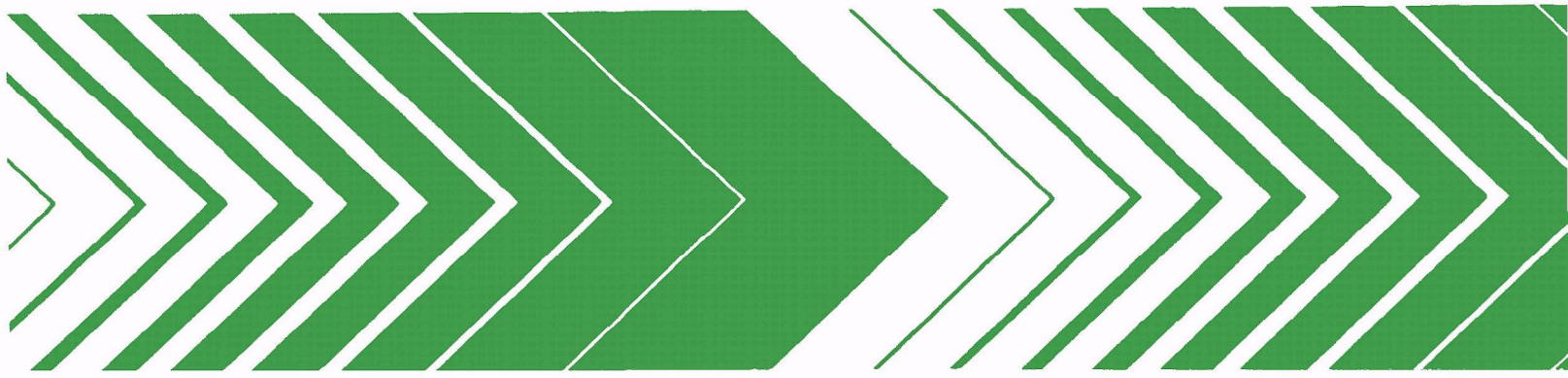


Research and Development



Color Removal from NSSC Mill Effluents by Ultrafiltration



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COLOR REMOVAL FROM NSSC MILL EFFLUENTS
BY ULTRAFILTRATION

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The subject of this report is to study the color removal from NSSC mill effluent by ultrafiltration. Results show that ultrafiltration is quite efficient in removing chromophore containing molecules from effluent. The capital requirements are about \$970 per cubic meter per day of effluent while operating cost is in the range of \$0.90 per cubic meter of effluent. With further developments in membrane technology and hardware, ultrafiltration may become an economically viable process for effluent treatment. Data on this report, coupled with pilot testing, will enable pulp and paper manufacturers to determine if UF is an economically feasible way for them to treat effluents.

For further information, please contact the Food and Wood Products Branch of the Industrial Environmental Research Laboratory, Cincinnati, Ohio.

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ABSTRACT

The feasibility of ultrafiltration in removing color from NSSC effluent was studied. The diluted shower water from the nearest NSSC mill of Green Bay Packaging, Inc. was used in all experiments. Commercially available tubular membrane modules with membranes (polysulfone, molecular weight cut off point between 6,000 and 20,000) on the outside of the tubes, were used in these experiments. Results show that ultrafiltration is feasible with operating cost of about \$0.90 per cubic meter of effluent. Color rejection was about 90%, and flux rate only about 25 l/m² hr. Permeate color was around 1000 mg/l.

Reasons for low color removal efficiency by lime treatment were examined. Our preliminary results indicate that carbohydrates are not responsible for the low efficiency.

The feed permeate and concentrate of one experiment were analyzed for thirteen toxic compounds. No chlorinated resin acids were detected. Rejection of the resin and fatty acids by UF membrane was greater than 90%.

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Special thanks to Mr. Gerald Walraven of Green Bay Packaging Inc. for supplying the Institute with feed samples.

SECTION 1

INTRODUCTION

The pulp and paper industry is one of the largest users of process or contact water. Proposed EPA regulations and strict enforcement regarding waste disposal have encouraged this industry to reduce the fresh water consumption. The pulp and paper industry has made significant progress by modifying their processes in order to reuse as much water as possible and also by using advanced treatment facilities to improve the quality of discharged effluent.

One of the problems that needs investigation is the reduction of color from pulp and paper mill effluent. At several stages of pulp and paper manufacturing, initial clear water picks up color bodies and its color becomes somewhere between pale yellow and dark brown. The discharge of colored effluent, if it is not toxic, may be regulated primarily for aesthetic reasons. Also, colored water blocks part of the sunlight and may interfere with the plant and animal life cycle.

Color bodies from pulp and paper mills are difficult to remove by conventional sedimentation and biological treatment. In the current practice 80 to 90% of the color is removed from kraft pulp and bleachery wastes by massive lime treatment (3). However, the color removal efficiency drops down when neutral sulfite semichemical (NSSC) effluents are treated in a similar way. Moreover, when partially decolorized effluent is subjected to biological treatment, color reversion has been observed (2). Reasons for this behavior of NSSC effluent are not entirely clear. Nevertheless, one must look for other ways to treat NSSC effluent.

Ultrafiltration appears to be a promising separation tool for this purpose since it is now well established in the engineer's list of separation processes. Its usefulness in purification, concentration and separation is well recognized in food, pharmaceutical, paint and other industries. However, at present, in the area of waste water treatment, ultrafiltration is considered to be feasible but uneconomical in most of the cases. The economic picture may improve as new, longer lasting membranes are developed.

The objectives of this project were:

1. to study the economic feasibility of ultrafiltration in removing color from NSSC effluent,
2. to study the effect of operating parameters, pressure, flow rate, concentration, and the effect of pretreatment and backwashing,

3. to study the performance of lime treatment prior to and after ultra-filtration, and

4. to study the removal of toxic chemicals, when present, by ultra-filtration.

The results from these studies helped determine the cost of removing color by pretreating with UF. The lime treatment studies elucidated the mechanism of color removal by lime treatment and also determined if lime treatment can be used on the UF concentrate to remove the remaining color.

Several resin and fatty acids and their chlorinated derivatives are toxic compounds. These compounds are found in some pulp and paper effluents (12). Objective 4 was included to briefly analyze for 13 of these compounds and determine if they can be separated from the effluent by UF.

SECTION 2

CONCLUSIONS

The experimental data show that color contained in a typical NSSC effluent can be concentrated by ultrafiltration. The effect of operating parameters on the performance of ultrafiltration can be summarized as follows:

1. Flux is relatively insensitive to changes in pressure from 445 kPa to 1480 kPa. Flux increases with increase in flow rate and decrease in feed color.
2. Color rejection improves with increase in pressure, feed rate or length of operation. Color rejection is not very sensitive to variations in feed color.
3. All long-term runs are characterized by an initial rapid flux decline. Color rejection appears to be invariant with time.
4. Prefiltering feed with 10 μm filter does not improve membrane performance.
5. Periodic membrane cleaning is essential. Five minutes backflushing with water increased flux to 90% of original value.

Preliminary economic analysis indicates that the concentration step will be expensive (about \$0.90/m³ of feed). The ultimate disposal costs must be added to these already expensive operating costs. The capital requirements are not excessive, being about \$970 per cubic meter per day of feed.

