FOREST PRODUCTS AGENDA 2020 PROGRAM
ENVIRONMENTAL PERFORMANCE

FINAL REPORT

RECYCLING OF BLEACH PLANT FILTRATES BY ELECTRODIALYSIS
REMOVAL OF INORGANIC NON-PROCESS ELEMENTS

by

Shih-Perng Tsai\textsuperscript{1}, Peter Pfommm\textsuperscript{2}, Michael P. Henry\textsuperscript{1},
Anthony T. Fracaro\textsuperscript{1}, Carl P. Swanstrom\textsuperscript{1}, and Paula Moon\textsuperscript{1}

\textsuperscript{1} Argonne National Laboratory
\textsuperscript{2} Institute of Paper Science and Technology

October 2000
TABLE OF CONTENTS

Executive Summary ............................................................................................................. 1

1. Introduction .................................................................................................................... 3
   1.1 Water Reuse of Bleached Kraft Pulp Mills ........................................................... 3
   1.2 Electrodialysis Technology ................................................................................... 3
   1.3 Goal and Objectives .............................................................................................. 5

2. Characterization of Bleach Plant Filtrates .................................................................... 7

3. Laboratory Desalting Electrodialysis Experiments ....................................................... 8
   3.1 Short-term Feasibility Experiments ...................................................................... 8
   3.2 Longer-term Experiments ..................................................................................... 9

4. Additional Laboratory Experiments ............................................................................ 11
   4.1 Membrane Fouling Characterization .................................................................. 11
   4.2 Chlorine Dioxide Tests ....................................................................................... 11
   4.3 Evaluations of Spacer Design ............................................................................. 12

5. Field Demonstration .................................................................................................... 16
   5.1 Laboratory Qualifying Experiment ...................................................................... 16
   5.2 Pilot Electrodialysis System ................................................................................ 18
   5.3 Field Tests ........................................................................................................... 19

6. Process Economics ....................................................................................................... 23

7. Conclusions and Recommendations ........................................................................... 24

8. Acknowledgments ........................................................................................................ 25

9. References .................................................................................................................... 26
EXECUTIVE SUMMARY

Water use in the pulp and paper industry is very significant, and the U.S. pulp and paper industries as well as other processing industries are actively pursuing water conservation and pollution prevention by in-process recycling of water. Bleach plant effluent is a large portion of the water discharged from a typical bleached kraft pulp mill. The recycling of bleach plant effluents to the kraft recovery cycle is widely regarded as an approach to low effluent bleached kraft pulp production. The focus of this work has been on developing an electrodialysis process for recycling the acidic bleach plant effluent of bleached Kraft pulp mills. Electrodialysis is uniquely suited as a selective kidney to remove non-process elements (NPEs) from bleach plant effluent before they reach the chemical recovery cycle. Using electrodialysis for selective NPE removal can prevent the problems caused by accumulation of inorganic NPEs in the pulping cycle and recovery boiler.

In this work, acidic bleach plant filtrates from three mills using different bleaching sequences based on chlorine dioxide were characterized. The analyses showed no fundamental differences in the inorganic NPE composition or other characteristics among these filtrates. The majority of total dissolved solids in the effluents were found to be inorganic NPEs. Chloride and nitrate were present at significant levels in all effluent samples. Sodium was the predominant metal ion, while calcium and magnesium were also present at considerable levels.

The feasibility of using electrodialysis to selectively remove inorganic NPEs from the acidic bleach effluent was successfully demonstrated in laboratory experiments with effluents from all these three mills. Although there were some variations in these effluents, chloride and potentially harmful cations, such as potassium, calcium, and magnesium, were removed efficiently from the bleach effluents into a small-volume, concentrated purge stream. This effective removal of inorganic NPEs can enable the mills to recycle bleach effluents to reduce water consumption. The electrodialysis process also effectively retained up to 98% of the organics and can reduce the organic discharge in the mill wastewater. By using suitable commercially available electrodialysis membranes, there were no indications of rapid or irreversible membrane fouling or scale formation, even in extended laboratory scale operations up to 100 hours. Results of laboratory experiments also showed that commercially available membranes properly selected for this process would have good stability to withstand the potentially oxidative conditions of the filtrate.

A pilot-scale field demonstration was also conducted at a southern mill, using the D0 filtrate from the bleach plant. During the field demonstration we found serious membrane
stack clogging problems, which apparently were caused by fine fibers that escaped through the 5-micron pre-filters, although such a pre-filtration method had been satisfactory in the laboratory tests. Additional R&D is recommended to address this pre-filtration or clogging issue with systems approaches integrating pre-filtration, other separation methods, and stack design. After the pre-filtration/clogging issue is overcome, laboratory development and pilot demonstration are recommended to optimize the process parameters and to evaluate the long-term process parameters. The key technical issues here include membrane lives, control and mitigation of fouling and scaling, and cleaning-in-place protocols.

From the data collected in this work, a preliminary process design and economic evaluations were performed for a model mill with 1,000-ton/day pulp production that uses a bleaching sequence based on chlorine dioxide. Assuming 3 m$^3$ acidic effluents to be treated per ton of pulp produced, the electrodialysis process would require a membrane area of about 361 m$^2$ for this model mill. The energy consumption of the electrodialytic stack for separation is estimated to be about $160/day, and the estimated capital cost of the electrodialysis system is $750,000 to $1,000,000 for this case. These economics seem attractive, although the overall costs will include additional operating and capital costs, which cannot be estimated at this time. It is recommended that a more detailed process design and economic evaluations be performed, when additional data are available.
1. INTRODUCTION

1.1 Water Reuse of Bleached Kraft Pulp Mills

Water use in the pulp and paper industry is very significant. About 50 million tons of bleached kraft pulp is produced in the United States per year. The effluent from typical bleached kraft pulp mills ranges from about 30 to 150 $m^3$ per ton of air-dried pulp produced (Mannisto et al. 1995). A typical pulp mill produces 1,000 tons of pulp per day and can cause considerable environmental stress in terms of water consumption and wastewater discharge. The U.S. pulp and paper industries as well as other processing industries are actively pursuing water conservation and pollution prevention by in-process recycling of water. This is motivated by the rapidly rising costs of raw water and wastewater disposal (Jessen and Kemp, 1996). For plants in certain geographic locations, plant water reuse is needed because fresh water is less available and/or there are limitations on wastewater discharge. An additional driver for pulp mills is to reduce the discharge of organics contained in the wastewater.

