Recovery Of Sodium Hydroxide From Embilipitiya Black Liquor By Electrodialysis

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ABSTRACT

A new type of electrodialyzer unit to fractionate the Embilipitiya black liquor into sodium hydroxide, lignin and organic acids has been proposed and experimented in this work. Lignin deposition on, and the consequent damage to, the anode-side cellophane membrane that are generally associated with black liquor electrodialysis have greatly been minimized in the proposed unit. Also, bubbling of liquor in the anode compartment has completely been eliminated. Even with the use of an ordinary membrane, such as cellophane, the cathode compartments of the proposed unit yield sodium hydroxide solutions of about 0.1N strength which has good market value. Lignin which has a very high fuel value can be isolated from the end products of electrodialysis by simple filtration. Most importantly the polluting black liquor, upon electrodialysis followed by filtration, yields a colourless liquor with a pH of 6 and a TDS of 0.2 g/l which could be discharged on land for irrigation purposes as per the environmental standards of Sri Lanka.

INTRODUCTION

Black liquor is a liquid effluent produced in pulp mills that are similar to the one in Embilipitiya, Sri Lanka, where sodium hydroxide is used to pulp the raw material for paper. The raw materials in the Sri Lankan case are mainly rice straw and sometimes wood. Black liquor is rich in valuable chemicals such as sodium, derivatives of lignin, and low molecular weight polysaccharides (Ray et al. 1992). Black colour of the waste liquor is owing to the presence of lignin which is isolated from the raw material during the pulping process in which the raw material is cooked with sodium hydroxide, known also as caustic soda, at specified pressure and temperature. In this soda-pulping process, lignin in the raw material is converted into sodium lignate which exists in black liquor as sodium ions and lignate ions. The concentration of the inorganic ions in black liquor, which are mainly sodium ions, is quantified by measuring the electrolytic conductivity of black liquor using the conductivity meter Hach 44600.

The electrolytic conductivity of black liquor samples from the Embilipitiya pulp mill ranges from 19 to 30 mS/cm which indicates the presence of considerable amount of dissolved solids in black liquor. The total dissolved solids (TDS) content of black liquor is about 64 g/l (according to a CISIR report dated 24th June 1994). Black liquor has a pH of about 10 when measured by the pH meter TOA HM-5ES. For an industrial effluent to be discharged on land for irrigation purposes, its TDS should be less than 2.1 g/l and its pH should be between 5.5-9.0 according to the National Environmental Act (1990). The Act also states that the biochemical oxygen demand (BOD) should be less than 30 mg/l and the chemical oxygen demand (COD) should be less than 250 mg/l if the effluent is to be discharged either onto land or into water bodies. For the Embilipitiya black liquor, BOD is

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about 3000 mg/l and COD is about 60,000 mg/l (according to the CISIR report dated 24th June 1994) which are about a 100 times more than the allowable limits.

An almost continuous release of black liquor of the above mentioned characteristics into a water body, as it is in the case of the Sri Lankan black liquor, has the potential to kill all life-forms in the water body and eventually turn it into a dead one (Shanthini & Arulanantham 1995; Wanigasundera 1995). Thus, black liquor is too hazardous an effluent to be let into the environment without treatment. This paper proposes a new type of an electrodialyzer unit in order to treat the Embilipitiya black liquor before it is discharged into the environment.

Recovery of chemicals from black liquor by fractionating electrolytes from non electrolytes of the black liquor by the process of electrodialysis has been reported to have tremendous industrial potential almost three decades ago (Basu 1968). Electrodialysis, in contrast to desilication followed by an extensive chemical recovery process, appears to be a suitable one step method to recover chemicals from black liquor. Spent sulfite liquor, for instance, has been successfully separated into pulping chemicals and lignosulphonic acids in pilot plant electrodialyzer units (Basu 1968; Mishra & Bhattacharya 1984). Investigations on the influence of operating parameters on the performance of a three-compartment electrodialyzer unit have been carried out with soda-pulped straw-based black liquor by Joshi & Basu (1973) and Mishra & Bhattacharya (1984). Both these works used cellophane membranes as well as cation-exchange membranes to recover sodium hydroxide from black liquor. No further work on electrodialysis has been reported in the literature to the best of our knowledge. We have been experimenting into electrodialysis of the Embilipitiya black liquor since 1992 and the results obtained on the electrodialysis of the Embilipitiya black liquor using a modified electrodialyzer unit proposed by us are briefly presented in this paper.

