Throughout the 1980s, there was significant progress in the development of polymers for high-performance membranes [1,2]. A wide range of materials has been developed that exhibits a broad spectrum of permeation properties. Moreover, a large database has evolved that allows the direct correlation of molecular structure with permeation properties, thereby providing the opportunity to tailor-make polymer materials for specific applications. These advances are resulting in rapid growth in the application of membrane technologies in existing as well as new markets.

This paper discusses three examples of potential membrane applications in the pulp and paper industry with respect to technical feasibility, process integration, and the economics of the mill-installed system. These are:

1. Effluent closure of mechanical pulp mills using ultrafiltration and reverse osmosis technology;
2. Incremental kraft recovery capacity and caustic soda production through the electrolysis of a fraction of weak black liquor;
3. Production of bleaching chemicals using bipolar membrane electrodialysis.

Effluent Closure

While some water recycling is practised in integrated mechanical pulp mills, complete recycling without treatment or partial purge is not feasible because of the accumulation of dissolved materials inside the plant. Direct reuse of mechanical pulping effluents, which are rich in extractives, leads to pitch problems in the paper machine and dark specks on the paper.

Hence, for increased recycling and reuse of water without compromising pulp and paper production and quality, additional separation processes have to be considered.

The criteria to be considered when assessing separation processes for effluent treatment are: (1) the regulatory limitations and receiving water conditions and (2) the effluent stream and volume to be processed. The first of these issues is site-specific and so is not further discussed in this paper.

If the final effluent is treated, then the volume to be processed depends on: (1) the production capacity of the mill and (2) the extent of internal water recycling. The effluent volume to be treated will determine the capital and operating costs of the process. The cost factors for scaling up are different for the various processes and could determine which ones will be cost-effective for the treatment of a particular stream [3].

For water recovery from mill effluents with low concentration (about 1% solids), our preliminary cost estimates indicate that ultrafiltration, with a membrane flux of 140 L/h.m² or higher, would be more economical than vapor recompression evaporation and freeze crystallization [4].

Technical feasibility: In ultrafiltration systems, a pressure of about 0.5 to 1 MPa (70 to 150 psig) is applied to drive water and salts through the pores of the membrane while macromolecules remain with the feed solution, Fig. 1a [5]. In reverse osmosis, the membrane pores are smaller for added selectivity, and, therefore, the required applied pressures are higher (3.5 to 5.5 MPa or 500 to 800 psig). In this case, essentially only water goes
Fe₂O₃, P₂O₅, Na₂O and K₂O.

Laboratory-prepared ash was an agglomeration of particles smaller than 10 μm. It had a complete melting point higher than 1400°C and did not appear to sinter at temperatures below 1050°C.

In-circuit ash appeared to be partially fused and had a much larger particle size than the laboratory prepared ash. The fused particles were exposed to much higher temperatures in the incinerator than the majority of the ash.

**Experimental**

Weighed sludge samples were dried for 24 hours at 105°C to determine moisture content. Ash samples were prepared in the laboratory by burning the dried solids in a furnace and heating the residue in an air muffler for at least 30 minutes at various temperatures from 500 to 1200°C.

The bulk chemical composition of the ash was determined by means of inductively coupled plasma spectroscopy (ICP) and X-ray fluorescence spectroscopy (XRF). The composition of individual particles in the ash was examined by wave-length dispersive spectroscopy (WDS). X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) were used for mineralogical and morphological examinations respectively.

Thermal analysis was done using a Seiko TA300 thermal analyzer for simultaneous thermal analysis/thermogravimetric analysis (DTA/TGA). Sample size was about 15 mg. Heating rate was 20°C/min. Both as-received sludge and dried sludge samples were analyzed for moisture content, ash content and heat released during combustion. The thermal behavior of the ash was also examined in air using DTA/TGA. Heating values for sludges were measured by bomb calorimetry on oven-dried samples.

**Acknowledgements**

The financial support provided by ABB Combustion Systems, Canadian Pacific Forest Products Limited, and the Natural Sciences and Engineering Research Council of Canada are gratefully acknowledged.