Bleach plant effluent is a large portion of the water discharged from a typical bleached kraft pulp mill. The recycling of bleach plant effluents to the kraft recovery cycle is widely regarded as an approach to low effluent bleached kraft pulp production (Johnson et al. 1996). Many bleach plant configurations and concepts are in use commercially. However, the principle of this approach can be illustrated in Figure 1-1, which shows the major common features of a generic modern bleach plant in a bleached kraft pulp mill. Generally, recycling of bleach plant effluents is achieved by counter-currently using bleach effluent for washing in the preceding bleaching stage, and finally washing the brown stock with the recycled bleach effluent, thus introducing bleach effluent to the kraft chemical recovery cycle. In this approach, the organics contained in the bleach effluents are to be oxidized in the existing recovery furnace, instead of being discharged as a dilute stream to the waste treatment plant. However, the presence of inorganic “non-process elements” (NPEs) in the bleach effluent is a significant issue. The term NPE loosely describes materials which are not needed in the process, but which are introduced through raw materials and replacement chemicals. The most detrimental NPEs are chloride, potassium, metals/transition metals, and calcium. Particularly, the acidic bleach effluent contains metals and transition metals extracted from pulp in the acidic stages, as well as chlorides from the use of chlorine dioxide for bleaching. Recycling the acidic bleach plant effluent directly without treatment will introduce a significant load of inorganic NPEs into pulping and bleaching, resulting in serious operational problems, such as fouling and corrosion of the recovery furnace, black liquor evaporators, and other processing equipment. This causes a strong need for a specific purge of inorganics (Rapson, 1967; Reeve, 1976). Additional discussions on water reuse in bleached kraft pulp mills were given earlier (Tsai et al. 1997; Tsai et al. 1999; Pfromm et al. 1999).

1.2 Electrodialysis Technology

The goal of this work is to develop electrodialysis technologies that will enable bleached kraft pulp mills to recycle acidic bleach plant filtrates by reducing the levels of inorganic NPEs in these filtrates. Electrodialysis is a membrane separation technology that uses the permselectivity of ion-exchange membranes and the electric potential driving force to remove,
concentrate, or separate ionic species in aqueous streams. Reviews of the principles and practices of electrodialysis can be found in the literature (Shaffer, 1980). Electrodialysis is an efficient means of separating the inorganic salts from the non-ionic and weakly ionic organic species, and, thus, is uniquely suited as a selective kidney to remove inorganic NPEs from bleach plant effluents, before they reach the recovery cycle, as illustrated in Figure 1-1. By using electrodialysis, the problems caused by accumulation of inorganic NPEs in the pulping cycle and recovery boiler can be prevented. Champion International has reported the first installation of its BFR™ process at Canton, NC (Caron and Williams, 1996), to remove metals from the acidic filtrate. The metal ion removal sequence requires significant pretreatment and is still subject to fouling. Electrodialysis is potentially superior since it requires no regeneration cycles and can tolerate organic foulants if modified membranes are used.

Electrodialysis has previously been proposed for use in the pulp and paper industry (Pfromm et al. 1999), including for NPE removal. An electrodialysis process was recently developed for chloride removal from the kraft pulping process; chloride was successfully removed by electrodialysis as sodium and potassium chlorides selectively from dissolved electrostatic precipitator dust, which contained a very high concentration of sulfate (Rapp and Pfromm, 1998). Electrodialysis of bleach plant effluent to remove inorganics, including

---

**Figure 1-1.** Schematic of a generic bleached kraft pulp bleaching operation using electrodialysis for water recycling (D: chlorine dioxide bleaching stage, E: caustic extraction stage).
chloride, has been proposed by Eka Chemicals (Gransson et al. 1995). However, an extensive pretreatment for the separation of the organic components before electrodialysis was proposed. Pretreatment leads to high investment and operating costs. In this work, we use membranes that are intrinsically fouling-resistant and eliminate the pre-treatment for removal of organic potential foulants. In addition, our process uses monovalent-selective anion-exchange membranes and preferentially removes chloride while simultaneously removing metals and transition metals from the bleach filtrate to be recycled.

1.3 Goals and Objectives

The efforts in this work have been focused on the effluent of the first acidic bleaching stage of bleached kraft pulp mills, because this effluent contains the highest concentrations of detrimental NPEs. The major technical issues for this process include the membrane selectivity for the NPEs to be removed, the maximum mass transfer rate per unit membrane area that can be achieved, and the resistance to membrane fouling. In addition, the process economics are crucial. The overall objectives of the work are to:

- Evaluate the feasibility of electrodialysis for NPE control of acidic bleach plant effluent, including ion selectivity and organic fouling resistance,
- Develop an efficient and economical electrodialysis process at the laboratory scale,
- Demonstrate the process performance at a mill site, and
- Transfer the technology to pulp and paper companies.

In this work, acidic bleach plant effluents from several mills using bleaching sequences based on chlorine dioxide were characterized. Laboratory-scale electrodialysis experiments using these effluent samples were conducted for feasibility evaluations and process stability testing. A preliminary economic evaluation was performed. A pilot-scale field demonstration was conducted at a southern mill. Additional information is given in the following chapters.
2. CHARACTERIZATION OF BLEACH PLANT FILTRATES

Acidic bleach effluents used in this work were obtained from three integrated bleached kraft pulp mills (designated as Mill A, Mill B, and Mill D). All these three mills use bleach sequences based on chlorine dioxide. The effluents were the acidic effluents obtained from washing after the first chlorine dioxide bleaching stage. Mill B is Champion International’s Canton, North Carolina mill, where a patented process for bleach effluent recycle is implemented (Maples, et al. 1994). Mill B effluent used in this work is the effluent that is fed to an ion-exchange treatment unit before being recycled. The bleach effluents from these mills were characterized with various chemical analyses and used in laboratory electrodialysis experiments.

Metals and transition metals were analyzed by ICP Emission Spectroscopy. Anions were analyzed by ion chromatography (Dionex LC20 ion chromatograph with ED40 electrochemical detector, Dionex AS-11 anion column). The total organic carbon (TOC) was determined with a Shimadzu Model TOC-5000A analyzer. Conductivity and pH were measured with commercial electrodes. Total dissolved solids (TDS) were analyzed gravimetrically.