EXPERIMENTAL SETUP

A three compartment electrodialyzer unit similar to the one described by Mishra and Bhattacharya (1984) was constructed with perspex and is shown in figure 1. This unit has a rectangular base of 38.9 cm x 7.2 cm and a height of 9.0 cm. The compartments were separated from each other by cellophane sheets. We used cellophane since it is the only membrane that is readily available in the Sri Lankan market and it is inexpensive. Black liquor used in the experiments was obtained from the Embilipitiya pulp mill and 900 ml of it was filled in the middle compartment. The outer compartments were each filled with 450 ml of distilled water. Two stainless steel electrodes, one per compartment, were placed in the two outer compartments. The electrodes were connected to a d.c. power supply unit such that one electrode acted as anode and the other as cathode. During the experiment, the current was maintained constant by manually varying the voltage.

During electrodialysis cations in black liquor, that are mainly sodium ions, moved through the membrane to the cathode compartment and sodium hydroxide was formed there. All the anions in black liquor moved towards the anode and of which the anions of organic acids passed through the membrane to the anode compartment where organic acids were formed.

The anions of sodium lignate were held by the membrane because of the colloidal nature of lignate macromolecules which could not penetrate through the pores of the cellophane membranes. Consequently, a lignin layer started to build up on the anode- side membrane.

The lignin layer formed on the anode-side cellophane membrane increased the cell resistance which in turn resulted in considerable increase in voltage required to maintain the constant current. Lignin deposition also caused damage to the anode-side membrane. In addition, bubbling of the liquor in the anode compartment due to rise in temperature and pitting of anode electrode were observed. These were problems that were encountered also by Mishra & Bhattacharya (1984). They reported that use of ion-exchange membranes in place of cellophane membranes improved the performance of the unit. We nevertheless decided to retain the inexpensive and locally available cellophane as the membrane in our experiments but to modify the electrodialyzer unit to improve its performance.

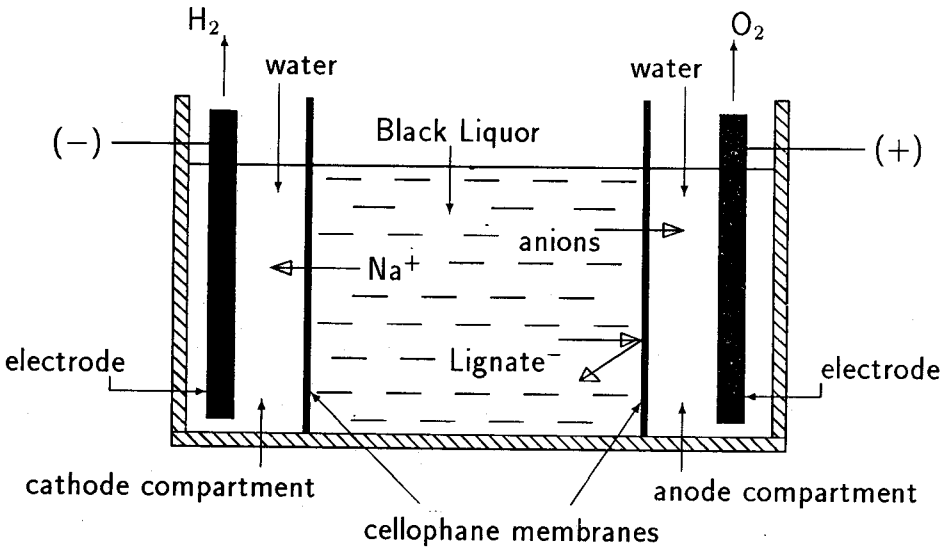

Fig. 1- A three compartment electrodialyzer unit similar to the one used by Mishra and Bhattacharya (1984).