**References**


Résumé: Les boues de déchiffage provenant de trois ateliers de déchiffage, ainsi que leurs cendres préparées en laboratoire et des échantillons de cendres provenant d'un incinérateur à boues de déchiffage, ont été caractérisées. Les boues contiennent des fibres celluloses décomposées mêlées avec des solides particulaires et de l'eau. Certaines boues contiennent de 30 à 55% de matières solides par unité de poids, ce qui consiste en 55 à 85% de matières volatiles et de l'15 à 45% de cendres. Les boues séchées ont des pouvoirs calorifiques allant de 12 à 16 MJ/kg et sont donc combustibles acceptables. Les boues ont été utilisées jusqu'à un degré hydrométrie faible. Les cendres consistent principalement de SiO₂, Al₂O₃ et CaO dérivés des produits de combustion; elles fondent à des températures supérieures à 1000°C et ne frittent pas sous 1050°C. Les particules de cendre de laboratoire sont plus petites que 10 μm, alors que les particules de cendre d'incinérateur sont beaucoup plus larges et partiellement fondues.

**Abstract:** Deinking sludges from three deinking plants, their laboratory-prepared ashes and ash samples from a deinking sludge incinerator were characterized. Sludges consist of degraded cellulose fibres mixed with particulate solids and water. As received, sludges contain 30 to 55 wt% solids which consist of 55 to 85 wt% volatiles and 15 to 45 wt% ash. Dried sludges have heating values ranging from 12 to 16 MJ/kg and are reasonable fuels if dried to a low moisture content. Ashes consist mainly of SiO₂, Al₂O₃ and CaO derived from coating materials. The cendres consist principally of SiO₂, Al₂O₃ and CaO. The bulk chemical composition of the ash particles are much larger and partially fused.

**References:**


**Keywords:** RECYCLING, DEINKING, SLUDGE, COMBUSTION, ASH, RESIDUES, THERMAL ANALYSIS, CHEMICAL COMPOSITION.
through the membrane (some methanol and ethanol would pass through as well) whereas salts and macromolecules remain with the feed solution, Fig. 1b.

In both ultrafiltration and in reverse osmosis systems, both the porous structure and the chemical nature of the membrane surface in contact with the feed solution determine the separation and permeability characteristics of the membrane. The nature of thefeed solution is also important. The major constituents of mechanical pulp mill effluents are: various suspended solids, wood resin, lignin fragments and hemicelluloses as well as smaller molecular weight (MW) components, such as sodium sulphite and sulphate salts.

When these membranes are exposed to the relatively complex feed solutions, represented by the effluents from mechanical pulp mills which, as previously mentioned, contain macromolecular solutes and/or suspended colloidal or particulate matter, several additional mechanisms of membrane transport may have to be considered as a result of the special chemistry of these systems.

Process integration: Figure 2 shows a simplified schematic of the proposed system for the treatment of mechanical pulp mill effluents. If process water discharge is reduced to less than 5 m³/adt of pulp through a variety of approaches currently under investigation (e.g., interstage bleaching and deresination [6]), then the costs associated with various effluent separation techniques compare favorably with biotreatment. At these low effluent flows, effluent treatment through ultrafiltration and reverse osmosis technology appears to be more cost-effective than vapor compression evaporation or freeze crystallization.

It is proposed that the effluents be first pretreated through an approach such as settling, screening or flotation to remove all suspended solids, followed by ultrafiltration and reverse osmosis, in series, to remove the high MW and low MW fractions, respectively, from the feed solution. As indicated in Fig. 2, the suspended solids and the high MW fraction components of the effluent would go to a concentration and disposal step such as incineration or landfill, whereas the purified water will go back to the mill for reuse.

Economics: The major economic factors to be considered are: (1) pretreatment for the removal of suspended solids through an approach such as settling, screening or flotation and (2) membrane properties such as flux, selectivity and life. Assuming a mill capacity of 500 adt/d, an effluent flow of 5 m³/adt of pulp, a membrane flux of 140 L/h.m² and a membrane life of 1.5 years, then, for such a system, the required capital investment would be $5.8 million, the operating costs would be $0.7 million/y and as credits one can claim compliance with government regulations. Table 1.

Note that these figures do not include the capital and operating costs associated with the concentration and disposal step shown in Fig. 2. We are now testing membrane properties such as flux, selectivity and life using a fully automated pilot unit recently constructed at the Pulp and Paper Research Institute of Canada (Paprican) in collaboration with the National Research Council of Canada. This unit was successfully operated at an Abitibi-Price mill for six months under mill conditions. If these trials are successful, we will then proceed to the demonstration plant level.

Weak BL Electrolysis

The chemical recovery system is often considered to be the bottleneck of the kraft pulping process due to its high capital cost. The key component of the conventional recovery system is the recovery furnace in which most of the black liquor's sodium and sulphur are recovered as sodium carbonate and sodium sulphide, and the organic solids are burned to produce heat for steam generation.

