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Electrochemical Treatment of Black Liquor from Straw Pulping

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ABSTRACT

The conventional black liquor regeneration process is not always suitable for pulping plants of nonwood fibers due to the unfavorable ratio of organic to inorganic solids. This paper presents an alternative treatment based on an electrolysis process of the soda black liquor from straw pulping. This alternative method minimizes the environmental impact by recovering the caustic at the same time that the liquor is acidified, which favors the later separation of the lignin.

INTRODUCTION

The alkaline pulping process involves cooking the cellulosic raw material in a solution of sodium hydroxide for soda pulping, or in a solution of sodium hydroxide and sodium sulfide for kraft pulping to obtain the fiber suspension. In the conventional processes the spent black liquor is washed from the pulp and treated to recover the cooking chemicals and regenerate the cooking liquor. The regeneration of chemicals, the realization of energy from incineration of organic residuals, the minimization of air and water pollution, together with the possibility of by-products determine the viability of a plant. However, this conventional process cannot be applied in small capacity plants because of its prohibitive capital investment and uneconomical operation or in plants using nonwood fibrous materials due to the unfavorable ratio of organic to inorganic solids. Therefore, it is necessary to develop alternative treatments of these black liquors in order to minimize the environmental impact of the mills.

Alkaline black liquors are a mixture of electrolytes (NaOH, Na_2CO_3, Na_2S, Na_2SO_4, organic sodium salts, etc.) and nonelectrolytes (hemicellulose and carbohydrate degradation products). Therefore, an electrochemical treatment is a suitable proposition to separate the components of the black liquor on the basis of their physical, chemical, and electrical properties and to recover the chemicals and the by-products, making the process economically attractive.

Various electrodialysis processes have been suggested for the separation of the components of spent liquors from sulfite and sulfate pulping (1). The application of electrodialysis for the regeneration of alkaline black liquors from a small capacity rice straw pulping plant has also been proposed (2–4). Another application of electrochemical treatment in the pulp industry is the electrolytic processing of a fraction of weak black liquor before it enters the recovery furnace in order to increase the recovery capacity and production of a conventional kraft mill (5–8). Based on this background, an alternative electrolytic process for the treatment of black liquor from the soda pulping process of wheat straw is proposed in this paper.

EXPERIMENTAL

The electrolyte processing of straw black liquor was carried out at the laboratory scale in the bath-recycle mode of operation using a 2-compartment cell and a 3-compartment cell with two platinum electrodes. Figure 1 shows a schematic drawing of the electrolysis concept.

The 2-compartment cell employed a cation-selective membrane (Nafion-450 of Dupont) between the two electrodes. The black liquor was fed into the anode compartment and a dilute sodium hydroxide solution (1 M) was fed into the cathode compartment (Fig. 2). When a voltage was applied between the two electrodes, the sodium ions migrated under the influence of the resulting electric field toward the negative electrode where they picked up hydroxide ions from the reduction of water at the cathode to form sodium hydroxide. In the anode compartment the sodium ions were replaced by hydrogen ions, which were produced from the oxidation of the water at the anode. The original black liquor at the anode tank was therefore acidified. If this liquor was acidified enough (pH 3), most of the lignin components precipitated out.