The modified electrodialyzer unit is shown in figure 2. The stainless steel electrodes placed in the two outer compartments containing 450 ml of distilled water each were turned into cathodes. An open box of 11.6 cm x 5.5 cm rectangular cross-section was constructed with a perspex bottom and four cellophane side walls of 5.0 cm height reinforced by a perspex grid. This box was filled with 400 ml of distilled water and a third stainless electrode was placed inside it. This third electrode was the anode. The whole set up was placed in the middle of the compartment holding 600 ml of black liquor. Placed in the black liquor was another open box of 17.3 cm x 5.9 cm rectangular cross-section and 9.0 cm height made entirely of plastic mesh which surrounded the small anode compartment on all four sides and at the bottom.

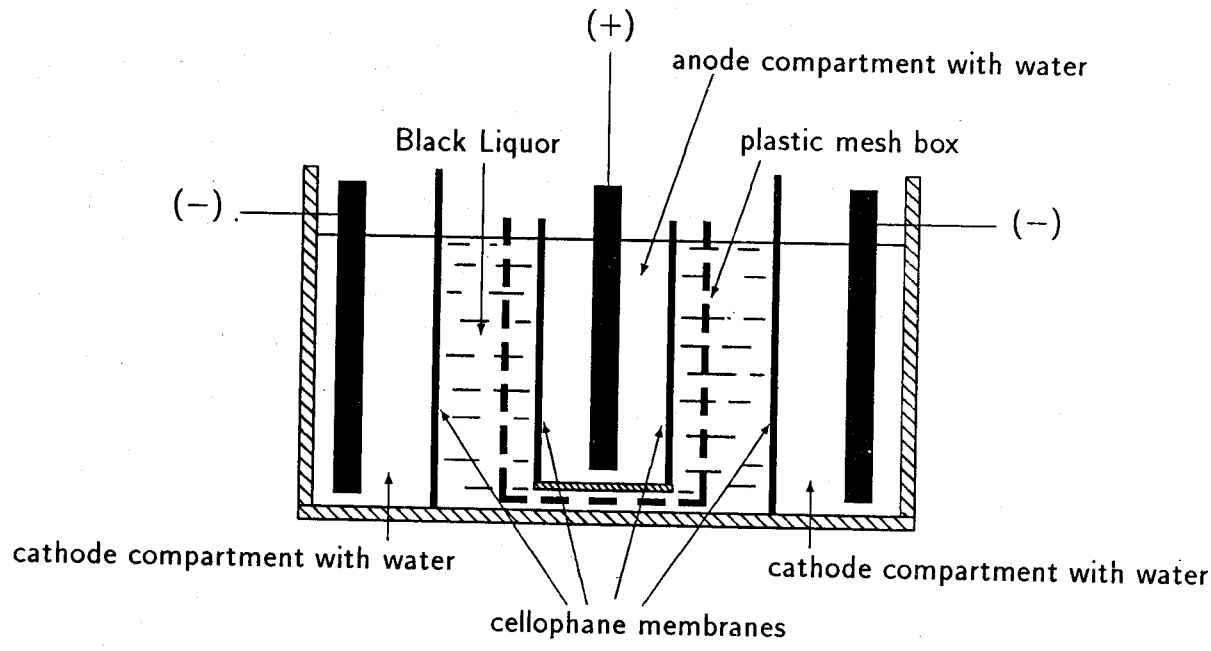

Fig. 2 - Modified electrodialyzer unit proposed in this study.

During electrodialysis, sodium ions in black liquor moved towards the cathode electrodes and sodium hydroxide solutions were formed in both the cathode compartments. Anions of organic acids moved towards the anode electrode and organic acids were formed in the anode compartment. Lignin did not deposit on the anode-side membrane, but was collected on the bottom of the mesh box. Because of the deposit-free anode-side membrane, the process of electrodialysis was continued until the black liquor in the middle compartment lost almost all its ions to cathode and anode compartments. Motion of the ions in the unit was monitored by periodically measuring the electrolytic conductivity of the solutions in the anode, cathode and black liquor compartments.

