectable losses of Cl^- ions and therefore little or no chlorine gas in the gas produced at the anode.

The results show that the presence of NaCl in the WBL does not have a significant effect upon the

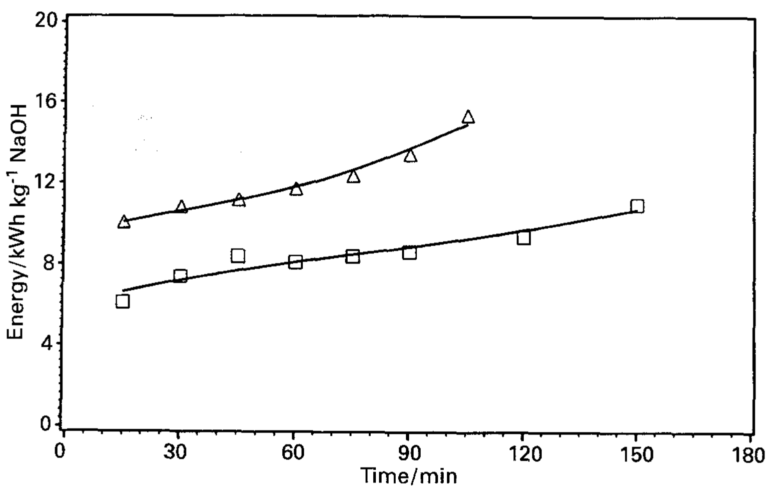

Fig. 9. Effect of current density on the specific energy consumption during electrolysis of softwood weak black liquor at 55° C. Current densities: (□) 250 and (△) 400 mA cm^{-2}.

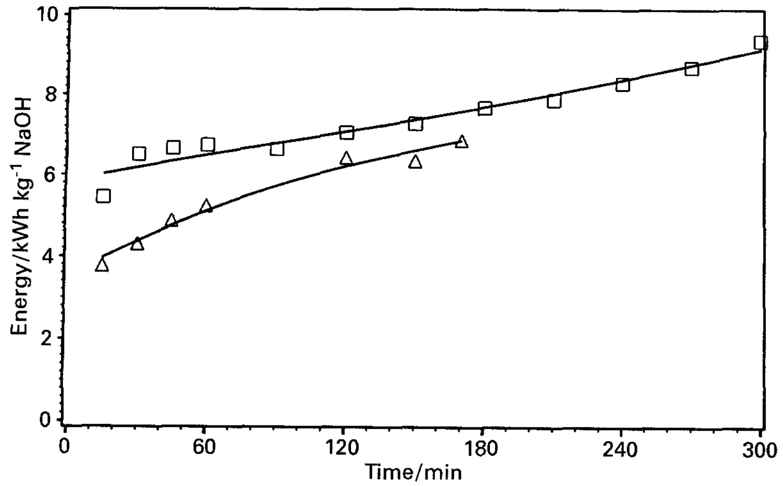

Fig. 10. Effect of temperature on the energy consumption during electrolysis of hardwood weak black liquor at 250 mA cm^{-2}. Temperatures: (□) 50 and (△) 80 °C.

performance of the cell. It did not decompose to chlorine gas. The sodium chloride remained in the depleted WBL. This could represent a new approach to bleed NaCl from the recovery system while recovering sodium from the other salts.

4. Discussion

During this study, we observed a rapid increase in cell voltage. The increase was due to (i) the reduction of liquor conductivity, and (ii) precipitated lignin accumulating on the anode. The lower conductivity inevitably contributes to increased voltage and consequently energy consumption. The cell performance may be improved by adding salt to the feed to increase conductivity. The precipitated lignin can efficiently be washed from the anode with a backwash system. The method was successfully tested and reported [3].

More than one hundred hours of continuous operation has been achieved. So far, membrane problems such as metals or lignin fouling have not been experienced. The voltage increase was due to anode fouling, which was solved by backwashing the anode compartment on a regular basis thus maintaining the cell performance. The average specific energy consumption was 7000 kWh tonne^{-1} of caustic produced [3].

5. Conclusion

The study of the effect of various operating parameters on the performance of the electrolytic cell showed that current density and temperature were critical to the operation. It was not possible to operate at the target maximum current density of 400 mA cm^{-2} and temperature of 90 °C. With the actual flow conditions used during the test, the operation of the cell was limited to a maximum current density of 300 mA cm^{-2} at a temperature below 80 °C. Optimization of these variables can significantly reduce the capital and operating cost. The addition of sodium sulfate by-product from the chlorine dioxide generator (and/or from the electrostatic precipitator) to the WBL could also be beneficial in terms of reducing the energy consumption and preventing the fouling from lignin and metal hydroxides. However, the residual acid content of the salt has to be minimized to avoid precipitation of lignin. The type of liquor (hardwood or softwood) had no significant effect on the energy efficiency. The Nafion® 324 membrane performed better compared to the R-4010. The Pt and IrO_2-coated anodes both showed a good performance. During these tests, at the same current density, the IrO_2-coated anode performed better, in terms of energy efficiency, than the Pt-coated anode. A durability test is required for evaluation of anode life. It was also shown that the presence of sodium chloride in the WBL did not produce chlorine gas within the pH range 5.4 to 13.

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