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ABSTRACT

Conservation of water in bleached kraft pulp mills by recycling the bleach plant effluent directly without treatment will cause accumulation of inorganic "non-process elements" (NPEs) and serious operational problems. In this work, an electrodialysis process is being developed for recycling the acidic bleach plant effluent of bleached kraft pulp mills. In this process, electrodialysis functions as a selective kidney to remove inorganic NPEs from bleach plant effluents, before they reach the recovery cycle.

Acidic bleach plant effluents from several mills using bleaching sequences based on chlorine dioxide were characterized. The total dissolved solids were mostly inorganic NPEs. Sodium was the predominant cation and chloride was present at significant levels in all these effluents. In laboratory electrodialysis experiments, selective removal of chloride and potentially harmful cations, such as potassium, calcium, and magnesium, were removed efficiently. Rejection of organic compounds was up to 98%. Electrodialysis was shown to be resistant to membrane fouling and scaling, in a 100-hour laboratory experiment. Based on a model mill with 1,000 ton/day pulp production, the economic analysis suggests that the energy cost of electrodialysis is less than $200/day, and the capital cost of the stack is about $500,000.

INTRODUCTION

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 [1]. 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.

Much of the water used in bleached kraft pulp mills is associated with the bleaching operation. The recycling of bleach plant effluents to the kraft recovery cycle is widely regarded as an approach to low effluent bleached kraft pulp production [2]. Many bleach plant configurations and concepts are in use commercially. However, the principle of this approach can be illustrated in Figure 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 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. This will result in such operational problems as fouling and scaling of the black liquor evaporators, fouling and plugging of the kraft recovery furnace, corrosion, and increased use of bleaching chemicals. The most detrimental NPEs are chloride, potassium, metals/transition metals, and calcium. This causes a strong need for a specific purge of inorganics [3, 4].

