New ultrafiltration membrane system for spent sulfite liquor recovery

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Recycling spent sulfite liquor from the digester of a sulfonated chemimechanical pulping process promotes both economic and environmental benefits.

In 1981, the SCMP (sulfonated chemimechanical pulp) process developed by Ford and Gardner (*1*) was introduced to one of Abitibi-Price's (A-P) newsprint mills to replace the old bisulfite pulping operation, chiefly for environmental reasons (*2*). This ultra-high-yield sulfite pulp is being used as reinforcement pulp for newsprint production. However, a small percentage of kraft pulp must be added to the furnish for better paper machine operation and paper quality.

Early studies revealed that both the cooking rate and pulp quality can be significantly improved if 0.05–0.1% of disodium salt of 1,4-dihydro-9,10-dihydroxy-anthracene (SAQ) is added to the continuous digester during sulfonation (*3*). Three mill trials had been performed so far with limited success. To make the SAQ addition more effective, a higher cooking temperature was necessary. However, raising the temperature caused a large drop in pulp brightness because of the formation of burned chips. This effect was attributed to the drastic difference between the heat transfer and chemical penetration rates (*4*). Further investigations revealed that the buildup of dissolved and colloidal organic compounds in the recycled weak liquor can significantly reduce chemical penetration on the chips and cause operational problems by plugging pipes in the liquor preparation system.

Ultrafiltration (UF) processes have been applied to fermented sulfite process liquors (*5*). Self-forming ultrafiltration membranes on various supports have also been observed (*6*). This concept was evaluated for removal of high-molecular-weight lignosulfonate and other colloidal organic compounds. The cooking chemical recovered in the permeate was refortified for testing. Several laboratory cooking experiments were performed, and results strongly demonstrated that both the pulping rate and the pulp brightness from using the refortified permeate were noticeably better than that achieved using the original weak liquor, and sometimes even better than that from using freshly prepared liquor. As part of A-P's strategy for improving the SCMP operation to totally eliminate kraft pulp usage and reduce overall mill effluent treatment cost, a Du Pont ultrafiltration system was installed in the summer of 1990.