Experimental data indicate that the low molecular weight carbohydrates are not the major reason for poor color removal from NSSC effluents by lime treatment. Conversion of the polymeric sugars to simple sugars by acid hydrolysis did not significantly improve color removal by lime treatment. Similarly, when these simple sugars were removed by ultrafiltration, no significant increase in color removal by lime treatment was observed. More work is needed to better understand mechanisms of color removal by lime treatment.

Lime treatment experiments on raw and ultrafiltered solutions show that the percent color removal by a given level of lime is constant. Additionally, the maximum level of color removal attainable is less than 80 percent. Thus, lime treatment of the ultrafiltration concentrate would probably not give satisfactory color removal even if the ultrafiltration process were economically feasible.

Small amounts of resin and fatty acids were detectable. No chlorinated acids were found. Although the data are questionable, the membranes rejected approximately 90% of the resin and fatty acids.

SECTION 3

RECOMMENDATIONS

It is important to know why color removal by lime treatment is not as effective with NSSC effluent as it is with kraft effluent. More work is needed to pinpoint chemical components, for example, lignin compounds, in NSSC effluent which lower the color removal efficiency.

Ultrafiltration is economical if useful products can be made from permeate and/or concentrate. Further research in this area could be quite fruitful. Some mills are already following this approach.

Membrane replacement cost accounts for about 40% of the operating cost. Less expensive and more durable membranes could improve the economics of using ultrafiltration.

SECTION 4

LITERATURE SURVEY

Principal color removal methods include:

1. lime or lime-magnesium precipitation
2. adsorption by ion exchange or activated carbon, and
3. membrane processes — reverse osmosis or ultrafiltration.

These and other miscellaneous color removal methods have been reviewed by Rush and Shannon (1).

Lime precipitation is one of the most common methods of removing color from mill effluent. The large amount of lime causes a big sludge disposal problem. Additionally, as shown by Dugal, *et al.* (2), lime treatment is not very effective in removing color bodies from NSSC effluent.

Two adsorption processes have been reported, one developed by a U.S. company, Rohm and Haas, and the other developed in Sweden and called the Uddeholm-Kamyr process (3,4). Even though 70 to 90% color removal from kraft bleach plant effluent is reported, two drawbacks of these processes are the requirement of low pH (≤ 2.5) for optimum efficiency and a possibility of buildup of chlorides in the pulping process. Activated carbon adsorption is primarily useful as a polishing step after precipitation (1).

Fremont, *et al.* (5) at Champion Papers, in an EPA supported project, studied decolorization of the first caustic extraction stage effluent by ultrafiltration. Color removals from 90 to 97% were obtained. Flux rates were in the range of 15 to 20 gal/ft² day (25 to 34 l/m² day). Recently, Maples and Lang (6) studied ultrafiltration and reverse osmosis in a pilot plant to remove color from caustic bleach effluent. Their calculations show that in-plant color removal by membrane processes is cost competitive with external treatments.

Considerable work has been done to treat pulp and paper mill effluents by membrane processes. Since some of the work done at the Institute has been summarized by Bansal and Wiley (7) in a review article, only the pertinent work will be considered in this report.

Collins, *et al.* (8) used ultrafiltration to study the separation of reducing sugars and lignosulfonates from calcium base and NSSC effluents. Flux rates were in the range of 10 gal/ft² day (17 l/m² day). They found that when a feed containing about 25% reducing sugar on solids is used, it is possible to get a permeate with about 52% reducing sugar on solids. If useful products

can be made from a concentrate containing a large fraction of lignosulfonate and from a permeate containing a significant amount of sugar, ultrafiltration can be economically attractive.

Bansal and Wiley (9) pointed out that ultrafiltration and reverse osmosis can be successfully used to fractionate and concentrate spent sulfite liquors. It was shown that a combined operation of ultrafiltration and reverse osmosis could reduce the thermal energy requirement to one-third of that required for conventional evaporators.

SECTION 5

EFFLUENTS AND EQUIPMENT

In order to cut the sample transit time, we elected to use effluents from the nearest NSSC mill — Green Bay Packaging, Inc. These effluents are more concentrated than most NSSC mills due to the extensive recycling of process water. For comparison, a visit was made to the Hoerner Waldorf Corporation NSSC mill in Minneapolis to obtain effluent samples from a mill with less extensive recycle.

These samples confirmed earlier speculation that the shower and press waters are the most highly colored. Analyses of these samples also showed that the Green Bay Packaging shower water is about four times the concentration (based on total solids and color) of that from an open mill. Therefore, we diluted the Green Bay Packaging shower water 4:1 in our ultrafiltration experiments. Grab samples were taken from process water storage tank at the Green Bay Packaging mill.

Western Dynamic's membrane modules were used in our experiments. In these modules, the membrane is outside the tube, and the permeate flows inside the tube. Tubular membrane modules have greater resistance to fouling and plugging and are easier to clean compared to compact units like spiral wound and hollow fiber modules. Each membrane module is about 3 m long and contains 7 membrane tubes. Each tube is 1.27 cm in diameter. The total membrane area per module is about 1 m². Two such modules arranged in series were used in this experiment, as shown in Fig. 1.

The polysulfone membrane used is quite stable at any pH and even at high temperature. The membrane molecular weight cutoff point is anywhere between 6,000 and 20,000. According to the manufacturer* polyethylene glycol (PEG) with molecular weight of 6,000 is rejected by only 5% whereas the mixture of 6,000 molecular weight PEG with 0.1% of 20,000 molecular weight PEG is rejected by 95%. Thus, molecular cutoff point is between 6,000 and 20,000 for this membrane.

*McLendon, Dr. H., Western Dynetics, Personal Communication.

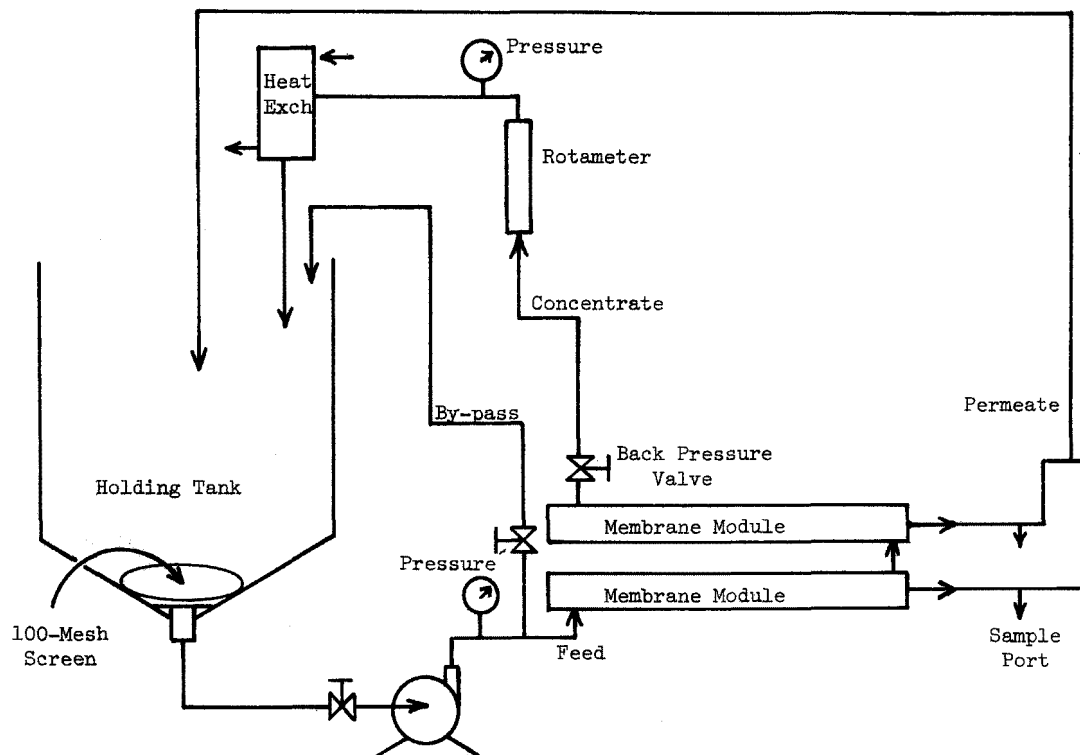


Figure 1. Experimental setup.