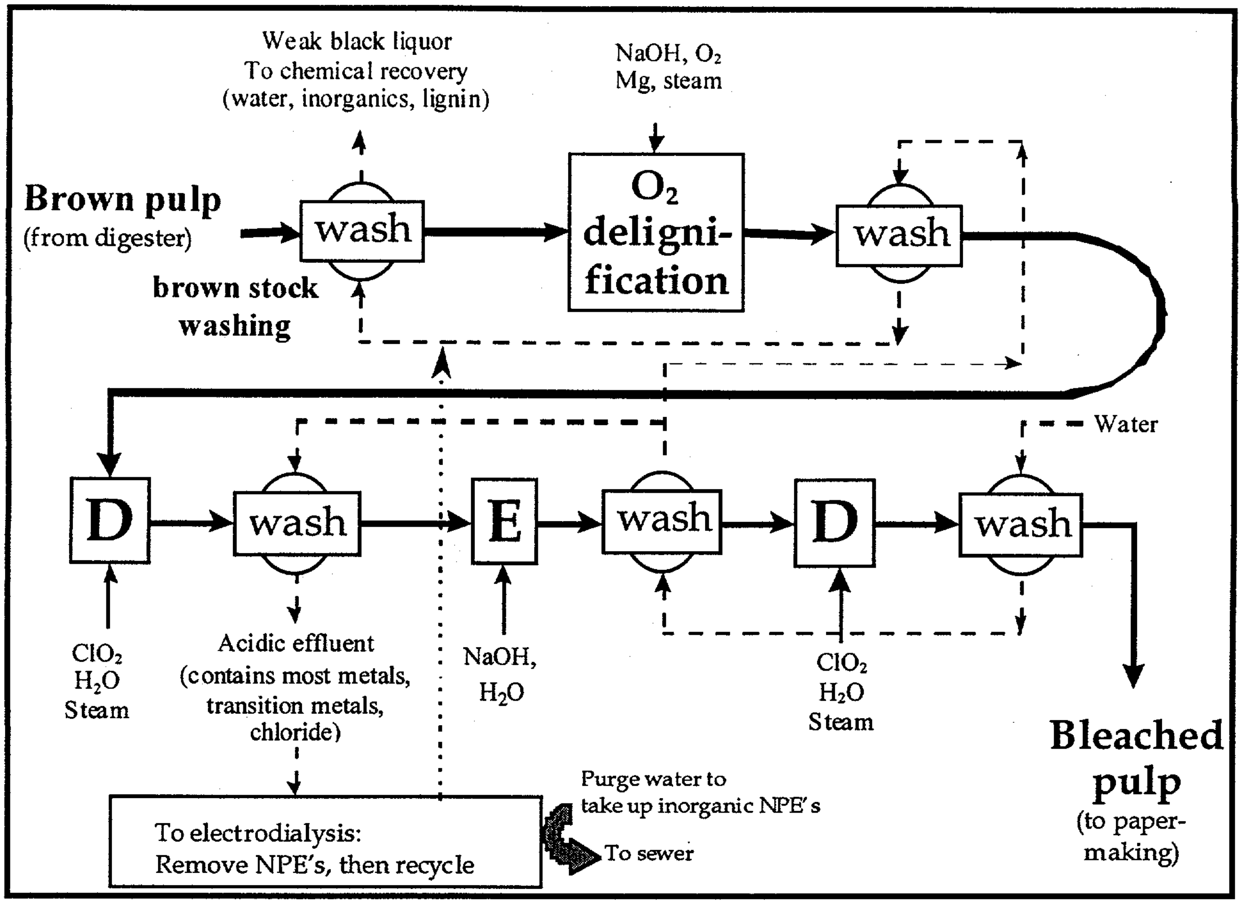

Figure 1: Schematic of a generic bleached kraft pulp bleaching operation with water recycling (D: chlorine dioxide bleaching stage, E: caustic extraction stage).

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 [5,6]. 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. By using electrodialysis, the problems caused by accumulation of inorganic NPEs in the pulping cycle and recovery boiler are prevented.

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 [7]. Electrodialysis of bleach plant effluent to remove inorganics, including chloride, has been proposed by Eka Nobel [8]. However, an extensive pretreatment for the separation of the organic components before electrodialysis was proposed. Pretreatment leads to high investment and operating costs. The process proposed here will employ membranes that are intrinsically fouling-resistant because of special polymer modifications. Champion International is currently testing the first installation of its BFR™ process at Canton, NC [9], to remove metals from the acidic filtrate. The metal ion removal sequence requires significant pretreatment and is still subject to fouling. Electrodialysis is superior since it requires no regeneration cycles and can tolerate organic foulants if modified membranes are used. Electrodialysis can remove chloride at the same time that metal ions are extracted, thereby preventing chloride from entering the recovery cycle.

EXPERIMENTAL

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 [10]. 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 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^{TM} 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 was used as the electrode rinse solution. Diluate and concentrate were recirculated at about 0.4 gpm (gal/min), and electrode rinse solutions were recirculated at about 1.6 gpm. System temperature was maintained at about 45 = B0C 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.

Two longer-duration laboratory scale experiments were carried out. The objectives were to test the longer-term process performance and to determine the requirements and efficacy of cleaning-in-place. A 50-hour electrodialysis experiment was completed using Sample B-2. This experiment consisted of two consecutive batch runs for a total run time of 50 hours without membrane cleaning during turnaround. Also, a 100-hour experiment was completed using Sample D-1. This experiment consisted of five consecutive batch runs, again, without membrane cleaning during turnaround.

RESULTS AND DISCUSSION

The general characteristics of acidic bleach effluents received from different mills are given in Table 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 1. General characteristics of acidic bleach effluent samples.

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

The anion profiles of the effluent samples are shown in Table 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 problems 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, but also to a large part with chlorine dioxide and its reaction products from the bleach plant.

Table 2. Anion profiles of acidic bleach effluent samples.