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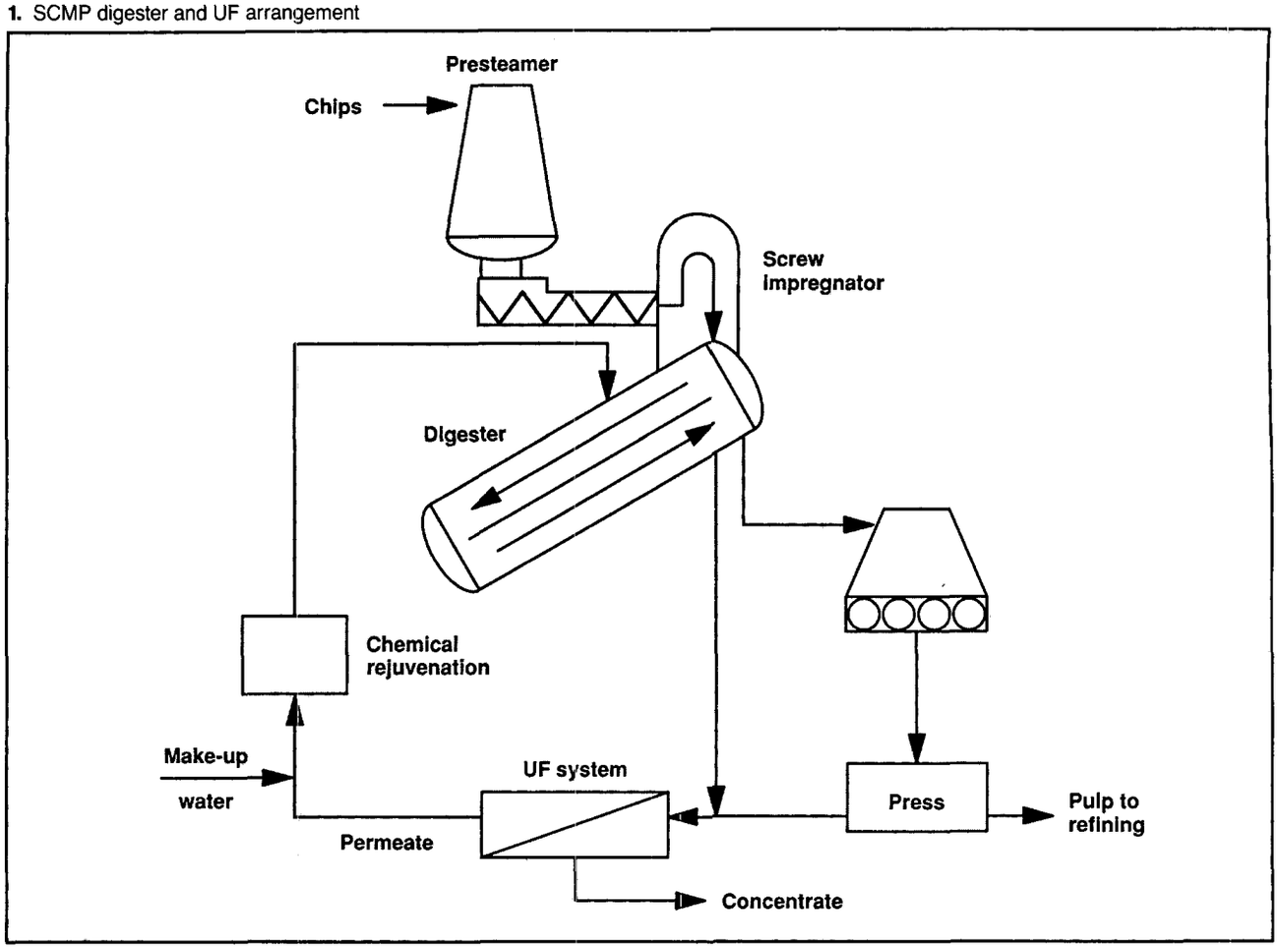
The SCMP process

The SCMP digestion process is depicted in **Fig. 1**. Chips are presteamed and fed to a plug-screw impregnator at a liquor temperature of about 155°C. Sulfonation is carried out in the digester using 12% chemical concentration as Na_2SO_3 at 7.5 pH and 150–155°C. Cooking time is about 48 min to give 90–92% yield. A French oil press is used to remove excess chemicals from the cooked chips discharged from the digester. The pressate and the weak liquor overflow were, prior to the installation of the unit, combined and refortified with fresh cooking chemical for return to the digester. Due to extensive recycling, solids tended to build up in the liquor system, reaching about 22% total solids. A major portion of the solids were dissolved and some were colloidal. Solidification of these materials was frequently encountered in the liquor preparation system. The solids, if carried over to the paper machine, will cause wet-end operating problems. Fresh water, combined with the permeate from the UF system, was refortified to supply the digester.