SECTION 6

EXPERIMENTAL PLAN

One of the objectives of this project, as mentioned earlier, is to study the effects of various operating parameters, pressure, flow rate, concentration, and the effects of pretreatment and backwashing. Accordingly, an experimental plan was designed where operating parameters were varied within their practical limits. This plan is presented below. For all runs temperature was maintained at 50°C — commonly encountered in closed mills. pH was not monitored.

In all but two experimental runs (VI and VII), both permeate and concentrate were recycled as shown in Fig. 1.

- I. The effects of feed rate and pressure were studied at the following operating conditions.

Pressure, kPa (psi): 1480(215), 800(116), 445(65)

Feed rate, l/min (gpm): 75 (20), 45(12), 30(8), 15(4)

- II. The effects of feed solids and color were studied at two selected operating conditions.

	Pressure, kPa	Feed Rate, l/min
1.	800	75
2.	445	75

- III. Flux decline rates were investigated by carrying out three long-term runs lasting for 72 to 96 hours at the following operating conditions.

	Pressure, kPa	Feed Rate, l/min
1.	800	75
2.	445	75
3.	445	30

- IV. The effects of feed pretreatment were studied by prefiltering feed through a 10 μ m filter.

- V. One run was carried out to study the effectiveness of backwashing.

- VI. A concentration run was carried out (where concentrate was recycled but permeate was not) to study the membrane performance as feed concentration

was continuously increased. Runs IV, V and VI were conducted at desirable operating conditions, viz., 800 kPa pressure with a feed rate of 75 l/min, as determined from experimental set I and II described above.

VII. Neither permeate nor concentrate was recycled in this run to duplicate practical ultrafiltration operation. This run was carried out at 445 kPa pressure with a feed rate of 30 l/min.

Results obtained from these experiments are presented and discussed in the next section, followed by results from the lime precipitation experiment, toxic chemical analyses, and some preliminary economic analysis.

SECTION 7

ULTRAFILTRATION RESULTS

THE EFFECTS OF FEED RATE AND PRESSURE

Results are presented in Table 1 and Fig. 2, 3 and 4. In all the runs, feed solids ranged from 5.5 to 7.7 g/l while feed color varied from 11,400 to 16,000 mg/l. Flux was about 25 l/m² hr at a low feed rate (15 l/min) and 47 l/m² hr at a higher flow rate (75 l/min). In two hours flux declined by 40% and 20% at low and high feed rates, respectively. Solids and color rejection varied from 40 to 70% and 80 to 98%, respectively.

Figure 2 shows that flux is more or less independent of pressure. This is due to the formation of a gel or slime layer. An increase in pressure merely increases the thickness of this gel layer such that the flux remains constant:

$$\text{Flux} = \frac{\text{Driving Force}}{\text{Resistance}}$$

The driving force is an applied pressure drop across the membrane, while the resistance depends on the nature and thickness of both membrane and the overlying gel layer.

Theoretically, as the wall shear is increased by increasing the flow rate, gel thickness decreases. Thus, at a fixed pressure, the effect of increasing the flow rate is to lower the resistance to permeate transports and hence increase the flux. This is confirmed by the results of Fig. 2.

The thickness of the gel or slime layer steadily increases with time, and consequently flux declines. The rate of flux decline decreases with increase in feed rate, as can be seen from Fig. 3. For the range of pressure studied, pressure has very little effect on the rate of flux decline.

Figure 4 shows that color rejection improves with increase in pressure or feed rate or time. Since the gel thickness increases with increase in time and pressure it is clear why the color rejection improves with increase in these two parameters. One would expect, for the same reason, that color rejection will improve as the feed rate decreases. However, this is not true, as can be seen from Fig. 4. One explanation is that as the feed rate increases, transport of "solvent" increases at a faster rate than the increase in the transport of "solute." One should note that in Fig. 4, the ordinate varies from only 80 to 100%, whereas feed rate increases from 15 to 75 l/min. Thus, we are talking about relatively small changes in rejection over a wider range of operating conditions. Another reason for the observed

TABLE 1. THE EFFECT OF FEED RATE AND PRESSURE *

Pressure, kPa	Feed			Permeate, initial/final (2 hr)			Rejection, %	
	Rate, l/min	Solids, g/l	Color, mg/l	Flux, l/m ² hr	Solids, g/l	Color, mg/l	Solids, initial/after 2 hr	Color, initial/after 2 hr
1480	75	6.76	15,300	46.7/34.5	2.26/2.01	480/288	66.6/70.3	96.8/98.1
1480	45	6.43	15,000	36.1/26.3	2.23/2.03	484/344	65.3/68.4	96.8/97.7
1480	30	6.53	14,580	30.8/22.8	2.39/2.06	560/350	63.4/68.5	96.1/97.6
1480	15	6.41	14,500	28.8/17.7	2.69/2.19	790/455	58.0/65.8	94.4/96.8
800	75	6.44	14,500	43.9/35.8	2.93/2.78	800/616	54.5/56.8	94.3/95.6
800	45	7.62	15,880	33.8/23.8	3.40/3.25	992/756	55.4/57.3	93.8/95.3
800	30	6.88	16,000	28.0/20.0	3.55/3.22	1320/800	48.4/53.2	91.8/95.0
800	15	6.84	15,880	27.1/17.6	3.99/3.24	2208/960	41.7/52.6	86.0/93.9
445	75	6.15	14,440	39.3/32.3	2.99/2.94	1150/940	51.4/52.2	91.8/93.3
445	45	5.91	14,000	31.3/24.3	2.95/2.87	1370/970	50.1/51.4	90.2/93.1
445	30	5.81	13,560	28.8/21.4	3.07/2.83	1740/1080	47.2/51.3	87.0/91.9
445	15	5.46	11,375	30.0/19.0	3.13/2.70	2272/1200	42.7/49.5	80.0/89.4

*(1) Color was measured in chloro-platinum units by the method of NCASI Technical Bulletin No. 253, December 1971.

(2) Solids were measured as total solids by gravimetric method.