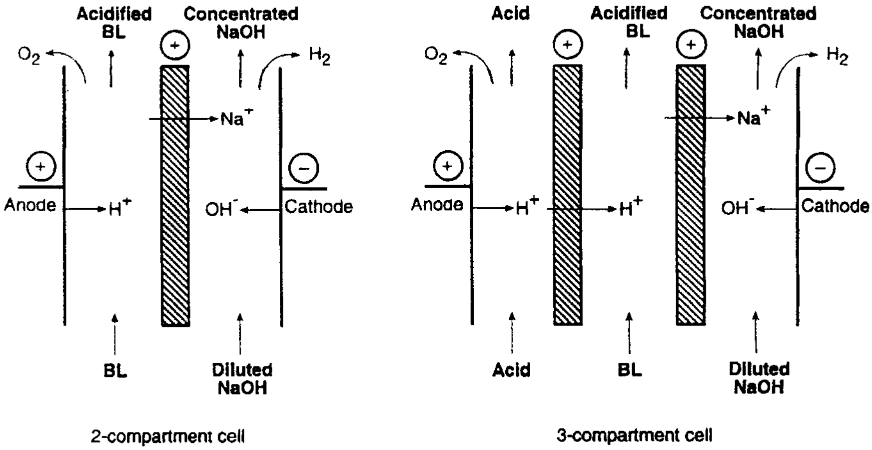

FIG. 1 Electrolysis concept for the 2- and 3-compartment cells.

Two cation-selective membranes were placed between the electrodes in the 3-compartment cell. The black liquor was fed into the middle compartment, the dilute sodium hydroxide solution into the cathode compartment, and a diluted sulfuric acid solution into the anode compartment (0.9 M) as shown in Fig. 3. The middle compartment was introduced to avoid fouling of the anode due to the deposition of the lignin at low pH.

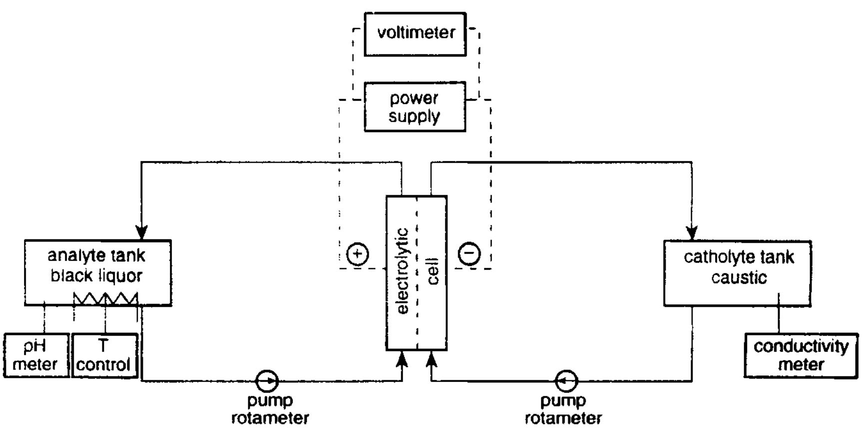

FIG. 2 Diagram of the 2-compartment cell process.

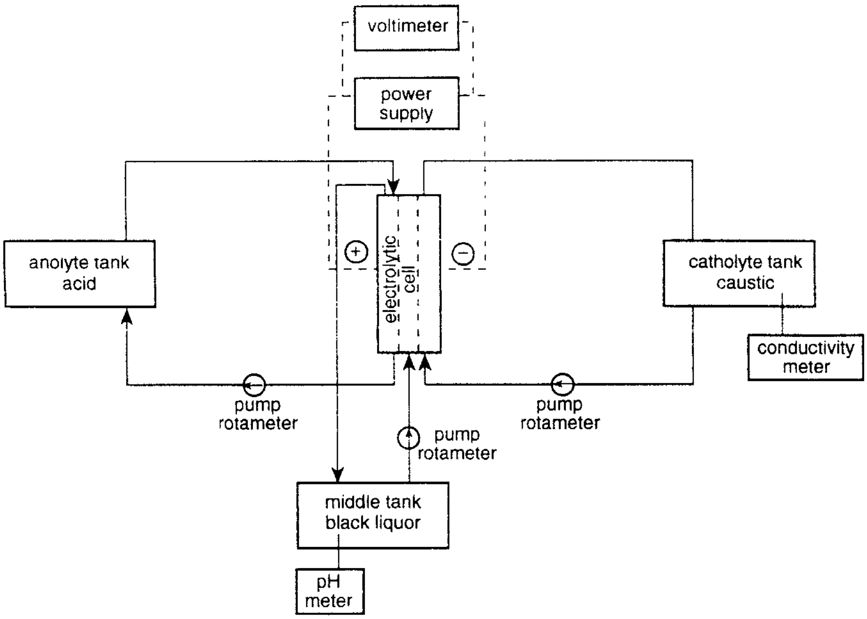

FIG. 3 Diagram of the 3-compartment cell process.