The general characteristics of acidic bleach effluents received from different mills are given in Table 2-1. The three samples from Mill A (Samples A-1, A-2, and A-3) were collected at different times over a two-week period, and did not appear to have significant variations among them. Samples B-1 and B-2 were both from Mill B, but B-2 was taken 8 months after B-1. These two Mill B samples had noticeably different concentrations. However, in all these effluents, the TDS was predominantly inorganic NPEs, and the TOC accounted for only a minor fraction (12–26%) of TDS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>TDS (g/L)</th>
<th>TOC (ppm)</th>
<th>Conductivity (mS/cm)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td></td>
<td>3.44</td>
<td>547</td>
<td>5.1</td>
<td>2.5</td>
</tr>
<tr>
<td>A-2</td>
<td></td>
<td>2.95</td>
<td>353</td>
<td>4.4</td>
<td>2.6</td>
</tr>
<tr>
<td>A-3</td>
<td></td>
<td>3.86</td>
<td>566</td>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>B-1</td>
<td></td>
<td>3.17</td>
<td>810</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>B-2</td>
<td></td>
<td>5.92</td>
<td>1,001</td>
<td>7.2</td>
<td>2.3</td>
</tr>
<tr>
<td>D-1</td>
<td></td>
<td>5.50</td>
<td>695</td>
<td>13.8</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The anion profiles of the effluent samples are shown in Table 2-2. Chloride and nitrate were present at significant levels in all effluent samples. The relatively high concentrations of sulfate in Samples A-1 and B-2 might be due to carryover of sulfate from the pulping process to the bleach plant. Many mills are trying to minimize this carryover by improving brown stock washing. Chloride is one of the more significant problem NPEs because of its good solubility in the kraft pulping liquors. It can cause plugging of the kraft recovery boiler through sticky dust, which results in costly shutdowns. Chloride is introduced into the pulping process with the wood
and replacement caustic, but also to a large part with chlorine dioxide and its reaction products if effluents are to be recycled from the bleach plant to chemical recovery.

Table 2-2. Anion profiles of acidic bleach effluent samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight Fractions (% of total detected anions)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F^-</td>
</tr>
<tr>
<td>A-1</td>
<td>5.2</td>
</tr>
<tr>
<td>B-1</td>
<td>6.2</td>
</tr>
<tr>
<td>B-2</td>
<td>3.4</td>
</tr>
<tr>
<td>D-1</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Results of ICP analyses showed that the metal and transition metal profiles of all these effluent samples were very similar (see Table 2-3). Sodium was the predominant metal ion. Calcium was also present at significant levels. Calcium is extracted from the wood fibers under acidic conditions (Ulmgren, 1997), while sodium is both carried forward from the pulping process, and is present in the wood fibers. Calcium is a potential problem because scales can form in the pulping process if bleach effluents are recycled. Magnesium and manganese were also present in these effluent samples. Magnesium is introduced through chemical addition in oxygen delignification, which is the last step before the pulp enters the bleach plant. In addition, potassium was present because of the potassium content of wood.

Table 2-3. Metal and transition metal profiles of acidic bleach effluent samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight Fractions (% of total detected metals and transition metals)</th>
<th>All Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Ca</td>
</tr>
<tr>
<td>A-1</td>
<td>80.11</td>
<td>12.99</td>
</tr>
<tr>
<td>B-1</td>
<td>79.07</td>
<td>11.56</td>
</tr>
<tr>
<td>B-2</td>
<td>81.81</td>
<td>10.38</td>
</tr>
<tr>
<td>D-1</td>
<td>76.47</td>
<td>16.55</td>
</tr>
</tbody>
</table>
3. LABORATORY DESALTING ELECTRODIALYSIS EXPERIMENTS

3.1 Short-term Feasibility Experiments

The electrodialysis experiments were conducted with a laboratory-scale electrodialysis system equipped with a Tokuyama TS-2 electrodialytic stack with 2–4 cell pairs. The TS-2 stack has a membrane surface area of 200 cm$^2$ per sheet of membrane. All membranes used were commercial Neosepta™ membranes available from Tokuyama Corp., Japan. The anion exchange membranes were ACS (strongly basic, mono-anion permselective), cation exchange membranes were CM-1 (strongly acidic, cation permeable), and two membranes of type CMX (strongly acidic, cation permeable, high mechanical strength) were used next to the electrode compartments. The membranes and stack were cleaned in place after each run by flushing the system with distilled water and sodium chloride solutions. The membranes were stored in 0.5 N sodium chloride between each run.

Each short-term feasibility experiment was conducted over a 2.5–4.6-h interval by using between 2.4 and 19 L of filtrate as the initial diluate and with 1.5–2.2 L of 3 g/L sodium chloride solution as the initial concentrate. A 30 g/L sodium sulfate solution was used as the electrode rinse solution. Diluate and concentrate were recirculated at about 0.4 gpm (gal/min). This corresponds to a superficial linear velocity in the cells of about 8 cm/s. Electrode rinse solutions were recirculated at about 1.6 gpm. System temperature was maintained at about 45° C with a water bath recirculator and heat exchanger on the diluate recirculation loop. Conductivity and pH were monitored continuously with sensors in the diluate and concentrate recirculation tanks, and temperature was monitored with an RTD probe in the diluate recirculation tank. Signals from these sensors, as well as voltage and current to the stack electrodes and desalting membranes were logged automatically to a PC. Samples of the beginning, midpoint, and end of each run were analyzed for cations, anions, conductivity, TDS, TOC, and pH to characterize the product streams and to calculate electrodialysis performance parameters.

Electrodialysis batch desalting runs were started at a current density of about 25 amp/m$^2$, selected on the basis of limiting current density tests that were conducted with the Mill B filtrate. This current density permitted operation at a good salt flux rate and minimized the voltage and power required for desalting. The current density was reduced step-wise as salt was depleted from the diluate (filtrate) tank to keep the cell voltage at or below 1.2 VDC/cell pair.