(3) % Rejection = $1 - \left[\frac{\text{Concentration in Permeate}}{\text{Concentration in Feed}} \right] \times 100.$

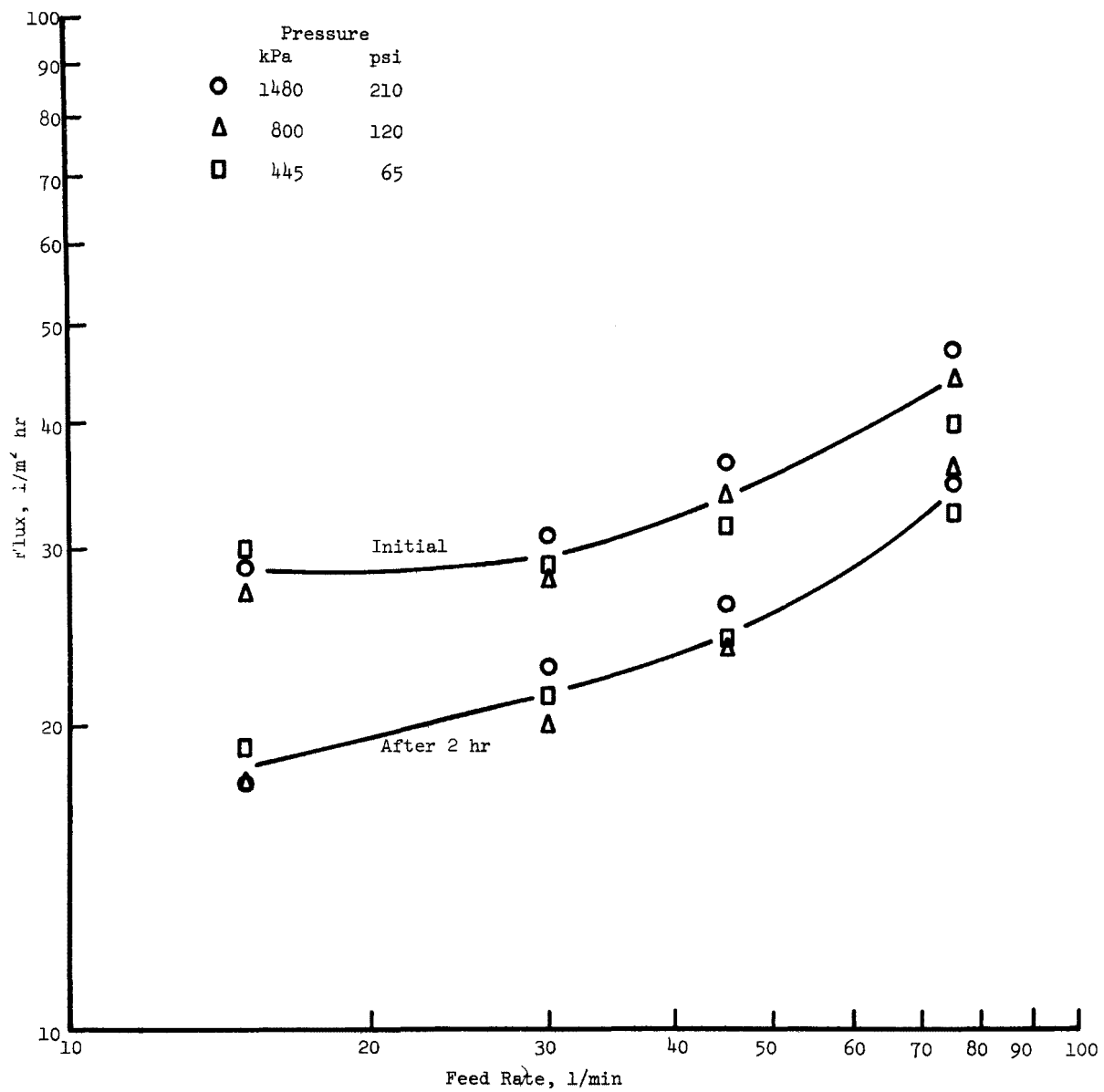


Figure 2. Variation of permeate flux with feed at different pressures.

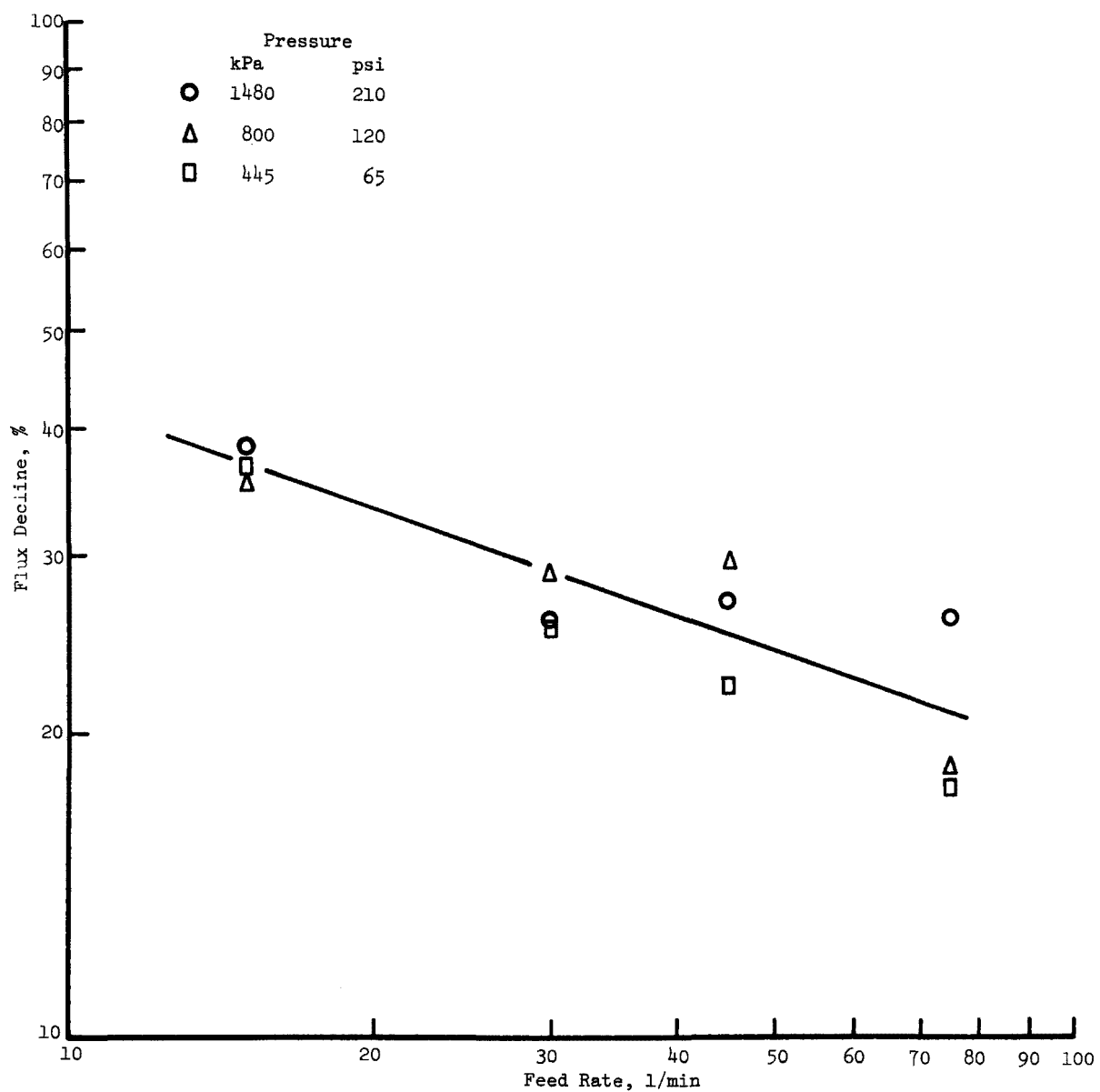


Figure 3. Flux decline in two hours as a function of feed rate.

