



*Institute of Paper Science and Technology
Atlanta, Georgia*

IPST Technical Paper Series Number 676

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August 1997

Submitted to
1997 AIChE Annual Meeting
Los Angeles, California
November 21, 1997

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Prepared for presentation at the 1997 Annual Meeting; Particle Separations and Membrane Processes
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INTRODUCTION

The reduction of water use by paper mills is currently one of the greatest concerns of the U.S. pulp and paper industry. The motivation is both to reduce the need for treatment of contaminated water (averaging 30 to 40 cubic meters per ton of paper), and to reduce the use of water as an increasingly rare and costly resource. Water use can be reduced by recirculation within the paper mill. The "white water" is the term for water that is removed during sheet formation of the paper. The white water is collected between the headbox and the press section. This water can be either internally reused or discharged and treated as effluent. Paper mill white water cycle closure is where white water that is currently being discharged is recirculated back into the process to replace fresh water. The white water contains particulates as well as dissolved organics and inorganics. Electrodialysis is investigated here to remove the dissolved inorganics. Fouling of the membranes is the focus of this work.

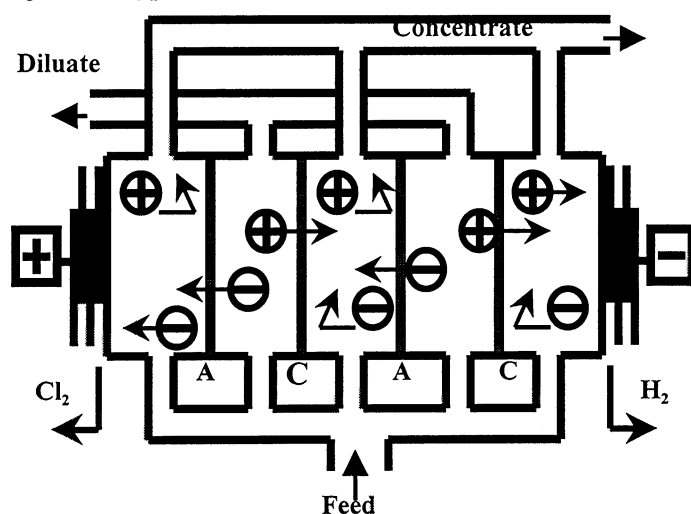
LITERATURE REVIEW

When white water is used where fresh water previously was added, three changes have been reported to occur to the white water. Increase in water temperature, total suspended solids (TSS), and total dissolved solids (TDS). Typical white water temperatures range from 110 to 120°F [1]. Temperatures have been reported as high as 160°F with closure efforts [2]. An increased white water temperature leads to increased drainage on the forming table. Increased temperature may also alter the population of biological growths. Efficient technology is already available for reusing suspended solids from the white water, so the TSS levels are not expected to increase significantly or otherwise be a problem. Going from a 0% closed system to a 100% closed system (reusing all water) could result in the TDS increasing by as much as 33-fold [3]. The TDS consists of organic macromolecules (organics) and inorganic salts (inorganics) (typically 500-5000 PPM TDS, 25-75% inorganic) [3-6]. Four problem areas are associated with increased levels of TDS: metallurgical, chemical, biological, and process/equipment related. Corrosion has been reported to increase with closure [3,6-8]. Chemical problems reported are precipitate/scale formation, decreased retention of paper fibers in the sheet that forms, decreased sizing (water resistance of the paper), loss of paper brightness, detrimental coloration, sheet mottling, and foam [3,6,8-13]. Increased levels of biological growths, slimes, and sheet odor have been reported [3,6,8,10]. Increased levels of dissolved solids can lead to increased felt plugging in the pressing operation to remove water from the paper [14,15]. For closure (reuse of white water rather than discharge) to proceed past the point where the above problems occur, a selective dissolved solids purge is needed. A separate purge for each of the organic and inorganic TDS fractions may be required.