Short-term feasibility experiments were performed in the laboratory electrodialysis system for all effluent samples received. The three Mill A effluent samples were pooled and concentrated 4.3-fold by evaporation to a TDS of 14,800 ppm, before the electrodialysis experiments. All other effluent samples were used as received. Selective removal of inorganic NPEs by electrodialysis was achieved successfully for all effluent samples. Although the TDS removal was not high (at only 31-66% removed), undesirable anions, especially chloride, were removed efficiently and selectively over sulfate. Potentially harmful cations, such as potassium, calcium, and magnesium, were also removed efficiently. The average current density (thus, NPE removal rate) for the concentrated Mill A effluent was higher than for other effluents, due to the higher ion concentrations and correspondingly higher conductivity.
Typical NPE removal results during these short-term feasibility experiments are shown in Figure 3-1 for Sample B-1. Chloride and other monovalent anions, such as fluoride and nitrates, were removed selectively over multivalent anions, as expected. Calcium and other potentially harmful cations were very effectively removed, despite the overwhelming concentration of sodium. Aluminum was an exception, possibly due to the size of aluminum complexes in water. Similarly, iron removal (not shown) was not conclusive. Notice that removal of the harmful NPEs was most efficient in the first 40 minutes, whereas the cation removed during 40-150 minutes was primarily sodium.

The electrodialysis process also rejected a high percentage (75–88%) of organic compounds. There were no indications of rapid membrane fouling or scale formation during these experiments. Removing chloride from bleach plant effluent before the effluent is introduced to the chemical recovery system can significantly reduce the size of the equipment required for the dedicated chloride removal system in the pulping process. The retention of organic compounds in the bleach plant filtrate prevents them from being discharged in the mill wastewater.

### 3.2 Longer-term Experiments

In the longer-duration experiments, 50- and 100-hour operations were successfully achieved with Samples B-2 and D-1, respectively. Figure 3-2 shows that inorganic NPEs were
effectively and consistently removed from Sample D-1 during the course of the 100-hour experiment, as well as in the short-term feasibility experiment. Sample D-1 contained chloride as the predominant anion. The electrodialysis treatment removed 64.7% of chloride, 81.9% of nitrate, 15.8% of fluoride, 9.8% of sulfate, and 1.1% of phosphate. Also, the total dissolved solids concentrations in the electrodialysis concentrate stream reached 30.8-37.1 g/L in both experiments, without precipitation or scaling problems. This means the non-process elements can be purged in a small volume of a concentrated stream, minimizing wastewater discharge and allowing efficient recycling of filtrates at a water recovery yield of greater than 90%. Results of ICP analyses showed that concentrations of metals in this inorganic NPE purge stream were well below RCRA (Resource Conservation and Recovery Act) regulatory levels, suggesting that this stream was nonhazardous. The rejection of total organic carbon in these longer-duration experiments was better than in the short-term experiments, at greater than 91% in the 50-hour experiment and greater than 97% in the 100-hour experiment. This means the total organic carbon can be effectively recycled to the recovery boiler and the discharge of organic compounds in the bleach plant effluent can be reduced by 10- to 30-fold. There were no indications of membrane fouling or significant increase of cell resistance in the longer-duration experiments. The time course of cell resistance in this 100-hr run (see Tsai et al. 1999 for data) exhibited a
consistent pattern in each batch, with the exception of the period from 90 to 100 hours. This suggests that membrane cleaning once every 80–100 hours should be adequate.
4. ADDITIONAL LABORATORY EXPERIMENTS

4.1 Membrane Fouling Characterization

As in all membrane separation processes, membrane fouling is an important technical issue that needs to be addressed. Bleach plant filtrates contain organics (e.g., lignin-derivatives) that have been known to cause membrane-fouling problems in some membrane applications. Therefore, a task was included in this work to evaluate an impedance spectroscopy method for the characterization of membrane fouling, with the goal of potentially providing a tool to understand and control membrane fouling. The basic principle of this method and details of the laboratory experiments have been described previously (Watkins and Pfromm, 1999). Results showed that the impedance measurements under conditions with no mass transfer were able to reliably detect the presence of foulants (sulfonated lignins). The increase in DC resistance from the investigated foulant adsorption was significant but did not increase after a layer of foulant was deposited on the membrane. Further work towards use of the technique under mass transfer conditions is recommended.

4.2 Chlorine Dioxide Tests

Laboratory experiments were carried out to evaluate the stability of electrodialysis membranes to chlorine dioxide exposure. Although chlorine dioxide is completely consumed during normal bleaching operations, it can be present in the filtrate at low concentrations during process upsets. Therefore, membrane stability over potential exposure to residual chlorine dioxide is of concern for the viability and economics of the proposed electrodialysis process. In these laboratory experiments, electrodialysis membranes were soaked in chlorine dioxide solutions in accelerated testing conditions that simulated extremely severe and unusual exposure. The treated membranes were evaluated and compared with untreated membranes for potential loss of physical integrity (e.g., formation of cracks and pinholes) or increase of electrical resistance, which would indicate that the membrane had been damaged by chlorine dioxide exposure.

To compare the effect of the membrane materials, different types of membranes were evaluated. They included the Tokuyama Neosepta membranes (ACS monovalent-selective anion-exchange and CM-1 anion-exchange) based on polystyrene divinyl benzene materials, Asahi Glass Seleion membranes (AMV anion-exchange and ASV monovalent selective anion-exchange) based on polystyrene divinyl benzene materials, and the Pall IonClad membranes (R4010 cation-exchange membrane and R4030 anion-exchange membrane) based on polytetrafluoroethylene (PTFE) materials modified by radiation grafting.

Two rounds of chlorine dioxide tests were carried out. The chlorine dioxide used in these tests was generated in-situ. An aqueous solution of 100 g/L sodium chlorite was added to 250 ml of 4 N sulfuric acid to generate chlorine dioxide. Nitrogen gas was used to purge the generated chlorine dioxide into chilled water (at 5 °C) to form chlorine dioxide solution. The typical pH was 3.75 for chlorine dioxide solutions prepared with this method. Membrane samples were then immersed in the chlorine dioxide solution in an amber bottle, which was swirled occasionally and warmed to room temperature (about 23-24 °C). After 24 hours, the membranes
were washed with deionized water then rinsed and soaked in 0.5 M sodium chloride before evaluations. The initial and final concentrations of chlorine dioxide were analyzed by iodometric titration. The average chlorine dioxide concentrations were 5.1 g/L (5.6 g/L initial and 4.6 g/L final) for the first test and 3.5 g/L (3.9 g/L initial and 3.2 g/L final). The treated and untreated membranes were evaluated for physical integrity by visual inspection and a dye penetration test. Electrical resistance (area resistance, in the units of ohm-cm$^2$) of the membranes was measured in a 0.5 N sodium chloride solution with the AC impedance method using a pair of electrodes at 100 kHz and 50 mV.