The essential separation

The spent liquor from the digester is a fluid that, without

1. SCMP digester and UF arrangement



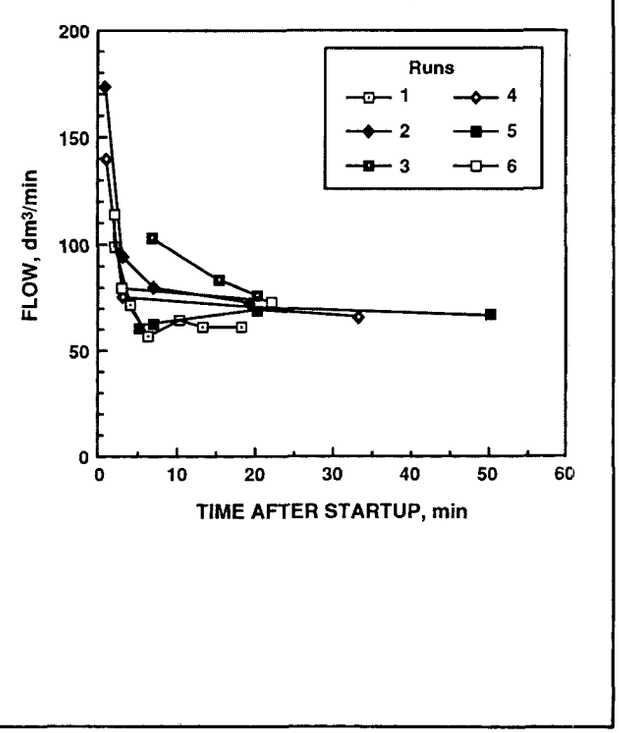
recycle, has about 12% solids distributed into three main groups. The first group is sodium sulfite, which represents about one-third of the total solids of value in recycle. The second group is also about one-third of the total solids and comprises the materials separated by the membrane. Large molecules, pitch, colloidal material, and much of the color bodies fill this group. The remaining group is the nonsulfite material found in the permeate. The permeate has been found to be uniformly clear, with some haze formation occasionally observed upon cooling. Color rejection is substantial and dependent upon conditions. Sulfite rejection is low and also depends upon conditions.

Preliminary testing of samples was conducted prior to the results reported herein to indicate proper membrane selection and to approximate flux expectations. Three membranes were tested: a microfilter, a polysaccharide membrane, and a zirconium-oxide membrane (*7*). A decision was made to pursue the zirconium-oxide (ZOSS) membrane because it offered better separation of color and little, if any, retention of the sulfite. We'll discuss the separation after we explain the establishment of the regular procedure.

The ultrafiltration unit

The ultrafiltration unit is a production-scale unit comprised of 12 modules in a flexible array. Each module

2. Initial responses of startups



is composed of 140 m (460 ft) in a serpentine arrangement of membrane tubing with an inside diameter of 1.54 cm (0.608 in.). The manifolds allow any desired parallel-series arrangement. An example is 6-3-2-1, representing six modules in parallel followed by three modules in parallel followed by two modules in parallel followed by the last single module. Other configurations used were 3-3-3-3, 3-3-3-2-1, 4-3-2-1-1-1, and an unusual 4-1-3-2-2-2 configuration. The control of the array allows for tailoring the average velocity in the fluid system within the allowable pressure-drop limitations.

The module array is fed by a Goulds multistage pump capable of 5.9-MPa (860 psi) pressure at 113 dm^3/min (30 gal/min) and 5.1-MPa (740 psi) at 151 dm^3/min (40 gal/min) flow. The module array exits through a control valve set to regulate the indicated concentrated flow. The fluid from the digester flows through a 100-μm screen to remove gross solids. The screen accepts flow from the overflow source or fluid from both sources but not from the press fluid separately. The flow enters a surge tank and is fed to the unit. Permeate from the unit is collected in a surge tank, augmented by makeup water as needed, and fed to the liquor preparation system for refortification with sulfite.

The membrane unit is serviced by a clean-in-place washing facility, comprising a 2-m^3 tank, a 30-dm^3/min (100 gal/min) pump, and a steam heat exchanger. A wash protocol has been developed. Twice-daily brief washings are conducted with a hot solution of sodium carbonate and detergent. The washing chemicals are circulated into the unit with the permeate blocked to prevent net flux. Soaking for about half an hour improves the effectiveness of this step. At intervals of about two to three weeks a more extensive washing is conducted adding a mild (pH 4) acetic acid wash and rinse.

Results and discussion

In a brief, off-site preliminary test we found that the permeability of the ZOSS membrane was such that a flux of 20 $dm^3/m^2 \cdot h$ (1 dm^3 = 1 L) was produced per megapascal of applied pressure (0.08 gal/ft^2/day/psi). This permeability held up to a point where further increases in pressure produced little increases in flux. This limiting flux depended on velocity and concentration. Its value was observed to be from 34 $dm^3/m^2 \cdot h$ to 136 $dm^3/m^2 \cdot h$ (20–80 gal/ft^2/day) in preliminary testing. It is commonly known that off-site testing will weakly indicate fluxes but normally give representative separation.