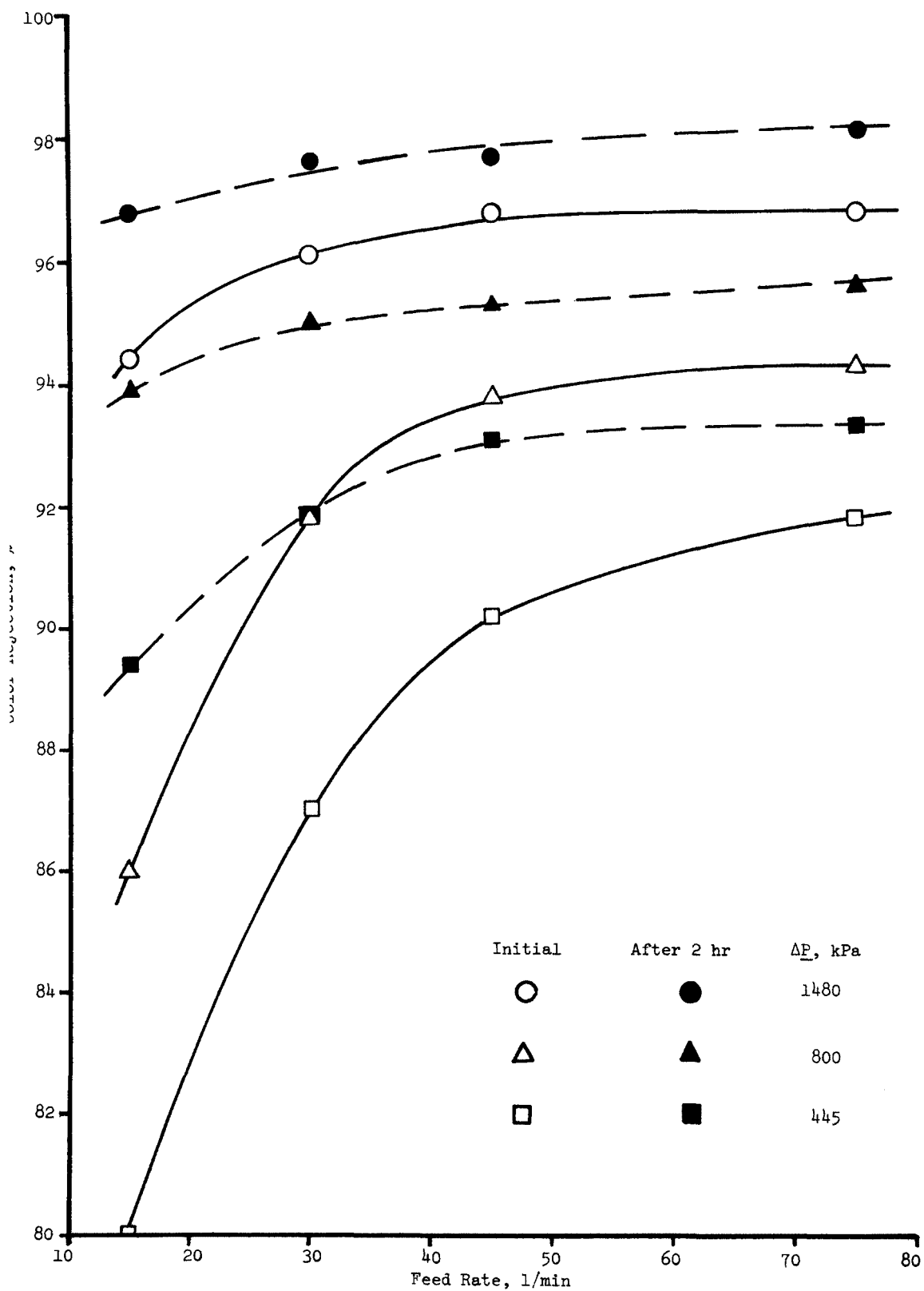


Figure 4. Variation of color rejection with feed rate, pressure and time.

variation of rejection with feed rate is concentration polarization. In other words, rejected species will accumulate in the vicinity of the gel layer, and the resulting concentration polarization becomes severe as flow rate decreases.

It is evident from the above qualitative arguments that instead of rejection, the variation of a total "solute" transported, or solute flux, should be considered. Solute flux is the product of solvent flux ($1/m^2$ hr) and permeate concentration, say, permeate color (mg/l):

$$\text{Solute Flux (mg/m}^2 \text{ hr)} = [\text{Solvent Flux (1/m}^2 \text{ hr)}] \times [\text{Permeate Color (mg/l)}]$$

Since feed color is not uniform in experimental runs presented in Table 1, its effect on solute flux must be removed by normalizing solute flux:

$$\text{Normalized Solute Flux (1/m}^2 \text{ hr)} = \frac{\text{Solute Flux (mg/m}^2 \text{ hr)}}{\text{Feed Color (mg/l)}}$$

The variation of normalized solute flux with flow rate at different pressures is shown in Table 2. As the flow rate decreases, the normalized solute flux first decreases and then increases. At high flow rates (75 and 45 l/min) concentration polarization is negligible due to turbulent flow. Consequently, as the flow rate is lowered, gel thickness increases and the normalized solute flux decreases. At lower feed rates (30 and 15 l/min), due to concentration polarization, decreasing feed rates increases the normalized solute flux.

The data in Table 1 were carefully analyzed to see if there is any correlation between performance parameters (flux and rejection) and operating parameters (feed flow rate and pressure). Since rejection is not a sensitive parameter, $100(1-R)$, where R is the fraction rejected, was selected as the parameter reflecting membrane selectivity. One would like to have a membrane with the highest value of the ratio of permeate rate to $100(1-R)$. Since this ratio depends on feed rate and pressure, a correlation of the following type is assumed:

$$A_1 [\text{Feed Rate, l/min}]^{b_1} [\Delta P, \text{kPa}]^{b_2} = \frac{[\text{Permeate Rate, 1/m}^2 \text{ hr}]^{b_3}}{100(1-R)}$$

where R is the fraction of solute rejected:

$$R = 1 - \frac{\text{Permeate Concentration}}{\text{Feed Concentration}}$$

It can be seen from Fig. 5 that correlation of this type applies quite well to the present data for the following values of constants which were evaluated by regression analysis:

$$A_1 = 6.73 \times 10^{-4}$$

$$b_1 = 0.783$$

$$b_2 = 1.033$$

$$b_3 = 1.24$$

Note that the effect of feed concentration is not taken into account here.

TABLE 2. NORMALIZED SOLUTE FLUX AT
DIFFERENT PRESSURES AND FEED RATES

Pressure	Feed rate	Normalized solute flux, l/m ² hr
1480	75	1.47
	45	1.17
	30	1.18
	15	1.57
800	75	2.42
	45	2.11
	30	2.31
	15	3.77
445	75	3.13
	45	3.06
	30	3.70
	15	6.00

$$\text{Normalized Solute Flux} = \frac{(\text{Permeate Rate, l/m}^2 \text{ hr})(\text{Permeate Color, mg/l})}{(\text{Feed Color, mg/l})}$$

It is expected that this type of correlation can be used to compare the performance characteristics of different membranes and membrane modules. One with higher values of A , b_1 , and b_2 and a lower value of b_3 should perform better than the other in terms of flux and/or rejection.