	Weight Fractions (% of total detected anions)				
Samples	F^-	Cl^-	SO_4^{2-}	NO^{3-}	PO_4^{3-}
A-1	5.2	37.2	36.3	18.7	2.7
B-1	6.2	41.6	9.4	40.8	2.1
B-2	3.4	31.2	44.4	20.3	0.7
D-1	0.7	75.1	1.8	21.5	0.8

Results of ICP analyses showed that the metal and transition metal profiles of all these effluent samples were very similar (see Table 3). Sodium was the predominant metal ion. Calcium was also present at significant levels. Calcium is extracted from the wood fibers under acidic conditions [11], 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 effluent enters the bleach plant. In addition, potassium was present because of the relatively high potassium content of wood.

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

	Weight Fractions (% of total detected metals and transition metals)									
Samples	Na	Ca	Mg	Ba	K	Si	Mn	Fe	Al	All Others
A-1	80.11	12.99	2.97	0.01	1.94	1.14	0.49	0.08	0.10	0.36
B-1	79.07	11.56	3.53	0.09	1.55	2.02	1.22	0.07	0.72	1.05
B-2	81.81	10.38	2.31	0.00	0.88	2.36	1.08	0.10	0.93	0.14
D-1	76.47	16.55	2.45	0.24	0.98	2.07	0.58	0.20	0.28	0.17

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-foild 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 2 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.

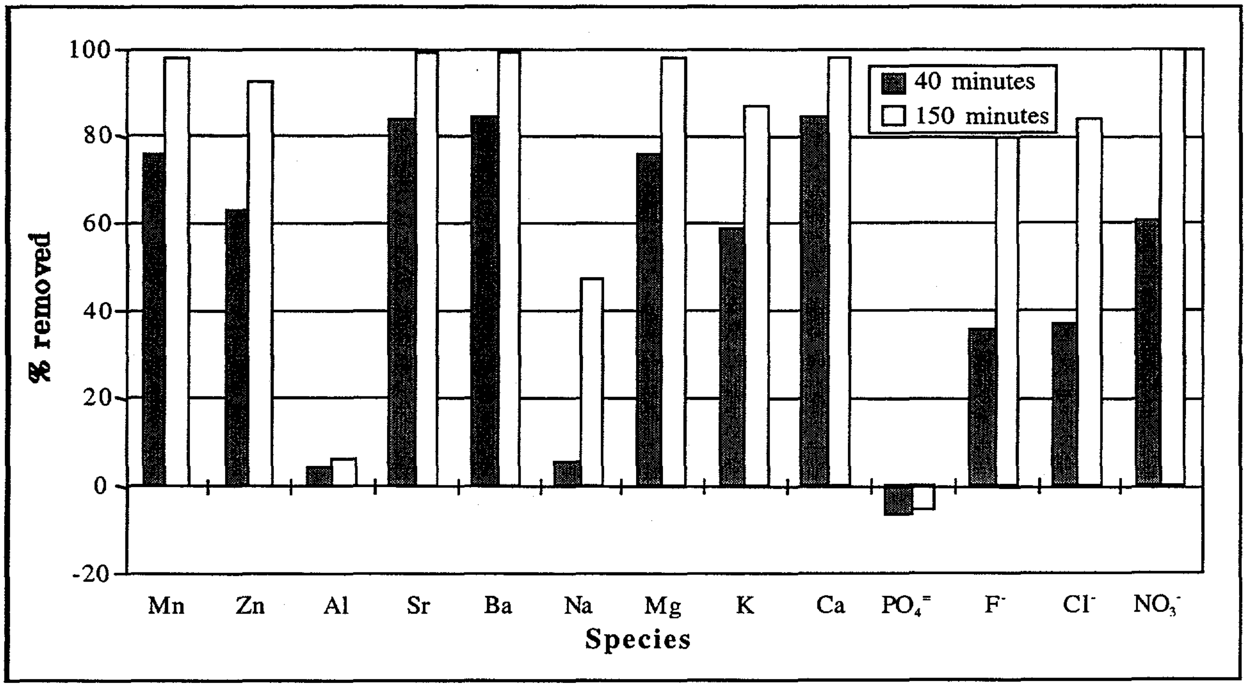

Figure 2: Removal of various NPE species during the electrodialysis run for Sample B-1 at 40 and 150 min (end of run).