Determination of electrolytic conductivity is performed by measuring the resistance occurring in an area of the test solution defined by the design of the test probe of the conductivity meter Hach 44600. The conductivity probe is not ion-selective but measures the sum total of the concentrations of the inorganic components of the solution. Solution temperature is measured by a thermistor network in the conductivity probe. Conductivity measurements are compensated by a coefficient of 2% per ^{0}C to provide a reading equivalent to what it would be at the reference temperature 25^{0}C.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 shows the experimental results obtained up to 3 hours of electrodialysis. Circles (o) represent the temporal development of the conductivity of the NaOH solution in the cathode compartment of Mishra & Bhattacharya type unit shown in figure 1. Pluses (+) represent the temporal development of the average conductivity of the NaOH solutions in the two cathode compartments of the modified unit shown in figure 2. Both results were obtained maintaining 500 mA current throughout the electrodialysis with stainless steel electrodes of 11.4 mm diameter.

It can be seen in figure 3 that the total inorganic ion concentration in the cathode compartment is always higher in the modified unit than in the unit duplicating the one used by Mishra & Bhattacharya for the same current of 500 mA. This observation can be attributed to the double-cathode setup of the modified unit as opposed to the single-cathode setup

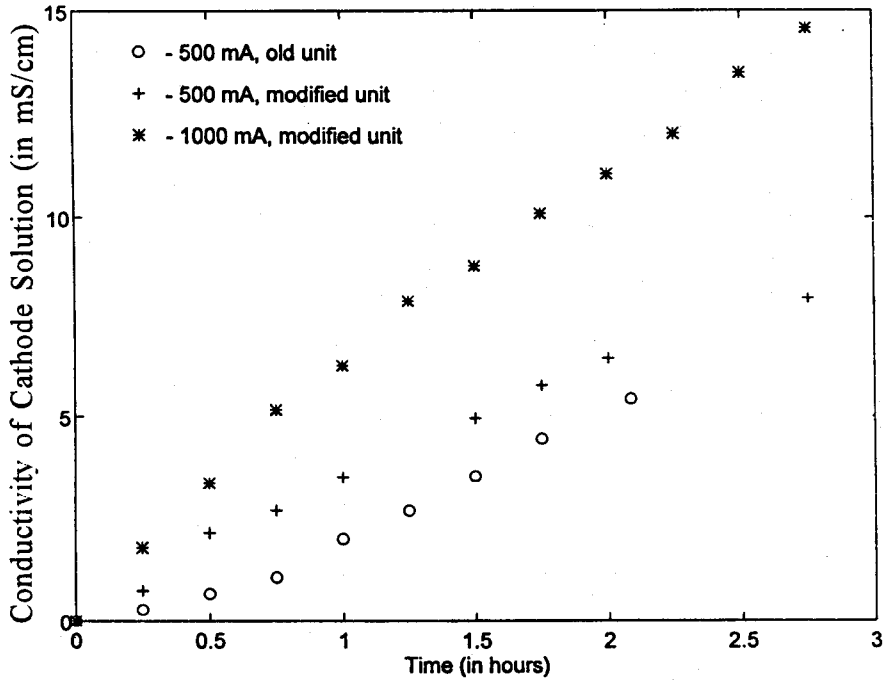

Fig. 3 - Temporal development of cathode solution conductivity during electrodialysis of Embilipitiya fresh black liquor in two different types of units.

of the old type unit. The modified unit can practically be described as two electrodialyzer units in series with one anode compartment in common, Whereas, the Mishra & Bhattacharya type unit is just one single electrodialyzer unit.

Electrodialysis was possible only for about 2 hours in the old type unit because of the increasing cell resistance owing to the lignin layer forming on the anode- side cellophane membrane. Whilst, electrodialysis in the modified unit was carried out for three hours and could have been carried out for more than three hours, if required. it was because most of the lignate ions moving towards the anode electrode of the modified unit did not form a lignin layer on the cellophane walls of the anode compartment but were collected on the bottom of the plastic mesh box.

Asterisks (*) of figure 3 represent the results obtained with the modified unit at 1000 mA current using stainless steel electrodes of 31.4 mm diameter. It is of considerable importance to note that the modified unit allowed currents as high as one Ampere owing to lignin-free cellophane as anode walls whereas such high current was not at all possible in the old setup with cellophane membranes. Higher current indeed resulted in higher ion concentration in the cathode compartment which meant better ion-removal from black liquor.