An electrodialysis (ED) inorganic purge appears attractive for maintaining the dissolved inorganics at an acceptable level. For desalination in a similar concentration range as the inorganics in white water, electrodialysis was found to be cost-effective compared to ion exchange, multistage flash evaporation, and reverse osmosis [16]. Figure 1 shows an example of desalination by electrodialysis. An ED stack is composed of compartments formed by alternating anion selective (A) and cation selective (C) membranes. A voltage gradient is applied across the compartments, which causes the charged species in solution to migrate toward the appropriate electrode. However, the arrangement of the membranes results in the ions concentrating in every other compartment while being diluted in the remainder. The attractive feature of ED is that the minority contaminant is removed from the bulk solution,

compared to removal of the bulk water (membrane filtration, evaporation). Thus, minimal energy is

Figure 1: Typical Electrodialysis Stack



expended on the bulk stream. In addition, the ion exchange membrane is not regenerated as ion exchange resins. However, fouling and cleaning or replacement of membranes often influences the cost of operation significantly. The Department of Energy identified fouling as the number one roadblock to further applications of ED [16].

Significant fouling research has been performed for microfiltration, ultrafiltration, and to a lesser extent, reverse osmosis [17-27]. The research has shown that adsorption of macromolecules from solution does contribute to fouling of the

membranes. ED, however, does not use a pressure-driven flow of water through the membrane, and the membranes have ion exchange capacity. Thus, we expect that the mechanisms and significance of adsorption phenomena could be quite different from cross flow filtration membranes. Some ED membrane fouling research has been conducted and has shown that macromolecular adsorption does occur and can be classified as reversible (cleanable) and permanent fouling [28-31]. The permanent fouling is a measurable fraction of the overall fouling and with time can lead to an unacceptably high stack resistance (power consumption) and replacement of the membranes. The mechanism of attachment of the permanent fouling is not entirely clear. Ion exchange resin beads have a similar composition as electrodialysis membranes. Fouling research with cross-linked styrene-divinylbenzene resin beads has shown that for porous beads, the mechanism of attachment is primarily by nonionic interactions [32-38]. However, for nonporous ion exchange resins or membranes, the importance of ionic and nonionic adsorption should be evaluated again. The high crosslinking and elimination of pores in the resin beads are similar to the structure of ED membranes [39]. We chose to initially perform experiments with gel-type ion exchange beads to investigate fouling mechanisms before testing membranes. Beads offer the great advantage of very large surface areas for adsorption, while maintaining the interfacial characteristics of a membrane.

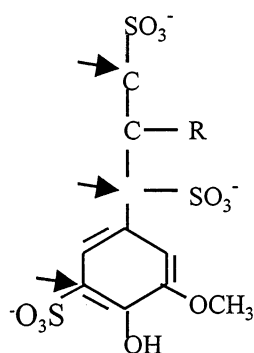
EXPERIMENTAL

Fouling is initially characterized by comparing the equilibrium adsorption of model macromolecules onto the surface of highly crosslinked resin beads with and without ion exchange groups. The direct measurement of adsorption on membranes is hampered by the very high sensitivity of analysis needed due to relatively low adsorption areas available in membrane sheets. The results from bead experiments are compared with impedance changes due to fouling of ED membranes with and without ion exchange groups.

The model white water used for experimentation includes model organic and model inorganic dissolved fractions. The model organics are sulfonated lignin and anionic polyacrylamide. There is

limited published information concerning white water organics. Sulfonated lignin was chosen to