Different direct and indirect approaches for obtaining incremental kraft recovery capacity have been reviewed elsewhere [7-11]. The removal of a portion of the organic material from the spent liquor before it enters the recovery furnace, represents an attractive means of providing incremental recovery capacity and production at kraft mills. One such approach is the electrolytic processing of a fraction (5 to 30%) of the weak black liquor (WBL) [12-15].

Technical feasibility: Figure 3 shows a schematic of a unit electrolysis cell. This cell employs an anode and a cathode, with a cation-selective membrane between the two electrodes. WBL is fed into the anode compartment and water (or a dilute sodium hydroxide solution) is fed
into the cathode compartment. When a voltage is applied between the two electrodes, under the influence of the resulting electric field, the sodium ions migrate towards the negative electrode where they pick up hydroxide ions from the reduction of water at the cathode to form sodium hydroxide. In the anode compartment, the sodium ions are replaced by hydrogen ions, which are produced from the oxidation of water, at the anode. The product from the anode compartment is, therefore, acidified WBL. If this liquor is acidified enough, either inside or outside the electrolysis cell, most of its lignin component precipitates out.

**Process integration:** Figure 4 is a simplified schematic of the proposed incremental kraft recovery system. In the conventional kraft recovery system, WBL goes through the multiple effect (ME) evaporator, where it is concentrated. It is then introduced into the recovery furnace. Once all the organic material is burned, the remaining inorganics are introduced into the causticizer to produce caustic-rich white liquor.

It is proposed that a portion of the WBL be diverted into an electrolysis cell where it is electrolyzed from pH 12.5 to pH 9.5, just before lignin begins to precipitate out, while at the same time producing high-quality caustic soda. The partially acidified WBL is further acidified outside the cell to pH 5.5, using waste acid from the chlorine dioxide generator, to precipitate out lignin. The lignin is then filtered and washed, and the depleted WBL is returned to the ME evaporator. A portion of the acidified anolyte and/or the wash water from the filtration step may be sewered.

**Economics:** Assuming a mill capacity of 700 adt/d, in which 13% of the WBL is processed, the credits would be: (1) an 8% increase in incremental kraft recovery capacity; (2) 56 t/d lignin recovered; (3) 7.7 t/d high-quality caustic soda produced. Assuming a membrane life of one year and an electrode life of two years, the capital costs for such an electrolysis plant would be $15.5 million, the operating costs $3.4 million/y and the credits $10.2 million/y. This translates into a payback of 2.3 years, Table II. Before this technology reaches the mill transfer stage, electrode and membrane durability studies need to be done. This is currently being done using a pilot unit recently constructed at Paprican.

**CHEMICALS FROM BME**

The consumption of chlorine in the pulp and paper industry is decreasing because of concern about the effects of chlorinated compounds on the environment. As caustic soda production is currently linked to chlorine production and the demand for sodium hydroxide has remained high, there is a need to find cost-effective approaches for saving or producing caustic soda [16-18].

One such method is bipolar membrane electrodialysis (BME). The BME process is an energy-efficient technology for the conversion of salts into their component acids and bases [19-23]. Using this technology, chemicals used in bleaching, such as caustic soda, and an acid, might be produced on-site, from a process stream, a waste stream or from a relatively cheap water-soluble salt.

**Technical feasibility:** The distinguishing component of BME systems is the bipolar membrane, Fig. 5. A bipolar membrane is basically a sandwich of an anion-selective and a cation-selective membrane, with an interface of water in between.

Assuming that such a membrane is placed between an anode and a cathode, then, under the influence of the electric field, the hydroxide ions from the dissociation of water are attracted to the positive anode, whereas the hydrogen ions from the dissociation of water migrate towards the negative cathode. If such membranes are placed in an electrolysis system, such as the one previously discussed, Fig. 3, one on either side of the cation-selective membrane, then, a BME system is obtained, Fig. 6.

A unit BME cell employs an anode and a cathode in between which the following membranes are placed: a bipolar membrane, a cation-selective membrane and a second bipolar membrane. If a salt solution, such as sodium chlorate, is fed between the first bipolar membrane and the cation-selective membrane, then the positive ions will migrate towards the negative cathode but, during ion transport, will pick up hydroxide ions produced from the dissociation of water within the second bipolar membrane, not the cathode as in the case of electrolysis, and produce base.