The procedure for the tests reported herein included several runs designed to evaluate the effect of operating parameters and establish the operating configuration of the system. At the same time, the frequency for washing and the protocol for washing were being evaluated. Also, samplings and observations of the permeate quality and effect on recycle were conducted. A typical run would be characterized by a short period (20 min) wherein the fluid filled the system and membrane acclimation occurred. Following the initial period, there follows a slow decline in permeation (fouling) until the decision is made to wash and subsequently return to processing.

The flux traces for the initial period of several runs are collected in **Fig. 2**. The typical response to a short-term asymptote within about 20 min is apparent. Before about 20 min the flux is not well organized and is highly variable. Run 5 is much different because the configuration, chosen to make a certain observation, caused much of the system to operate at reduced pressure. There is a systematic relationship of the flux to the velocity within the system. The velocity was lower in Run 1 and generally increased during the run sequence.

During the early part of Run 1, but after the initial period, data were obtained on the permeation rate as the outlet module flow was varied. In the configuration 6-3-2-1 of Run 1, the velocity in the last module was directly proportional to the outlet flow; the velocities in all modules were systematically affected but to a lesser degree. The resulting flux for the last module was related to the outlet flow velocity raised to a power of about 0.5. The flux for the entire system was slightly less affected, that is, to a power less than 0.5. Between Run 1 and Run 2, the configuration was changed from 6-3-2-1 to 4-3-2-1-1-1. The result was a substantial increase in pressure drop from 1.2 MPa to 3.7 MPa (180-540 psi) and an increase of around 50% in the cross-flow velocity. The increase in the 30-min flux from Run 1 to Runs 2–6 is attributed to the difference in velocity. Substantial further increases in velocity could not be accommodated since the inlet pressure of 5.5 MPa (800 psi) is only modestly higher than the 3.7-MPa (540 psi) pressure drop of Run 2.

The short-term effect of concentration of the fluid has been measured in three ways. First, individual modules of the system were isolated and the respective permeate flows determined. The range of concentrations observed in this way extend to about a four-fold concentration factor. Here concentration factor pertains to a perfectly rejected component of the original feed stream. A four-fold concentration factor implies that three-fourths of the original feed stream has been permeated.

Second, a batch of fluid representing approximately 100 dm^3/m^2 of membrane (2.5 gal/ft^2) was concentrated by allowing the permeate to exit and by retaining the reject flow mixed with the feed batch. Thus, the batch was raised to a concentration factor of 7.7, at which point the exit of the operating system was passing fluid raised beyond a concentration factor of 10.

Third, one of the runs was conducted using fluid partly diluted with water. The fluxes were observed on diluted fluid which was necessarily also diluted in energy. The temperature was used to judge the dilution, and the flux was corrected based on established estimates for the effect of temperature.

The data for the first method are for individual modules having nearly uniform conditions. The data for the concentration and dilution runs is for an entire system with conditions not so uniform. Part of the observation during the concentration run is for the last module to have nearly uniform conditions at the greatest concentration. There was a drop in temperature (from 76°C to 66°C) of the batch fluid during the execution of the concentration run, the effect of which has not been adjusted. The results of the observations, despite the difference in techniques, is reasonably consistent.

Fouling was observed to occur in a consistent manner during the test. A simple theory of fouling at constant pressure operation may be hypothesized wherein a

resistant layer is deposited in proportion to the volume of fluid passing the surface of the membrane. This layer-type fouling means that the inverse square of the flux is proportional to time. Further, the resistance of the layer-membrane assembly should be linearly related to the total volume passed through the membrane. By looking at the inverse flux squared versus time, we satisfied this hypothesis within the error bounds of data uncertainty indicated. When we plotted resistance vs. volume for Runs 1 and 2, where the temperature (T) varied, the resistance was compensated using an anticipated tendency of resistance proportional to $\exp(2500/T)$. Even so, the dilution causing the lowering of temperature also resulted in diminished fouling. The runs past number three have similar trends and slope at a consistent value, indicative of a predictable trend, unvarying from day to day.