All membrane samples remained physically intact after chlorine dioxide exposure; there were no cracks or pinholes detected. Results of electrical resistance measurements are summarized in Table 4.1. There were no significant changes in electrical resistance in any of the cation-exchange membranes tested. One type of anion-exchange membrane (Neosepta ACS) was found to have a considerable (130%) increase in electrical resistance. However, the change in electrical resistance was insignificant for all other anion-exchange membranes tested, including the Selemion ASV membrane, which is an equivalent alternative to the Neosepta ACS membrane. Therefore, it is concluded that suitable membranes with good resistance to chlorine dioxide are available for the process.

### Table 4.1 Effects of Chlorine Dioxide Exposure on Membrane Electrical Resistance

<table>
<thead>
<tr>
<th>Membranes</th>
<th>[ClO$_2$] (g/L)</th>
<th>Membrane Electrical Resistance (ohm-cm$^2$)</th>
<th>Change in Electrical Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Untreated</td>
<td>Treated</td>
</tr>
<tr>
<td>IonClad R4010</td>
<td>5.1</td>
<td>1.08</td>
<td>0.91</td>
</tr>
<tr>
<td>Neosepta CM-1</td>
<td>5.1</td>
<td>2.04</td>
<td>1.95</td>
</tr>
<tr>
<td>IonClad R4030</td>
<td>5.1</td>
<td>2.25</td>
<td>2.14</td>
</tr>
<tr>
<td>Neosepta AMX</td>
<td>3.5</td>
<td>5.76</td>
<td>6.30</td>
</tr>
<tr>
<td>Selemion AMV</td>
<td>3.5</td>
<td>2.79</td>
<td>3.03</td>
</tr>
<tr>
<td>Neosepta ACS</td>
<td>5.1</td>
<td>9.20</td>
<td>21.97</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>8.61</td>
<td>20.26</td>
</tr>
<tr>
<td>Selemion ASV</td>
<td>3.5</td>
<td>3.57</td>
<td>4.38</td>
</tr>
</tbody>
</table>

#### 4.3 Evaluations of Spacer Design

The Environmental Performance Task Group of the American Forest and Paper Association (AF&PA, charged with monitoring this the DOE/OIT Agenda 2020 Forest Products program) raised the issue of whether the electrodialysis process would to be tolerant to suspended fibers in the bleach plant filtrates and what kind of pre-filtration would be required for the electrodialysis feed. In our laboratory experiments using the Tokuyama TS-2 stack with the standard mesh screen spacer design, filtrates are routinely filtered through a 5-micron bag filter before they are fed to the electrodialysis system, according to Tokuyama’s recommendations. In
this subtask, we conducted laboratory evaluations to determine if electrodialysis could be operated without prefiltration. Different types of membrane spacer netting were evaluated, but all of them resulted in rapid plugging of flow channels by fibers and consequent pressure increase in the test flow cell. Several spacer designs, which did not use netting at all, appeared to have much less plugging of the flow cell. However, cross-compartment leakage occurred in the stack using the netting-free spacers and the electrodialysis performance was compromised. According to recent discussions with Eurodia, a leading electrodialysis equipment supplier, a wide variety of membrane spacers have been designed to meet the requirements of different applications, but there was none that could be recommended for feed streams containing fibers. Therefore, it was decided that pre-filtration with a 5-micron bag filter would continue to be used in subsequent laboratory and pilot-scale electrodialysis runs.

The evaluations of several spacer designs were conducted by using a test cell and a test solution that contained 30 ppm of suspended pulp fibers in water. The test cell was made of Plexiglas plates with the same dimensions as the Tokuyama TS-1 laboratory scale electrodialytic stack, which had an effective area of 100 cm² per cell. The use of clear Plexiglas material allowed observation of the flow distribution and clogging within the flow compartment.

Three types of spacer designs were evaluated, each with one of the following flow distributors in the compartment window:

- Type A: with the standard Tokuyama mesh screen,
- Type B: with a parallel strip flow distributor,
- Type C: with a perpendicular strip flow distributor.

In each experiment, the test solution was recirculated through the test cell containing one type of spacer, at a superficial velocity of 5 cm/sec, which was typical for common electrodialysis processes. Observations were made for accumulation of fibers inside the compartment and pressure drop across the test cell. With the Type A spacer, fibers were trapped easily by the mesh screen and the pressure drop increased quickly (to 9 psi in 10-35 minutes). Obviously, the Type A spacer was not suitable for the feed solution containing suspended fibers. With the Type B and Type C spacers, the results were much better. For the Type B spacer, the pressure drop remained low at below 1.5 psi and there was no accumulation of fibers within the compartment in an experiment that lasted for 150 minutes. For the Type C spacer, there was no significant increase in pressure drop in an experiment that lasted for 55 minutes; however, there was a gradual accumulation of fibers at several dead zones in the compartment (see Figure 4-1). Based on these results, the Type B spacer was selected for further evaluations in a desalting experiment using a TS-2 stack.
The desalting experiment in the TS-2 stack was carried out with a feed solution containing 3 g/L of sodium chloride and 30 ppm of suspended fibers in water. The stack was assembled with ACS and CMX membranes and the Type B spacers for 4 cell pairs. A batch desalting experiment was conducted and data were collected to determine the process performance. During the experiment, it was observed that the stack was prone to internal leakage between the diluate and concentrate compartments. This was attributed to the absence of screens to support the membranes and potential leakage between the inlet and outlet ports of the feed gaskets. In addition, the electrodialysis desalting performance in this run was found to be significantly compromised, compared with the performance of a control experiment, as shown in Table 4.2 below. The lower current efficiency in this study case is indicative of internal leakage from the concentrate to diluate compartment. The much higher power consumption was probably a much more severe concentration polarization in the diluate compartment in the absence of the mesh screen, which redirects the flow toward the membranes and reduces the concentration boundary layer thickness. Because of the poor performance results, it was concluded that the Type B spacer design was not suitable either.
Table 4.2. Comparative electrodialysis performance results in spacer evaluations.