THE EFFECTS OF FEED SOLIDS AND COLOR

Two operating conditions were selected to study the effects of feed concentration:

	Pressure, kPa	Feed Rate, l/min
1.	800	75
2.	445	30

Results are presented in Table 3. Data from Tables 1 and 3 are plotted in Fig. 6 to show the variation of flux with feed color at the above two operating conditions. Figure 6 also shows initial flux and flux after two hours of operation.

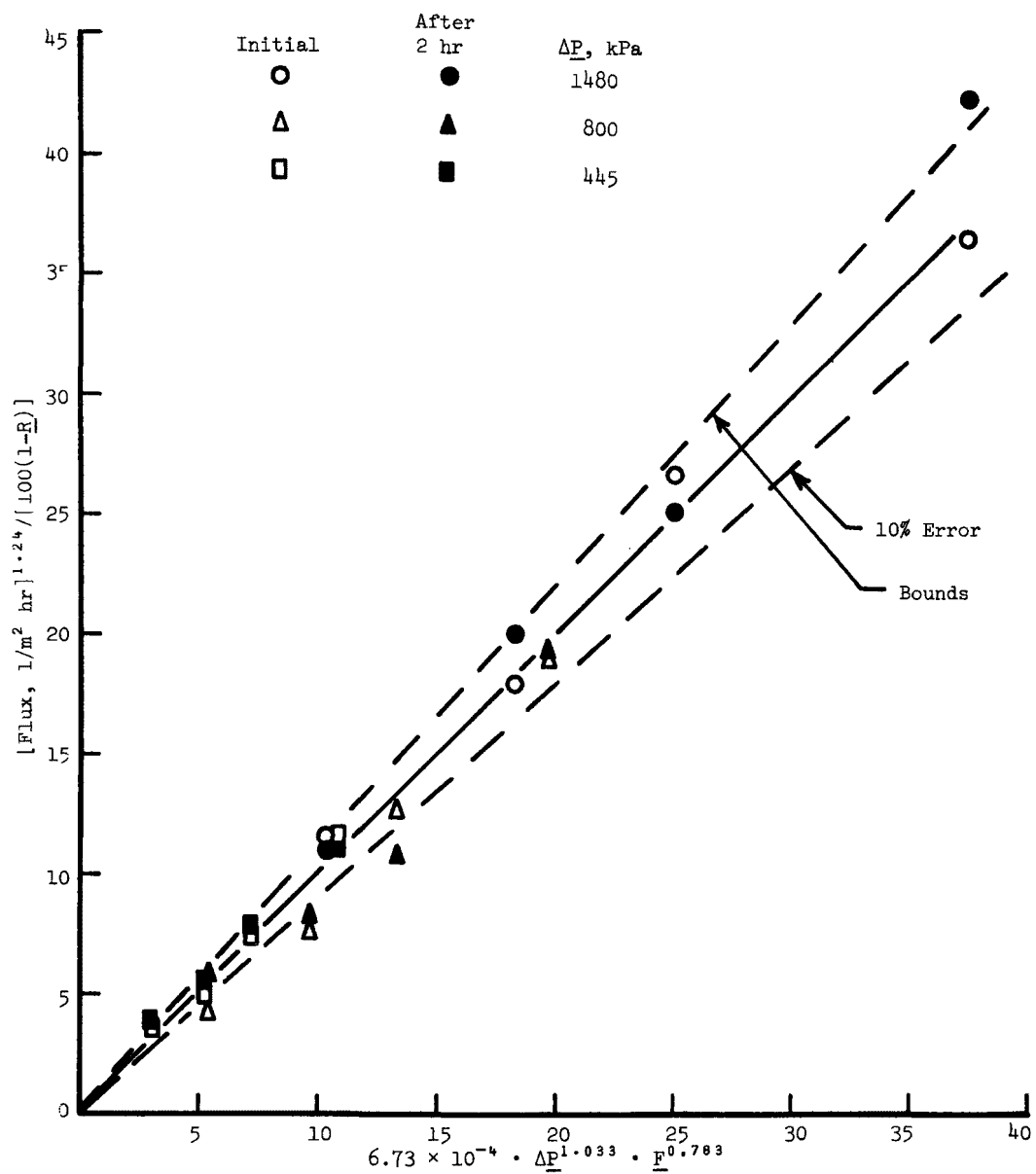


Figure 5. Correlation of flux and rejection with feed rate and pressure.

TABLE 3. THE EFFECT OF FEED SOLIDS AND COLOR

Pressure, kPa	Rate, l/min	Feed		Permeate, initial/final (2 hr)			Rejection, %	
		Solids, g/l	Color, mg/l	Flux, l/m ² hr	Solids, g/l	Color, mg/l	Solids, initial/ after 2 hr	Color, initial/ after 2 hr
800	75	11.0	20,300	38.9/31.5	5.11/5.08	1260/1088	53.5/53.8	93.9/94.7
445	30	10.4	19,690	29.0/19.6	5.83/5.71	2140/1750	43.9/45.1	88.9/91.0
800	75	16.1	34,200	31.8/24.0	7.88/7.66	2200/1900	51.1/52.4	93.5/94.4
445	30	15.9	32,000	16.9/10.9	9.4/9.32	3680/3400	40.9/41.4	88.5/89.4
800	75	10.9	22,200	33.5/22.1	4.81/4.70	1225/1012	55.9/56.9	94.5/95.5
445	30	10.5	20,800	21.2/15.1	5.81/5.60	2320/1920	44.7/46.7	88.8/90.8