Presence of plastic mesh walls near the anode compartment walls is a factor that solely contributed towards the advantageous phenomenon of lignin-free cellophane as anode walls which in turn considerably improved the performance of the electrodialyzer unit. The mesh seemed to offer physical resistance to the colloidal macromolecular lignate ions moving towards the anode walls and consequently provided a site for the lignate ions to settle on. The lignate ions turned to lignin solids by accepting the hydrogen ions that seeped out of the anode chamber.

Figure 4 shows results that were obtained with stainless steel sheets of 43.5 mm x 2 mm cross-section as electrodes with mesh outer box. A current value of 1000 mA was maintained initially. Because of the decreasing electrolytic conductivity of black liquor with time, it became increasingly difficult to maintain 1000 mA current. After about 10 hours of electrodialysis, the unit was to be run at the

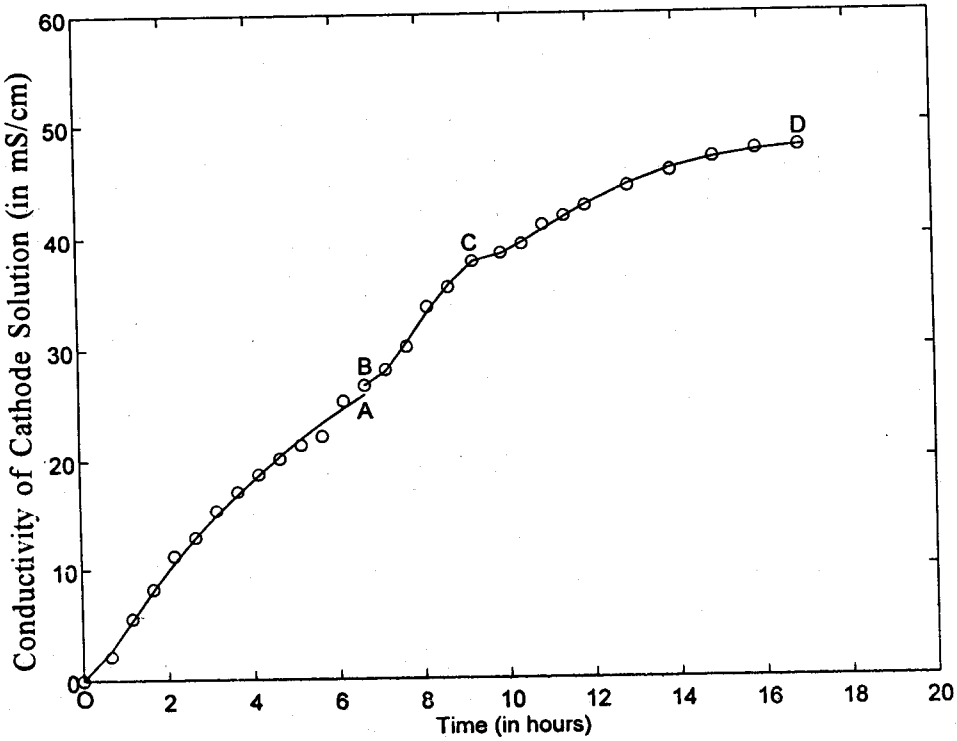

Fig. 4 - Cumulative conductivity of cathode solution during electrodialysis of fresh black liquor in the modified unit with mesh outer box.

maximum voltage of 140 V which meant the current passed was only about 100 mA.

The circles of Figure 4 fit in three distinctly different curves labeled OA, BC, and CD. These three curves represent three different runs that were carried out one after the other with one single batch of black liquor. Each of the three runs was however started with fresh distilled water in anode and cathode chambers. The equations describing the curves were developed using mathematical models to describe the electrodialyzer performance and the details of which shall be presented in a future paper.

Curve OA of figure 4 spanning from 0 to 6.67 hours represents the first run during which the conductivity of black liquor decreased from 19 mS/cm to 13 mS/cm and the average conductivity of cathode solutions increased from 0 to about 27 mS/cm. At the beginnning of the run, the flow of sodium ions from black liquor chamber to cathode chambers was caused by the favourable concentration gradient as well as the electric potential gradient. Towards the end of the run, however, the concentration gradient became adverse and hence the flow of sodium ions from black liquor chamber to cathode chambers slowed down as shown by the decreasing gradient of curve OA.