<table>
<thead>
<tr>
<th>Conditions/Performance Parameters:</th>
<th>Study Case</th>
<th>Control Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack</td>
<td>TS-2 with Type B spacers (parallel strip flow distributor)</td>
<td>TS-2 with Type A spacers (standard mesh screen)</td>
</tr>
<tr>
<td>Initial NaCl feed conc. (g/L)</td>
<td>3.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Suspended fibers in feed (ppm)</td>
<td>30 ppm</td>
<td>None</td>
</tr>
<tr>
<td>Diluate Inlet Pressure, psig</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Percentage desalination</td>
<td>43.7%</td>
<td>50.9%</td>
</tr>
<tr>
<td>Current efficiency</td>
<td>53.0%</td>
<td>77.9%</td>
</tr>
<tr>
<td>Power consumption (kW-hr/kg NaCl)</td>
<td>1.2</td>
<td>0.19</td>
</tr>
</tbody>
</table>

*Conditions or performance parameters that are not reported were same or similar for both cases.*

Subsequently, discussions regarding this issue took place with Eurodia, a leading electrodialysis equipment supplier. According to Eurodia, a wide variety of membrane spacers have been designed to meet the requirements of different applications, but there was none that could be recommended for feed streams containing fibers. Therefore, it was decided that prefiltration with a 5-micron bag filter would continued to be used in subsequent laboratory and pilot-scale electrodialysis runs.
5. FIELD DEMONSTRATION

5.1 Laboratory Qualifying Experiment

Mill E, a southern bleached kraft pulp mill using a chlorine dioxide-based bleaching sequence, was selected for hosting the field demonstration. A sample of the D0 filtrate from Mill E was characterized, and the results are shown in Tables 5-1 to 5-3. This filtrate contained a considerable level of chloride at about 1,000 ppm and, therefore, the removal of chloride from the filtrate by electrodialysis would be important to avoid chloride accumulation in the pulping cycle, if this filtrate is to be recycled to the chemical recovery process. The cation profile of this filtrate is similar to that of previous filtrate samples, with sodium being the most abundant cation followed by calcium and magnesium.

Table 5-1. General characteristics of the D0 filtrate sample from Mill E.

<table>
<thead>
<tr>
<th>TDS (g/L)</th>
<th>TOC (ppm)</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.40</td>
<td>494</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Table 5-2. The anion profile of the D0 filtrate sample from Mill E.

<table>
<thead>
<tr>
<th>Weight Fractions (% of total detected anions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
</tr>
<tr>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 5-3. The metal and transition metal profile of the D0 filtrate sample from Mill E.

<table>
<thead>
<tr>
<th>Weight Fractions (% of total detected metals and transition metals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
</tr>
<tr>
<td>56.66</td>
</tr>
</tbody>
</table>

A laboratory electrodialysis experiment was performed with the Mill E D0 filtrate sample, using the laboratory-scale electrodialysis equipment and procedures described earlier in Chapter 3 Laboratory Desalting Electrodialysis Experiments. The experiment was carried out as a batch desalting run, which lasted for 240 minutes. The conductivity of the treated filtrate was reduced to 2.2 mS/cm, indicating successful purge of inorganic NPEs. Results of NPE removal are shown in Figures 5-1 and 5-2. Harmful NPEs (such as calcium, chloride, and potassium shown in Figure 5-1) were preferentially removed by electrodialysis. The organics were effectively retained at greater than 87%, as shown in Figure 5-3. From results of this experiment, the parameters to be used in the filed demonstration were determined.
Figure 5-1. The time course of NPE removal in the laboratory experiment using Mill E D0 filtrate sample using 4 cell pairs, 10 liters initial feed volume, 2 liters initial concentrate volume, and a current density of 23 amp/m².

Figure 5-2. Percentage removal of NPEs at 60 and 120 minutes in the laboratory experiment using Mill E D0 filtrate sample using 4 cell pairs, 10 liters initial
feed volume, 2 liters initial concentrate volume, and a current density of 23 amp/m².

Figure 5-3. Retention of organics in the laboratory experiment using Mill E D0 filtrate sample using 4 cell pairs, 10 liters initial feed volume, 2 liters initial concentrate volume, and a current density of 23 amp/m².

5.2 Pilot Electrodialysis System

The pilot-scale electrodialysis system used for the field demonstration was constructed by Benham-Electrosynthesis (Lancaster, New York). The system was equipped with a Tokuyama Model TS-10-100 electrodialytic stack with 100 pairs of CMX cation-exchange and ACS anion-exchange membranes. The effective membrane area was 0.1 m² per sheet of membrane (20 cm wide by 50 cm tall), the cell thickness was 0.7 mm and the total membrane area of the stack was 10 m². (Notice that in the convention used in the electrodialysis field, this means 10-m² of cation-exchange membrane and 10 m² of anion-exchange membrane.) The diluate and concentrate inlet lines were located near the bottom of the stack and on opposing sides from each other. Stack inlet lines for diluate and concentrate were the electrodes were stainless steel 316 cathode and platinized titanium anode. The stack had polypropylene endplates and PVC spacer-gaskets. There was a DC power supply, capable of up to 50 amps and 150-volt output. Piping material of construction was primarily CPVC. Instrumentation included cell flow rates (feed & concentrate), temperature (feed), pH (feed, concentrate, and electrode rinse), conductivity (feed, concentrate, and electrode rinse), current, and stack voltage.

The pilot scale electrodialysis system was transported to and installed at the field demonstration host mill in August 1999. A 1-½ inch PVC line was installed by the host mill to deliver the on-site D0 filtrate to the test area. A 50-micron bag filter in a stainless steel housing was fitted to the end of the D0 filtrate supply pipe. The 50-micron filter was installed to remove
the bulk of any suspended solids that might be in the stream. The ED system skid contained a 5-micron bag filter to protect the membrane stack.

5.3 Field Tests

For the field demonstration, based on results of the laboratory electrodialysis experiment using the filtrate sample from the host mill, the optimal operating window was determined to be the one that corresponds to 30-40% removal of total dissolved solids. Under such conditions, 40-70% removal of chloride, 70-95% removal of calcium, and over 90% retention of total organic carbon were expected. With 10 m² of membrane area, the pilot scale electrodialysis system was expected to treat up to 5 gallon-per-minute of the acidic filtrate. With the ED system operated in the feed-and-bleed mode, the key target operating parameters were as follows.