RESULTS AND DISCUSSION

The main characteristics of the black liquor from straw digestion are given in Table 1.

The effects of various parameters on the performance of the electrolytic cell were studied in relation to the current efficiency and sodium recovery. After each experiment the membranes were examined in order to detect the presence of any deposit which could cause membrane fouling.

The results show that a rapid increase in cell voltage is obtained due to fouling of the anode in the 2-compartment cell. In the 3-compartment arrangement the cell voltage increased due to fouling of the membrane facing to the anode compartment. The current efficiency was higher with the 2-compartment cell (95%) than with the 3-compartment cell (83%). After the first set of experiments it was decided to use the 2-compartment cell, adding a current reverse system to clean the anolyte compartment and minimize both the fouling of the anode and the energy requirements. The main variables considered for the different electrolysis arrangements are summarized in Table 2.

TABLE 1
Analysis of Black Liquor

Total solids (g/L)	100–120
Organic solids (g/L)	75–90
Suspended solids (g/L)	5–10
Conductivity (mS/cm)	19.7
pH	8.9
Viscosity (cP)	1.5
Density (g/L)	1.0–1.1
Total alkalinity (g $CaCO_3$/L)	14–16
SiO_2 (g/L)	2–4
Sulfates (g/L)	2–3
Chlorides (g/L)	2.5–3.0
Sodium (g/L)	12
Calcium (g/L)	1.0–1.5
Magnesium (g/L)	0.1

To reduce the energy consumption the experiments have to be stopped before an excessive electrical resistance is caused by lignin precipitation (pH < 4.5). Further acidification of the black liquor could then be carried out by traditional acid precipitation in order to obtain the lignin and a clarified stream. Only a small amount of acid is required for this. The voltage drop with the standard solution shows that no fouling was present when the cell was operated with current reversal. However, analysis of

TABLE 2
Operational Conditions and Main Results from Electrolysis of Black Liquor

Operational conditions	2-compartment cell	3-compartment cell	2-compartment cell
Current density (mA/cm^2)	50	50	50
BL feed rate (mL/min)	300	300	500
Cell voltage (V)	4.5	7.4	4.5
Reverse current (30 s/5 min)	No	No	Yes
Temperature (°C)	20	20	20–50
Residence time (min)	166	180	140–160
Current efficiency (%)	57	83	100
Final BL conductivity (mS/cm)	19	10	13.2
Final pH	4.0	4.0	3.9–3.7
Final cell voltage	10.5	8.3	8.7
Cell voltage after cleaning	4.5	7.0	4.7
NaOH recovered (%)	44	73	64–75

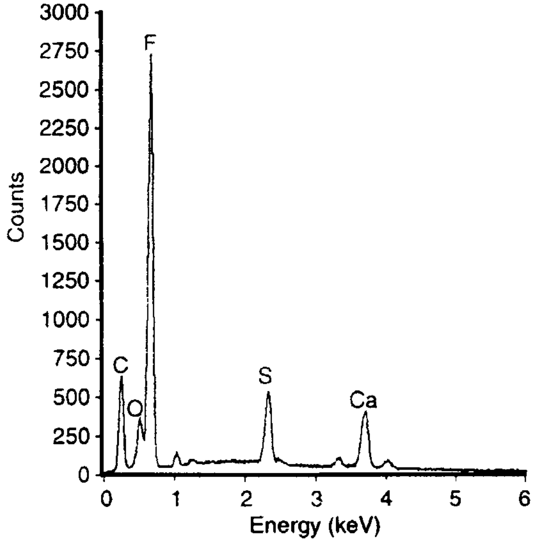

FIG. 4 Overall analysis of the membrane.