From this, we concluded that the effects of fouling, velocity, and concentration are substantially predictable. We presumed that temperature has a predictable effect, and a production configuration was chosen for extended operation. The system was shortened somewhat to a 3-3-3-2-1 configuration and the outlet pressure maintained at 0.69 MPa (100 psi). Thus, the velocity was maintained at about 3 m/s (10 ft/s) to obtain maximum benefit.

The operation of the unit for practical implementation resulted in the selection of an operate-clean cycle of 12 h, based on a number of factors. A cleaning protocol to remove the fouling layer was investigated. The ZOSS membrane pH limits range from about pH 4 to pH 11. Cleaning with sodium carbonate and nonionic detergent (Triton X-100) proved effective in restoring flux within about 10 min but later was improved by soaking for about 30 min. The cleaning solution at 80°C is flowed into the modules arranged in parallel at a rate to displace the process fluid in about a minute. After two to three minutes the fluid is allowed to soak. During the entire operation, the permeate exit is closed to prevent net permeation. Twice-daily washings for some 38 cycles resulted in a slight decline in system flux.

After 38 regular wash cycles, we added an acetic acid wash at pH 4 and a subsequent rinse. The following run, made on August 1, then was compared to two runs made in June. The results of all three runs are substantially the same. The June runs were selected because they were the earliest runs having the same module configuration (3-3-3-2-1) and operated with an outlet pressure of 0.69 MPa (100 psi). We added a biweekly acid wash to the cleaning protocol of twice-daily washes, and the unit may be kept on-line for approximately 22 h per day.

Details of separation

We conducted simple analysis of fluid samples: total solids, sulfite, and color absorbance. The pH of all samples was about 7. We compared rejections of color, total solids, and sulfite to elapsed times for each run. Except for two low rejections in Run 2, the color rejections are uniformly around 95%. Early in Run 2 the operation was accompanied by considerable dilution both uncharacteristic of the application and harmful to color retention.

Similarly, the sulfite can be retained by the membrane when diluted. Dilution occurred in Runs 1 and 2 to a greater degree. Other runs have no known dilution. Sulfite rejection in the non-diluted cases begins at about 5% and rises to about 10% by the end of the half-day cleaning period. If the cleaning cycle were longer, the rejection rate would continue to climb. Apparently the fouling layer is capable of causing separation of sulfite to some degree.

The total solids rejection is not so sensitive to dilution as the others, varying from 30% to about 50%. Total solids rejection also increases as the fouling layer is deposited. Since the sulfite comprises one-third of the total solids, a significant portion of the solids rejection increase is that of the sulfite component. We believe that during the operating cycle the sulfite will be rejected by less than 10%, the color removed by about 95%, and the total solids reduced by one-third. These separations produce an acceptable recycle stream, though presently they represent only a fraction of the total stream to the digester.

Conclusions

Ultrafiltration of SCMP spent liquor using ZOSS membranes has been shown to retain color, pass sulfite, and retain turbid material to produce a permeate estimated to be satisfactory for continuous recycling. The effects of cross-flow velocity and concentration have been determined and are observed to control the initial flux of operation. The establishment of a regular, predictable fouling tendency is quantified following a short period to establish initial conditions. A twice-daily washing protocol of short duration and biweekly extended cleaning allow for 90% on-line operation at an average flow rate of about 57 dm^3/min (15 gal/min) from the unit.

A complete economic benefit analysis is site-dependent. The benefits include recycle of sulfite and energy in the permeate and environmental factors. These factors include reduction in toxic discharge, compression of the waste stream leading to more effective management, and reduction in maintenance arising from buildups associated with recycling of untreated liquor. Compared with pulp produced using untreated recycle, pulp strength is improved with ultrafiltration.□

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