Figure 2:
Sulfonated Lignin



represent the worst case foulant (Figure 2). Sulfonated lignin possesses both aromatic and charged groups so that nonionic and ionic interactions with the aromatic and charged groups of the membrane are possible [46]. Arrows in Figure 2 show the carbon atoms where sulfonation is expected to occur. It has been found that sulfonated aromatics are very serious foulants [31,35]. Anionic polyacrylamide is a high charge density polyelectrolyte that is used on paper machines. Polyacrylamide has no aromatic groups. Due to the higher charge density and no aromatic groups, it is expected that the polyacrylamide will exhibit a higher proportion of ionic adsorption than nonionic adsorption compared to the sulfonated lignin. The model white water inorganics are based on the averages found for unbleached kraft paper mills, which was the majority of literature data [40-43]. Only sulfate,

chloride, aluminum, and calcium concentrations were reported consistently. Below pH 7, carbonate species total less than 1 PPM in solution. The reported averages were 790 PPM sulfate, 24 PPM chloride, 1 PPM aluminum, and 124 PPM calcium. The average pH was 5.6, and the remainder of the positive charge is obtained using sodium. Using simulation software (OLI Incorporated) and laboratory results, the aluminum was found to exist as an ionized species in solution at 23°C but > 99% precipitated as aluminum hydroxide at $\geq 25^\circ\text{C}$. Inorganic precipitates are not desired during the experiments so the aluminum is not included in the model white water.

The highly crosslinked styrene divinyl benzene resin beads were chosen for their similarity in composition to ED membranes. Some heterogeneous ED membranes use resin beads cast into films. The resin beads offer a large surface area-to-volume ratio so that the concentration change of the macromolecule in solution can be easily detected after adsorption. Fluorescence is being used to determine the sulfonated lignin concentration, while inductively coupled plasma (ICP) and electrophoresis are being used to determine the inorganic concentrations. Image analysis techniques have been developed for determining the surface area per dry gram of the beads. Thus, adsorption can be expressed per unit surface area. The experiments are equilibrium adsorption experiments where adsorption is allowed to take place with mixing. The next step is cleaning (regeneration) of the resin. The sulfonated lignin that remains adsorbed after regeneration is the permanent fouling. Isotherms of the amount adsorbed will be generated as a function of concentration and of time. These will be compared to the resins with and without ion exchange groups.

The ED membrane test cell will be used to measure the impedance change that occurs to a membrane with fouling [44]. The impedance is calculated from the measured resistance, capacitance, and frequency. The capacitance can be determined from the phase angle shift of an ac signal across the membrane. Simultaneously the resistance is measured. The impedance can then be calculated from $Z = (R^2 + (1 / (2 * \pi * f * C))^2)^{0.5}$ where Z is the impedance; f is the frequency; and C is the capacitance [45]. The impedance will be measured of an anion exchange membrane and a base substrate membrane before and after fouling. The base substrate membrane has no ion exchange groups. The experiments will be performed with sulfonated lignin and then with anionic polyacrylamide as the foulant. The test cell is shown in Figure 3. The anionic foulant is added into the foulant stream and will move toward the anode. However, it will encounter the membrane and then attach. The

electrodes will be used to measure the impedance change of the membrane with adsorption of the foulant.