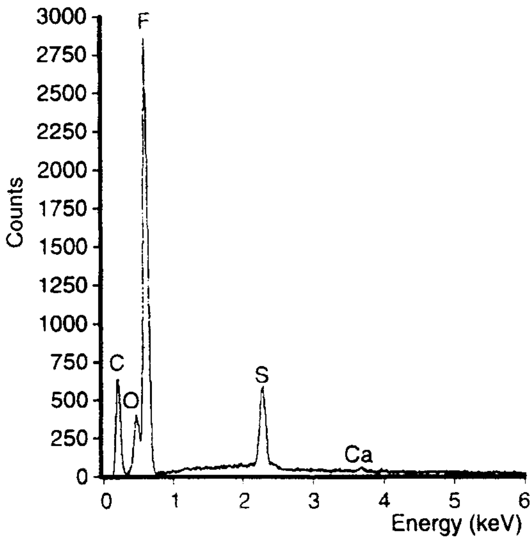

FIG. 5 Overall analysis of the membrane after acid washing.

the membranes after the experiments showed the presence of a white deposit on the membrane. In order to identify the deposit, SEM and XRMA analyses were performed on both sides of the membrane and on the cross section. The overall analysis of the membrane is presented in Fig. 4.

The results show a high concentration of Ca on the two surfaces of the membrane and a very low concentration of Na, Mg, and Si. It is important to notice that most of the deposits are found on the membrane surface. Thus, a new set of experiments was set up, incorporating an acid wash of the membrane to dissolve the deposits and reverse the possible fouling of the membrane (9). The overall analysis of the membrane cross-section after the acid wash process is presented in Fig. 5. It is observed that the calcium deposits in the membrane have been removed during the washing stage with acid. Thus, the fouling of the membrane can be reversed.

CONCLUSIONS

The results show the technical feasibility of the electrolytic process as an attractive alternative for recovering the caustic from the straw black liquor and acidifying the black liquor when the conventional process cannot be applied. Further acidification of the black liquor should be carried out in a separate vessel outside the electrolyte cell.

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REFERENCES

1. M. S. Mintz, R. E. Lacey, and E. W. Lang, "Separation of Pulping Liquor Components with Electrodialysis Processes," *Tappi*, *50*(3), 137–146 (1967).
2. K. Radhamohan and S. Basu, "Electrodialysis in the Regeneration of Paper Mill Spent Liquor," *Desalination*, *33*, 185–200 (1980).
3. A. K. Mishra and P. K. Bhattacharya, "Alkaline Black Liquor Treatment by Batch Electrodialysis," *Can. J. Chem. Eng.*, *62*, 723–727 (October 1984).
4. A. K. Mishra and P. K. Bhattacharya, "Alkaline Black Liquor Treatment by Continuous Electrodialysis," *J. Membr. Sci.*, *33*, 83–95 (1987).
5. J. N. Cloutier, M. K. Azarniouch, and D. Callender, "Electrolysis of Weak Black Liquor. Part I: Laboratory Study," *J. Pulp Pap. Sci.*, *19*(6), J244–J248 (1993).
6. J. N. Cloutier, M. K. Azarniouch, and D. Callender, "Electrolysis of Weak Black Liquor. Part II: Effect of Process Parameters on the Energy Efficiency of the Electrolytic Cell," *J. Appl. Electrochem.*, *25*, 472–478 (1995).

7. J. N. Cloutier, M. K. Azarniouch, and D. Callender, "Electrolysis of Weak Black Liquor. Part III: Continuous Operation Test and System Design Considerations," *Pulp Pap. Can.*, *95*(5), 68–72 (1994).
8. M. Paleologou, J. N. Cloutier, P. Ramamurthy, R. M. Berry, M. K. Azarniouch, and J. Dorica, "Membrane Technologies for Pulp and Paper Applications," *Ibid.*, *95*(10), 36–40 (1994).
9. E. C. Milton and H. P. Gregor, "Membrane Processes for Treatment of and Recovery of Components from Kraft Black Liquors," US Patent 4,775,480 (1988).

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