- The maximum membrane stack voltage was to be limited to 60 volts.
- The maximum membrane stack current was to be limited to 4.0 amps.
- The conductivity of the recirculating concentrate stream was to be maintained at no greater than 40 mS/cm (~3.7% dissolved solids) by adding water.

The shakedown wet test was performed using sodium chloride (NaCl) dissolved in plant process water as the feed. The system was operated for 2 hours and 15 minutes with the current maintained at 4.1 amps to simulate anticipated operating conditions when feeding D0 filtrate. This wet test was successfully completed, and all system components operated as designed.

Subsequently, a test was performed using the D0 filtrate from the plant. The test run lasted only 6.5 hours due to the following problems:

- The filters, which were installed upstream of electrodialysis to remove the suspended particulates and fibers, became overloaded rapidly and required frequent replacement.
- Even with the filters in service, the electrodialysis membrane stack became clogged and the recirculation flow rate dropped to a level too low to operate.

However, data collected showed that NPEs were effectively removed during the run. The estimated chloride removal was 45%. Several attempts to clean the membrane stack and resume the testing were not successful. Due to the technical problems and funding constraints, the field demonstration was terminated. Additional information on the conditions and results of this run is given below.

The feed tank was filled with 132 gallons of the D0 filtrate. During the feed tank filling, it was observed that the fill rate was declining and the 50-micron bag filter was replaced twice. When the system feed tank had received about 50 gallons of D0 filtrate, a 25-micron bag was used to replace the 50-micron bag. The test was then started. At the start-up, the stack was drawing 4.0 amps at 37 volts as anticipated. The system was operated for 32 minutes in the batch mode to reduce the conductivity of the D0 filtrate in the feed tank from 3.9 mS/cm to 2.8 mS/cm as planned. At this time, the diluate bleed pump was started and the D0 filtrate automatic fill circuit was energized and set for approximately 3.7 gpm. Water was added to the
concentrate recirculation tank to keep the conductivity below 40 mS/cm. At 110 minutes the system was turned off to replace the 5-micron filter because the diluate recirculation rate had dropped from 14.5 gpm to 6.5 gpm, corresponding to superficial velocities of 6.4 and 2.8 cm/sec, respectively. After 8 minutes the system was restarted and the recirculation rate was approximately 10 gpm. After 10 minutes of operation the recirculation rate had dropped below 6 gpm. Again, the system was shut down to replace the 5-micron bag filter on the ED skid. Upon restarting the system, the recirculation rate was about 12.1 gpm. The total elapsed time at this point was 2 hours and 25 minutes. At 2 hours and 52 minutes, the 5-micron bag filter was again replaced. Upon restarting the system, the recirculation rate was about 8.6 gpm. At about 3 hours and 25 minutes the recirculation pump pressure was increased from 10.0 to 11.0 psi. This brought the recirculation rate up to almost 10 gpm. This recirculation rate held relatively constant till about 5 hours and 50 minutes. By 6 hours and 30 minutes the recirculation rate had dropped to about 4.2 gpm even though the recirculation pressure had been increased to 12.5 psi. This indicated that in addition to the problem of plugging the 5-micron filter bag on the ED skid, the membrane stack was also becoming plugged. At this point, the test run was terminated.

Samples of the diluate and concentrate streams were collected during this 6.5-hour run and analyzed to for metal ions by ICP-MS, anions by capillary ion electrophoresis, and total organic carbons by TOC analyzer. The analytical data suggest that the following NPEs were partially removed: Cr, Fe, Ni, Cu, Zn, Al, P, Cl, Sr, S, Na, Mg, K, and Ca. The estimated chloride removal was 45%. Removal of NPEs was also indicated by reduction of conductivity in the diluate stream from 3.9 mS/cm in the initial feed to about 3.2 mS/cm at steady state in the recirculation feed tank (which contained the fresh feed mixed with the returned effluent; the conductivity of the effluent was not measured but is estimated to be about 2.6 mS/cm). TOC data showed almost complete retention of total organic carbon. Quantitative results could not be calculated, because this run was intended for preliminary testing and was not designed to generate data for material balances.

ANL engineers made several attempts to clean the membranes and stack in place by reverse flushing using water and chemical/ enzymatic solutions. However, this did not effectively unclog the stack and restore the flow rate to an acceptable level. Additional efforts to solve the problem were hampered by the inclement weather conditions (evacuation due to approaching hurricane) at the field site. Due to the technical problems and funding constraints, this field demonstration was terminated.

There are two possible causes of membrane stack clogging:

- The filters did not completely remove all the suspended fibers and the fibers that passed through clogged the flow channels inside the stack.
- The acidic filtrate (D0 filtrate) contained colloidal materials (e.g., lignin- or cellulose-derivatives) that passed through the filters but became unstable and precipitated inside the stack due to localized physical or chemical conditions. It is possible that such colloidal materials were not present in the filtrate used in the earlier laboratory experiment, because they might have precipitated during shipping and were filtered out.
The clogged stack was later opened for inspection. Solid materials were found to accumulate in the diluate compartments and be trapped by the mesh screen spacer (see Figure 5-3). Samples of these solids were examined under the microscope, and they appeared to be fibrous materials. Therefore, it appears that very fine fibrous matter passed through the 5-micron bag filter and was trapped by the mesh screen spacer, and clogged the membrane stack.
The electrodialytic stack (Model Tokuyama TS-10-100) used in this field test was of the thin channel design with fine mesh screens, which made it vulnerable to clogging by suspended solids. In principle, a thicker channel design with coarse mesh spacers should be less vulnerable to clogging. A commercial size electrodialysis stack of such a design was used in pilot scale work on dissolved electrostatic precipitator ash by one of the co-Principal Investigators of this work (Rapp and Pfommm, 1998). This stack operated for extended times without any pre-filtration on a feed that contained macroscopic flocs consisting of a mixture of organics and inorganics. Due to the relatively large fluid passages and a coarse spacer design with relatively large membrane spacing a stack like this might be more suitable for the process proposed here. However, removal of fibers by pre-filtration may still be necessary since fiber entanglement can cause a problem, as suggested by our results reported in Section 4.3, Evaluations of Spacer Design. Advanced spacer designs may overcome the need even for this simple pre-treatment of the feed, but based on discussions with Eurodia, a leading supplier of electrodialysis equipment, there is currently no known stack design that can reliably tolerate suspended solids in long-term operations. Therefore, we recommend that appropriate filter systems or other separation methods be used to effectively remove fine fibers to avoid membrane stack clogging, if this electrodialysis process is to be used for filtrate recycling.
6. PROCESS ECONOMICS

For a model mill with 1,000-ton/day pulp production that uses a bleaching sequence based on chlorine dioxide, preliminary process design and economic evaluations were performed. In this process, the acidic D0 bleach filtrate is assumed to be treated without pre-concentration. In addition to the electrodialysis step for purging NPEs, the process may also include an optional pre-filtration step for removal of fibers prior to electrodialysis.