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.

In the longer-duration experiments, 50- and 100-hour operations were successfully achieved with Samples B-2 and D-1, respectively. Figure 3 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 concentration 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 regulatory levels, suggesting that this stream was nonhazardous. The rejection of total organic carbon in this 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. As shown in Figure 4, the cell resistance 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.

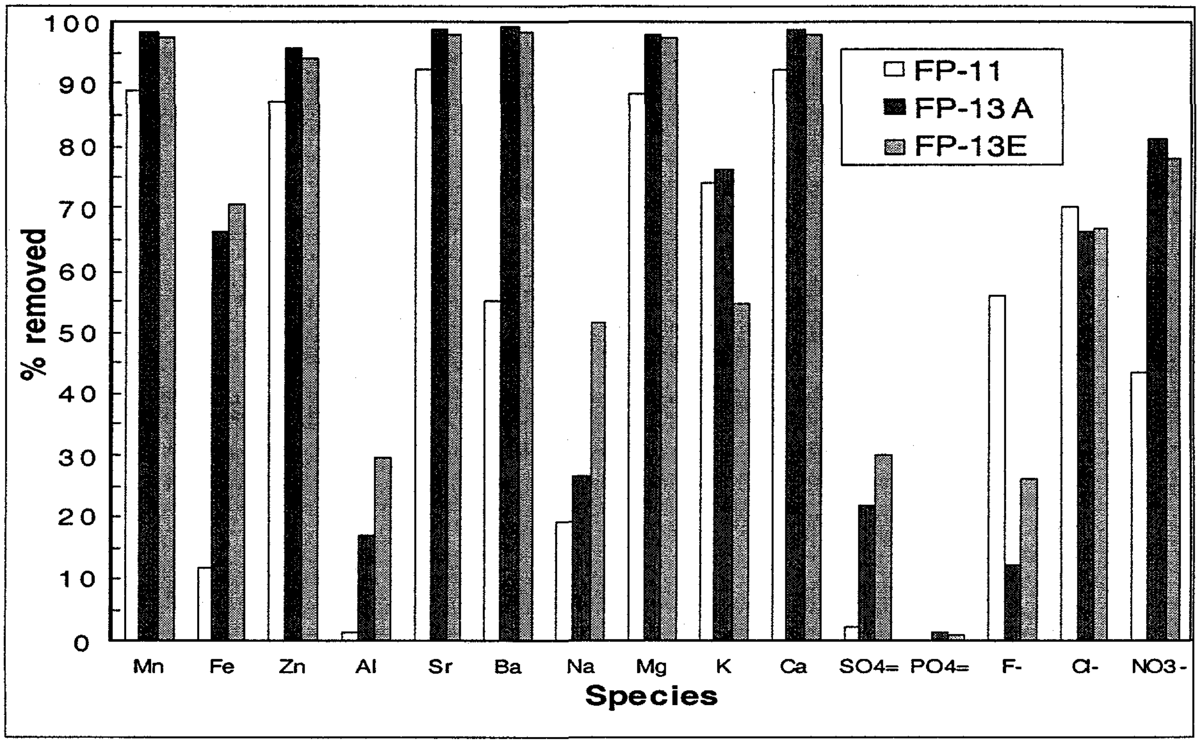

Figure 3. NPE removal from Sample D-1 in the short-term experiment (FP-11), the first batch of the 100-hour experiment (FP-13A), and the fifth batch of the 100-hour experiment (FP-13E).