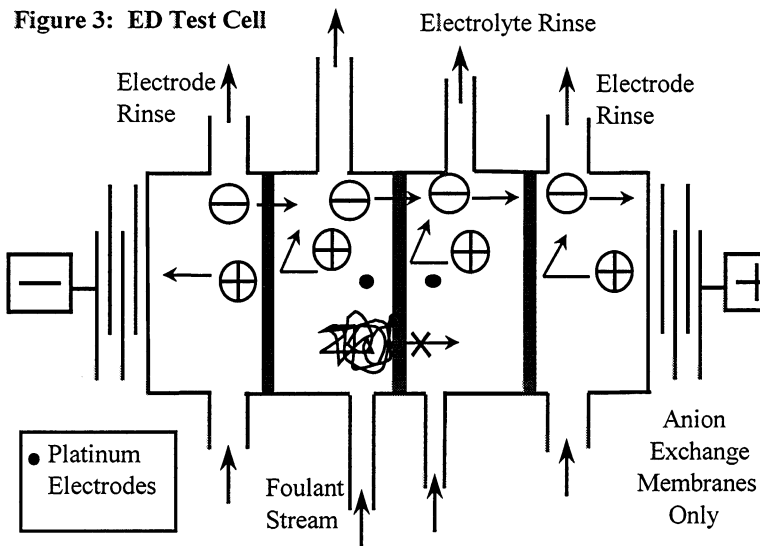


Table 1: Anion Exchange Resin Adsorption

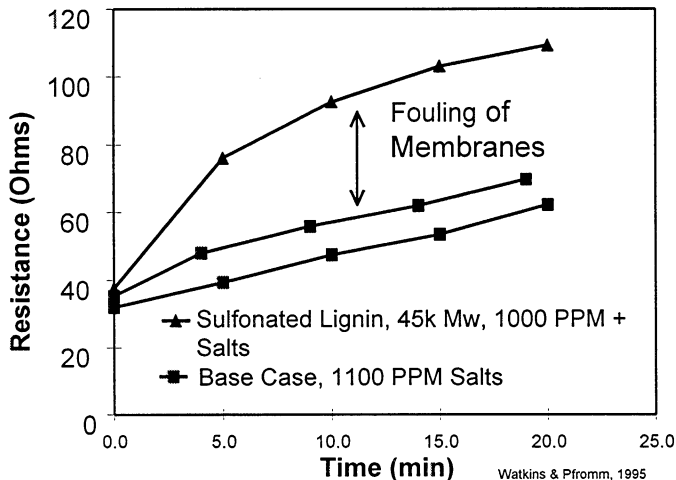
34 mg adsorbed
1.45 mg desorbed using 8 rinses of 1 N HCl
0.35 mg using 2 rinses of 2000 PPM Na_2SO_4
0.43 mg using 1M Hot Na_2SO_4
2.23 mg total desorbed

repulsion prevents adsorption onto the cationic resin. In addition, the adsorption onto the anion exchange resin was predominately of the permanent type, with only 6.6% desorbing with 11 regeneration steps.

RESULTS AND DISCUSSION
Initially sulfonated lignin adsorption experiments were conducted using porous anion and cation exchange beads. The resin beads are styrene divinyl benzene with quaternary ammonium and sulfonic ion exchange groups for the anion and cation beads, respectively. The sulfonated lignin had an average molecular weight of 65,000 grams/mol and was added at a concentration of 100 PPM. No

measurable adsorption of the sulfonated lignin occurred for the cation exchange resin. For the anion exchange resin, a total of 6.6% of the sulfonated lignin desorbed leaving 93.4% adsorbed (Table 1). This shows that the sulfonated lignin measurably adsorbs to the anion exchange resin, while it was not found to adsorb to the cation exchange resin. It may be that charge

Figure 4: Stack Electrical Resistance vs. Time



Pilot-scale experiments were conducted to determine if the sulfonated lignin measurably fouled ED membranes. The inorganic electrolyte used for all streams was approximately 1100 PPM with 693 PPM of SO_4 , 149 Ca, 190 Na, and 50 Cl. The results of the trial are shown in Figure 4. The sulfonated lignin was found to significantly foul the membranes. The sulfonated lignin run included the base case salts.

CONCLUSIONS

For paper mills where water use and effluent discharge become more restricted, white

water cycle closure will be necessary. An inorganic dissolved solids purge will be required to maintain acceptable levels. In regard to membrane separations (electrodialysis) as a purge method, fouling can be a significant cost factor. However, the nature of how permanent foulants remain attached to the membrane is not well understood. Research to investigate the mechanisms of permanent fouling is under way. Sulfonated lignin and anionic polyacrylamide are being used as foulants with a model white water system. Adsorption studies are being carried out with resin beads and membranes. Sulfonated lignin has demonstrated significant adsorption onto both of these mediums. Fouling of ED membranes by sulfonated lignin and 'permanent' adsorption onto anion exchange resin beads has been observed. Experiments using substrates with and without ion exchange groups should help clarify the mechanism of attachment for the adsorption (model fouling) observed.

ACKNOWLEDGEMENTS

We graciously acknowledge the free use of OLI Inc.'s ESP simulation software. Portions of this work were used by E. J. W. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology.

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