We assume the electrodialysis step is operated in a continuous flow-through mode. The characterization and electrodialysis performance data for Filtrate Sample B-1 are used for this design. The analysis is based on the cations Ca and Mg. Anions are assumed to be removed in balance to the cations. The NPE removal achieved in 40 minutes is selected as the target removal (see Figure 3-1; Cl 36.7%, Ca 84.0%, Mg 76.0%). The scale up from the batch data to a continuous process is straightforward since the current density was unchanged at 23 mA/cm² during the first 40 min. The electrical current efficiencies for removal of Ca and Mg were assumed to be as measured for the first 40 min of the batch run (η_{Ca}=25.1%, η_{Mg}=11.5%). Assuming 3-m³ acidic effluent to be treated per ton of pulp produced, a membrane area of about 361 m² (361 m² each of anion- and cation-exchange membranes) would be needed for this model mill, which generates 3,000-m³ effluents per day from the production of 1,000 tons of pulp per day. This membrane area can be contained in one or two commercially available stacks marketed by the existing electrodialysis equipment suppliers (for example, Eurodia, Asahi Glass, and Tokuyama).

Assuming a voltage drop per cell pair (one diluate and one concentrate compartment) of 1.6 volt, the energy consumption is estimated to be about 3,200 kWh per day or $160 per day at an electricity cost of $0.05/kWh. This translates to $0.16 per ton of pulp produced. This calculated energy consumption is needed for the electrodialytic stack (i.e., separation) only, excluding pumping. For electrodialysis processes, the pumping energy consumption is generally comparable to or lower than the stack energy consumption. In addition, there are other operating costs, which cannot be estimated at this time due to limited data, such as the costs of membrane replacement, cleaning chemicals, operators, etc.

The capital cost of the electrodialysis membrane stack(s) for 361 m² is estimated to be about $275,000. The cost of the complete electrodialysis plant, including the stacks, pumps, rectifiers, instruments, piping, valves, tanks, engineering, etc., is estimated to be $750,000 to $1,000,000. This estimate is based on the cost of electrodialytic stacks of existing, commonly used designs. If a new stack design is needed (for example, to overcome clogging without pre-filtration), the cost is likely to be higher. In addition to the electrodialysis equipment cost, the overall capital cost may include the costs for installation, building and site preparation, and the pre-filtration system.
7. CONCLUSIONS AND RECOMMENDATIONS

Analyses of the bleach plant effluents showed no fundamental differences in the inorganic NPE composition or other characteristics among the first stage acidic filtrates from three bleached kraft pulp mills using different bleaching sequences based on chlorine dioxide. Chloride and nitrate were present at significant levels in all effluent samples. Sodium was the predominant metal ion, while calcium and magnesium were also present at considerable levels.

The feasibility of using electrodialysis to selectively remove inorganic NPEs from the acidic bleach effluent was successfully demonstrated in laboratory experiments with effluents from all these three mills. Although there were some variations in these effluents, chloride and potentially harmful cations, such as potassium, calcium, and magnesium, were removed efficiently from the bleach effluents into a small-volume, concentrated purge stream. This effective removal of inorganic NPEs can enable the mills to recycle acidic bleach effluents to reduce water consumption. The electrodialysis process also effectively retained up to 98% of the organics and can reduce the organic discharge in the mill wastewater. By using suitable commercially available electrodialysis membranes, there were no indications of rapid or irreversible membrane fouling or scale formation, even in extended laboratory scale operations up to 100 hours. Results of laboratory experiments also showed that commercially available membranes properly selected for this process would have good stability to withstand the potentially oxidative conditions of the filtrate.

The pilot-scale field demonstration found serious membrane stack clogging problems caused by fine fibers that escaped through the 5-micron pre-filters, although such a pre-filtration method had been satisfactory in the laboratory tests. Additional R&D is recommended to address this pre-filtration or clogging issue with systems approaches integrating pre-filtration, other separation methods, and stack design. Attention should be given to verify that results obtained in laboratory tests, which use “old” filtrate samples, are reproducible with “fresh” filtrates generated in the bleach plant. A particular issue is whether settling of fine suspended fibers or precipitation of colloids might have taken place in the samples used in laboratory tests, during shipping, storage, and handling. After the pre-filtration/clogging issue is overcome, laboratory development and pilot demonstration are recommended to optimize the process parameters and to evaluate the long-term process parameters. The key technical issues here include membrane life, control and mitigation of fouling and scaling, and cleaning-in-place protocols.

A preliminary process design and economic evaluations were performed for a model mill with 1,000-ton/day pulp production that uses a bleaching sequence based on chlorine dioxide. Assuming 3-m³ acidic effluent to be treated per ton of pulp produced, a membrane area of about 361 m² would be needed for this model mill. The energy consumption of the electrodialytic stack for separation is estimated to be about $160/day, and the estimated capital cost of the electrodialysis system is $750,000 to $1,000,000 for this case. These economics seem attractive, although the overall costs will include additional operating and capital costs, which cannot be easily estimated at this time. It is recommended that a more detailed process design and economic evaluations be performed, when additional data are available, especially with respect to the pre-filtration requirement and site-specific stream volumes and compositions.
8. ACKNOWLEDGMENTS

The work reported here was supported by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, under Contract W-31-109-Eng-38. This project was part of the “Agenda 2020-Forest Products Industries of the Future Program” by the U.S. Department of Energy, Office of Industrial Technologies, in collaboration with the American Forest and Paper Association. The authors would also like to gratefully acknowledge the support of R. Caron of Champion International for supplying some of the bleach effluent samples. The support of additional companies and their personnel, who wish to remain anonymous, are also appreciated for supplying the effluent samples and collaborating on the field demonstration.
9. REFERENCES