For a model mill with 1,000 ton/day pulp production that uses a bleaching sequence based on chlorine dioxide, a preliminary process design and economic evaluations were performed. A continuous flow-through process was assumed, with the NPE removal achieved in 40 minutes as the target (see Figure 2). The scale up from the batch data to a continuous process here is straightforward since the current density was unchanged during the first 40 minutes. Assuming 3 m^3 acidic effluent to be treated per ton of pulp produced, a membrane area of about 810 m^2 (810 m^2 each of anion- and cation-exchange membranes) would be needed for this model mill. This membrane area can be contained in one single commercially available stack marketed by the existing electrodialysis equipment suppliers. The capital cost of the electrodialysis membrane stack of this size is estimated to be about $500,000 and the electrodialysis electricity cost is estimated to be less than $200/day.

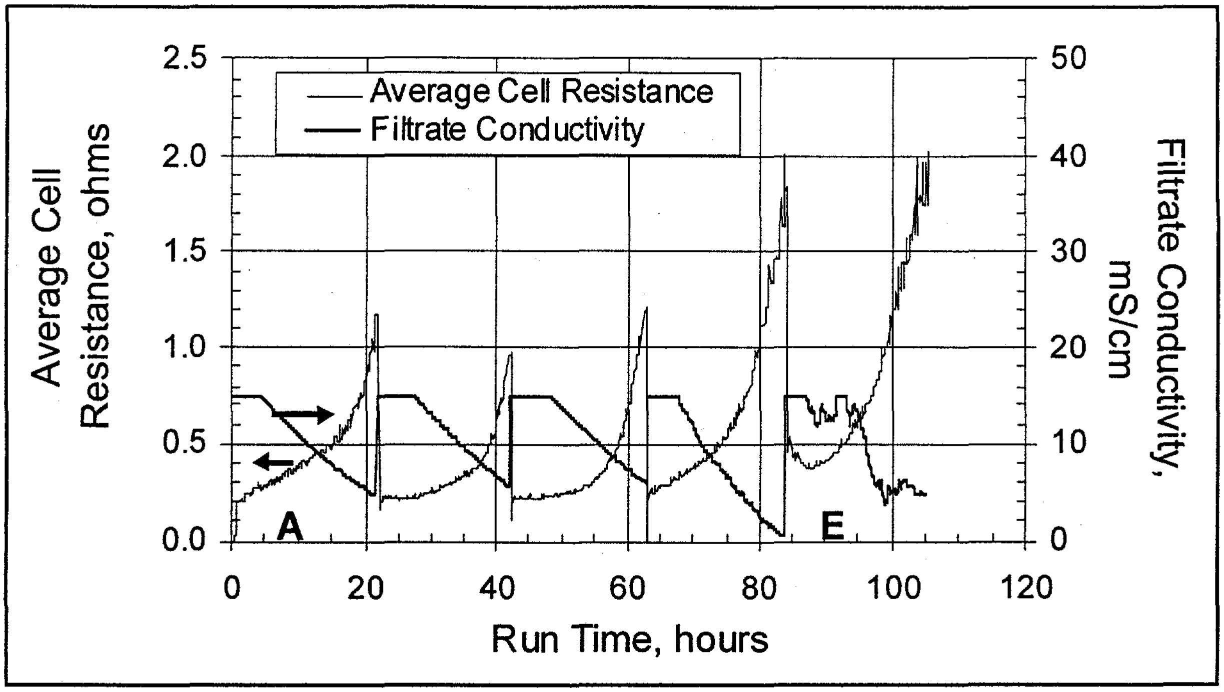

Figure 4. The time course of average cell resistance in the 100-hour experiment with Sample D-1.

CONCLUSIONS

The feasibility of using electrodialysis to selectively remove inorganic NPEs from the acidic bleach effluent was successfully demonstrated in laboratory experiments with effluents from three mills using bleaching sequences based on chlorine dioxide. 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. 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 membranes, there were no indications of rapid or irreversible membrane fouling or scale formation, even in extended laboratory scale operations up to 100 hours. A preliminary process economic evaluation suggests that the energy cost of electrodialysis in this process is low, at less than $200/day for a 1,000 ton per day pulp production; the estimated capital cost of the stack is about $500,000 for this case. A pilot scale field demonstration of this process at a mill site is planned in mid-1999.

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