At the end of the first run, the cathode solutions of 27 mS/cm conductivity were removed and the cathode chambers were once again filled with 450 ml of fresh distilled water each. As can be seen from the gradient of the second curve of circles BC, the flow of ions from black liquor chamber to cathode chambers immediately improved owing to the favourable concentration gradient experienced by the sodium ions in addition to the electric potential. The curve BC spanning from 6.67 to 9.25 hours represents the second run during which the conductivity of black liquor decreased from 13 mS. cm to 7 mS/cm and the average conductivity of cathode solutions increased from 0 to about 11 mS/cm. The curve CD spanning from 9.25 to 17 hours represents the third run during which the conductivity of black liquor decreased from 7 mS/ cm to 0.4 mS/cm and the average conductivity of cathode solutions increased from 0 to about 10 mS/cm.

The respective average conductivity of the cathode solutions obtained at the end of each of the three runs with the plastic mesh were about 27, 11 and 10 ms/cm. These values are equivalent to that of 0.14N, 0.06N and 0.05N NaOH solutions, respectively, according to the linear relationship,

$$\text{Normality of NaOH solution} = \frac{(\text{conductivity in mS/cm} - 0.63)}{183.5}$$

which was obtained by calibrating the conductivity readings against NaOH solutions of known concentrations. Figure 4 also shows that at the end of 17-hour electrodialysis, the cumulative value of the average conductivity of the cathode solutions went up to about 45 mS/cm. To obtain a NaOH solution of 0.24N at the end of 17 hours of electrodialysis, however, all the resulting cathode solutions must be added together and the volume be reduced to the original 900 ml by evaporation. Market value of NaOH solutions of 0.1N (that is, 4 g/l) strength and above is indeed very admirable. Purity of the NaOH sulutions of the cathode compartments has not yet been analysed owing to lack of adequate funds.

At the end of the 17-hour electrodialysis, the cumulative conductivity of the cathode solutions changes only marginally with time. This feature of figure 4 signals the end of electrodialysis for the batch of black liquor processed. Conductivity of black liquor at this state was about 0.4 mS/cm. At condctivity as low as 0.4 mS/cm, almost all the sodium ions in black liquor had been lost to the cathode compartments. And, the original black liquor in the middle compartment was observed to have become a light brown liquor with suspended and settled solids. When these dark coloured solids, mostly lignin, were removed from the liquor by filtration, an almost colourless liquor was obtained as the filtrate. Thereby, the black colour of the black liquor has been successfully removed by the process of electrodialysis carried out in the unit proposed in this study.

The original black liquor had a TDS of about 64 g/l and the TDS of the colourless filtered liquor was only 0.2 g/l which is much less than the stipulated limit 2.1 g/l of TDS for an industrial

effluent to be discharged on land for irrigation purpose as per the environmental standards for Sri Lanka (National Environmental Act 1990). The pH of the original black liquor was 10 and the pH of the filtrate was 6 which falls within the acceptable pH-range of 5.5-9.0 for a liquid effluent to be discharged onto the environment as per the environmental standards of Sri Lanka (National Environmental Act 1990).

The major drawback of the electrodialyzer unit was that the liquor in the anode compartment, comprising mainly of organic acids, offered high resistance to the flow of electricity. For example, at the end of the 17-hour electrodialysis, electrolytic conductivity in the anode chamber went only up to 2 mS/cm indicating the comparatively high resistance prevailing in the anode chamber. Such high resistance in the anode chamber led to comparatively large energy dissipation in the anode chamber which in turn increased the temperature of the anode liquor as high as 80°C. Such high temperatures resulted in bubbling and evaporation losses of anode liquor as well as leaks at the joints of the perspex unit. All these adverse features were avoided when the temperature of the anode liquor was maintained below 65°C. A series of runs were carried out with anode liquor at 60°C by circulating the anode liquor through a water-cooler by use of a pump.

Figure 5 shows the results obtained in the modified unit with and without cooling. Both the results shown were obtained with stainless steel sheets as electrodes and with 1000 mA initial current. After about 10 hours of electrodialysis, the unit was to be operated at the maximum voltage of 140 V which permitted only about 100 mA current in both cases of with and without cooling. It can be observed in figure 5 that the overall recovery of sodium ions with cooling is better than the recovery obtained without cooling. The initial rate of recovery of sodium ions, however, exhibits an entirely opposite feature. Preliminary investigations indicate that maintaining the anode liquor at about 60°C temperature yields the best recovery of sodium ions from black liquor. Maintaining the temperature of the anode liquor temperature at 60°C or below, most importantly, saved the unit from developing leaks. Besides, bubbling of anode liquor and evaporation losses of anode liquor are all completely eliminated.