The migrating sodium ions are

---

**TABLE II. PRELIMINARY ECONOMICS OF THE PROPOSED INCREMENTAL KRAFT RECOVERY CAPACITY SYSTEM.**

<table>
<thead>
<tr>
<th>Description</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital investment</td>
<td>$15.5 million</td>
</tr>
<tr>
<td>Operating costs</td>
<td>$3.4 million/y</td>
</tr>
<tr>
<td>Credits</td>
<td>$10.2 million/y</td>
</tr>
<tr>
<td>Payback</td>
<td>2.3 years</td>
</tr>
</tbody>
</table>

**Assumptions:** Mill capacity: 700 adt/d; WBL processed: 13%; electrode life: 2 years; membrane life: 1 year.
replaced by hydrogen ions, which are produced from the dissociation of water within the first bipolar membrane, not the anode as in the case of electrolysis, thus producing an acidified salt stream from this compartment.

One great advantage of this technology, is that one is able to stack as many as 200 unit cells between the two electrodes, Fig. 7; this means that a given Faraday of electricity does a significant amount of useful work in travelling from the cathode to the anode, before being dissipated in the production of gases at the two electrodes. This means low operating costs.

What one is essentially doing here is replacing electrode area with bipolar membrane area. Since bipolar membrane area is about one-half as expensive as electrode area, the capital costs are reduced significantly as well.

**Process integration:** In the case of existing R8 chlorine dioxide generators, concentrated sodium chlorate and sulphuric acid solutions are fed into them and allowed to react to produce chloric acid and sodium sulphate saltcake. In the generator, the chloric acid is subsequently reduced to chlorine dioxide through reaction with the reducing agent, methanol.

This process, however, suffers from three major problems: (1) it consumes sulphuric acid; (2) it wastes the caustic value associated with sodium chlorate; (3) it produces an unneeded by-product, sodium sulphate. How can these problems be resolved?

It is proposed here that a BME step be placed ahead of the conventional R8 chlorine dioxide generator, Fig. 8. Sodium chlorate is fed into the BME system, and split into sodium hydroxide that can go to bleaching, and into chloric acid that is subsequently fed into a modified chlorine dioxide generator. There, in the presence of a reducing agent, the chloric acid is reduced to chlorine dioxide. As Fig. 8 shows, this system does not consume sulphuric acid, it does extract the caustic value associated with sodium chlorate and, in addition, it does not produce any of the unneeded by-product, sodium sulphate, if all of the sodium chlorate is treated [22,23].

**Economics:** Assuming a mill with a chlorine dioxide production of 30 t/d, in which 34% of the sodium chlorate is treated by BME and, also assuming a membrane life of one year, then the credits will be the caustic soda produced and the sulphuric acid saved.

For such a system, the required capital investment would be about $1.1 million, the operating costs $0.7 million/yr, the credits $1.4 million/yr, which translates to a payback of 1.6 years, Table III.

Note that these preliminary economic estimates do not include such indirect costs as engineering and construction management, taxes and insurance. A more detailed economic analysis, including all costs associated with mill installation will be published in the near future.

We are now testing membrane durability because, ultimately, it is membrane life and cost which are the principal factors that will determine the economic viability of this process. For this purpose,
we have recently built at Paprican a BME pilot unit. This is a fully automated unit equipped with the necessary controls to operate on a 24-h schedule with minimum attention.

**Future Plans**

In summary, for all three membrane technologies discussed in this paper, the technical feasibility has been established and various process options identified. In addition, preliminary economic analyses defined the technological challenges that must be met to maximize the economic attractiveness of each process. What remains is to complete the ecosystem recovery boiler computer simulations defined the technological challenges that must be met to maximize the economic attractiveness of each process.

**Acknowledgements**

The authors acknowledge the expert technical assistance provided by R. Harland, D. Callender, M. Dubé, H. Barclay, D. Kolovos, A. Thibault, R. Thompson and P.Y. Wong.

The contributions of the following organizations to the various membrane-based projects are also acknowledged: Zenon Environmental Inc.; Cowan SNC Lavalin Inc.; National Research Council of Canada; Abitibi-Price Inc.; IC1 Chemicals & Polymers Ltd.; Dupont Company, Polymer Products Div.; Eltech Research Inc.; Abitibi-Price Inc.; IC1 Chemicals & Polymers Ltd.; Dupont Company, mechanical pulp, and various process options identified.

**References**