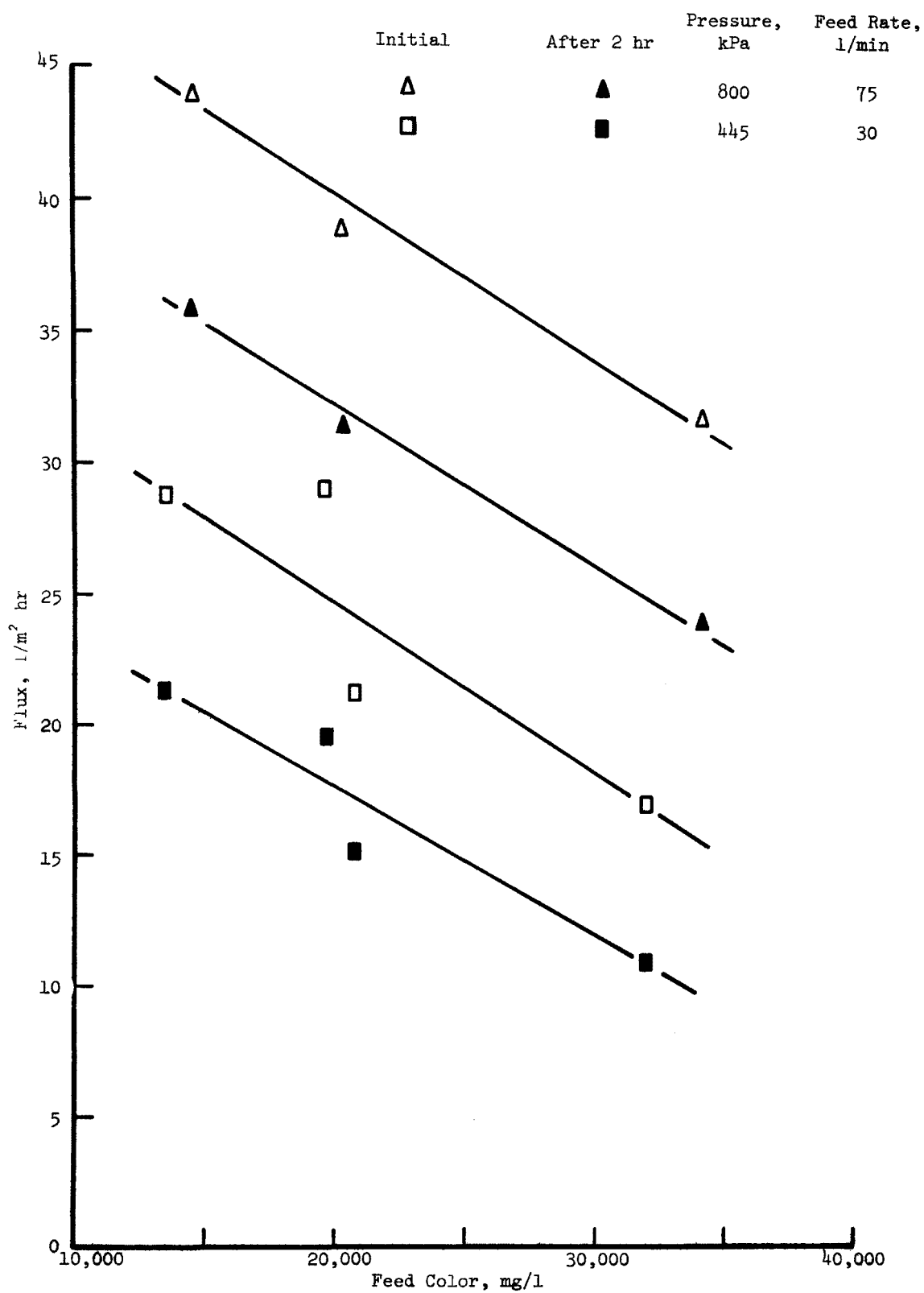


Figure 6. The effect of feed color.

For a given pressure and feed rate, flux decreases with increase in feed color. This is not surprising, since, as explained earlier, gel thickness increases with increase in feed color. Thus, resistance to the transport of solvent increases as color concentration in feed increases.

Rate of flux decline also increases with increase in feed color. For example, at 445 kPa pressure and 30 l/min flow rate, flux declines in two hours were 26 and 36% at feed colors of 13,600 and 32,000 mg/l, respectively. This can be attributed to the relatively rapid buildup of gel layer when feed color is high.

LONG-TERM RUNS

Three runs were made to study membrane performance over a period of 72 to 96 hours. Results are summarized below, and details are given in Tables 4-6.

In all three runs permeate and concentrate were recycled instead of using fresh feed. This was done to avoid handling large volume of feed which could not be done within the project budget. Since the results obtained by recycling or with fresh feed are indistinguishable, as will be shown later, recycling is justified.

Table no.	Pressure, kPa	Feed rate, l/min	% Flux decline in 74 to 76 hr	Time for 50% flux decline, hr	Av. solid rejection	Av. color rejection
4	800	75	64	11.5	55.9	95.4
5	445	30	81	7.5	48.9	92.4
6	445	75	63	12.0	52.8	93.3

It is clear from the above results that membrane performance is highly sensitive to feed rate and relatively insensitive to the applied pressure. Thus, long-term results are in concurrence with the short-time results discussed earlier.

One of the characteristics of all long-term runs is initial rapid flux decline. Thus, flux declined by about 50% in the first 8 to 12 hours and by 60 to 80% in 70 to 80 hours. Figure 7 shows that flux leveled off in about 50 hr.

One would expect that as gel thickness increases with time, rejection should improve with time as shown in Fig. 4. However, Tables 4 to 6 show that the rejection of color and solids does not show systematic variation with time. As discussed earlier, rejection is not the proper parameter to be considered, since it depends on the relative changes in the solute and solvent transport rates. Instead, solute flux or normalized solute flux should be considered. Indeed, results of Tables 4 to 6 indicate that solute flux does decrease with time, as expected.

TABLE 4. LONG-TERM RUN

Time, hr	Pressure, kPa	Rate, l/min	Feed		Flux, l/m ² hr	Permeate		Rejection, %	
			Solids, g/l	Color, mg/l		Solids, g/l	Color, mg/l	Solids	Color
1	800	75	10.73	26,150	27.5	4.93	1731	54.1	93.4
5	800	75	10.85	27,310	18.7	4.76	1461	56.1	94.7
21	800	75	* 8.05	28,080	13.0	6.52	1423	19.0	94.9
28	800	75	* 8.08	29,610	11.9	6.51	1816	19.4	93.9
45.5	800	75	10.93	22,500	10.8	4.77	870	56.4	96.1
53	800	75	10.98	23,090	10.5	4.81	1058	56.2	95.4
69	800	75	10.90	23,680	10.1	4.83	980	55.7	95.9
74	800	75	11.07	24,080	10.0	4.86	995	56.1	95.9
93.5	800	75	11.09	23,290	10.0	4.82	995	56.5	95.7
99	800	75	11.15	22,900	9.7	4.85	790	56.5	96.6
Average			10.96	24,125		4.83	1110	55.9	95.4
*(omit 3rd & 4th reading)								±1.2	±1.6
Std. Dev.			0.14	1,705		0.054	320		

THE EFFECT OF FEED PRETREATMENT

In many cases, the feed may have to be treated prior to ultrafiltration to avoid excessive fouling. Feed pretreatment may be useful if it improves membrane performance, particularly by increasing flux rate and lowering the rate of flux decline without significantly affecting rejection. The only pretreatment tested in this program was filtering through a 10 μ m cartridge filter. (Effluent was not prescreened at the mill.)

The ratio of solids in the filtrate to solids in feed was 0.98. It appears that feed consists largely of suspended matter and macromolecules, less than 10 μ m in diameter, which are responsible for membrane fouling.

Results obtained with prefiltered feed are presented in Table 7. These results should be compared with those for unfiltered feed (Table 4). Note that the feed color in the two runs is significantly different and, consequently, these results should be compared together with Fig. 6.

It can be seen from Tables 4 and 7 and Fig. 7 that flux decline in 2 hr is about 25% when feed is prefiltered, compared to 21% when no prefiltration

was carried out. Thus, prefiltering does not help. In fact, the result of prefiltering is to increase the rate of flux decline. The difference is significant when one notes that feed color in the prefiltration run was much lower compared to that in the no prefiltration case (Table 6). One may argue that by removing relatively larger particles, a compact, less porous fouling layer is formed when the feed is prefiltered. However, in view of the fact that we do not have a reproducible feed, the evidence is not conclusive.