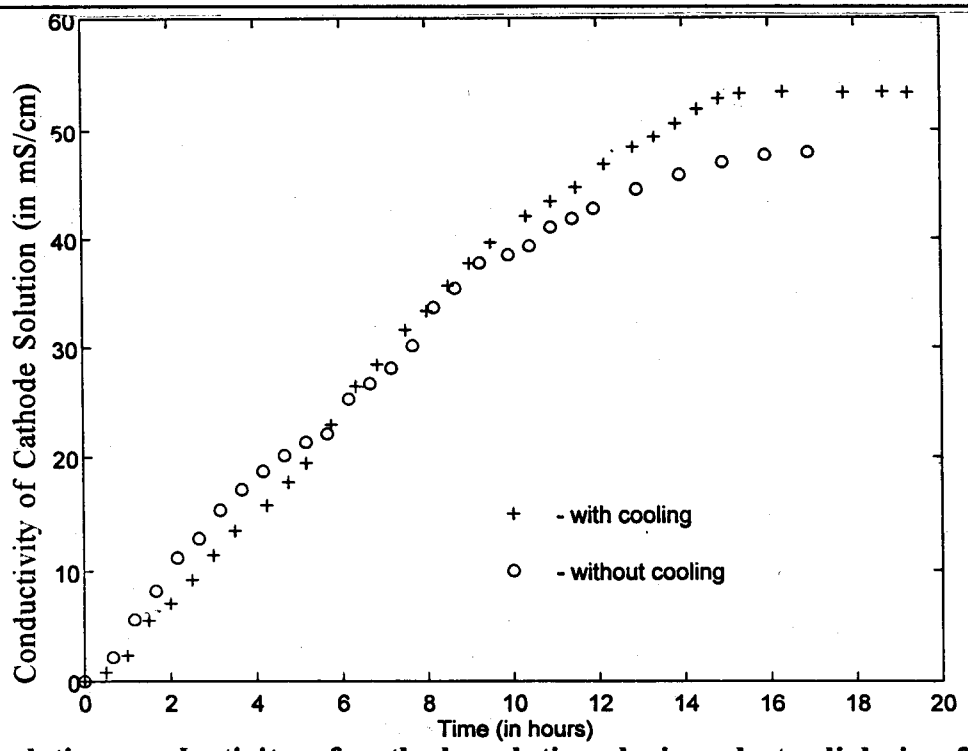

Fig. 5 - Cumulative conductivity of cathode solution during electrodialysis of fresh black liquor in the modified unit with and without cooling of anode liquor.

CONCLUDING REMARKS

Black liquor of the Embilipitiya pulp mill is fractionated by the process of electrodialysis in the modified unit into sodium hydroxide, lignin and organic acids. Damage to the anode-side cellophane membrane due to lignin deposition and bubbling of liquor in the anode compartment, both are problems generally reported with electrodialysis of black liquor, have been eliminated in the unit proposed by us in this paper.

The modified unit even with the cellophane membrane gives valuable caustic soda solutions of about 0.1N strength of more. Black liquor after the process of electrodialysis and filtration is changed into a colourless liquor of 6 pH and 0.2 g/l TDS. This liquor is qualified to be discharged on land for irrigation purpose as per the environmental standards for Sri Lanka as far as the pH and TDS are concerned. The environmentally hazardous black liquor can therefore be transformed into an environmentally friendly liquor with valuable byproducts.

ACKNOWLEDGEMENTS

We greatly appreciate Mr. W.G. Gunaratne of the Department of Chemical Engineering for his invaluable assistance in constructing the electrodialyzer units and Dr. K.S. Walgama of the Department of Engineering Mathematics for his indispensable contribution in turning the black liquor into a colourless liquor. Most importantly, we are extremely grateful to the one and only source of financial and moral support to this research work which in indeed the University of Peradeniya, itself.

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