TABLE 5. LONG-TERM RUN

Time, hr	Pressure, kPa	Feed			Permeate			Rejection, %	
		Rate, l/min	Solids, g/l	Color, mg/l	Flux, l/m ² hr	Solids, g/l	Color, mg/l	Solids	Color
1.5	445	30	9.55	28,800	15.1	4.80	1026	49.7	96.4
19.5	445	30	9.39	21,620	6.8	4.86	1792	48.2	91.7
27	445	30	9.36	21,430	5.8	4.90	1823	47.6	91.5
42.5	445	30	9.21	24,350	4.5	4.78	1870	48.1	92.3
50.5	445	30	8.97	21,430	3.8	4.60	1901	48.7	91.1
66.75	445	30	8.94	20,650	3.2	4.52	1823	49.4	91.2
74	445	30	9.03	20,840	2.9	4.54	1886	49.7	91.0
	Average		9.21	22,731		4.71	1732	48.9 ±1.1	92.4 ±2.7
	Std. Dev.		0.24	2,943		0.16	314		

One can definitely conclude that prefiltering with the 10 μ m filter does not improve membrane performance. Pretreatment was, therefore, not considered further.

THE EFFECT OF BACKWASHING

Since flux declines as the operation time increases, it is important to know the effect of backwashing on membrane performance. Results obtained by backflushing for 5 min with tap water are presented in Table 8 and Fig. 8.

Flux declined by about 30% in 4.2 hr (Fig. 8). Backflushing with tap water for 5 min increased the flux to 90% of the original value. We think more vigorous washing methods, by using chemicals like Biz or detergent (11), could increase the flux to close to 100% of the original value.

Flux decline rate after washing is not too different from that prior to washing. Flux returns to the prewashing value in about 2 to 2.5 hr. Thus, the effect of washing is to improve the flux but not the rate of flux decline.

This is one of the problems with membrane processes. If the rate of flux decline is reduced, efficiency of membrane processes could be improved.

TABLE 6. LONG-TERM RUN*

Hr	Feed		Flux, l/m ² hr	Permeate		Rejection, %	
	Solids, g/l	Color, mg/l		Solids, g/l	Color, mg/l	Solids	Color
2	7.91	19,740	28.0	2.35	1550	70.3	92.1
5	7.85	18,750	24.0	3.83	1140	51.2	93.9
22	7.80	22,300	13.8	3.80	1180	51.3	94.7
29	7.78	23,450	12.0	3.88	1200	50.1	94.9
46	7.61	18,900	10.8	3.82	1200	50.2	93.7
53	7.65	18,530	10.5	3.85	1380	49.7	92.6
70	7.71	18,530	10.5	3.82	1360	50.5	92.7
76	7.61	17,820	10.5	3.88	1450	49.0	91.9
Average	7.74	19,750		3.65	1310	52.8	93.3
Std. Dev.	0.113	2,020		0.53	150	7.11	0.0116

*Pressure, 445 kPa; feed rate, 75 l/min.

TABLE 7. FEED PREFILTERED THROUGH 10 μ m FILTER*

Hr	Feed		Flux, l/m ² hr	Permeate		Rejection, %	
	Solids, g/l	Color, mg/l		Solids, g/l	Color, mg/l	Solids	Color
0.5			38.8				
1.0	5.57	11,450	35.9	2.20	440	60.5	96.2
1.5			32.4				
2.0			30.8				
2.5	5.59	11,450	29.2	2.09	350	62.6	96.9
18.0	5.95	11,800	20.6	2.10	440	64.7	96.3
22.0	3.36	13,250	19.2	2.10	475	37.5	96.4

*Pressure, 800 kPa; feed rate, 75 l/min.

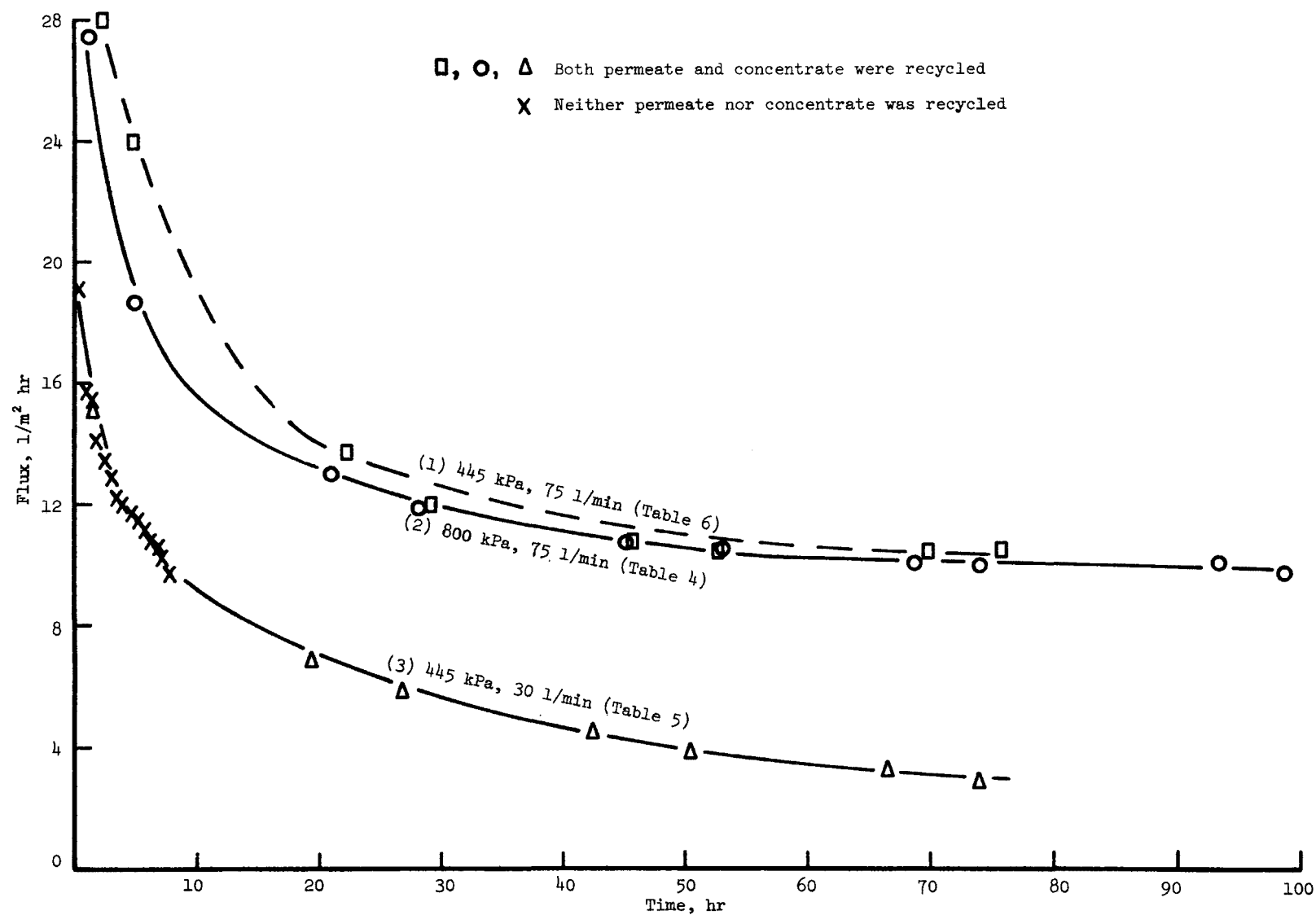


Figure 7. Long-term flux decline effects.

TABLE 8. THE EFFECT OF BACKWASHING*

Hr	Feed		Flux, l/m ² hr	Permeate		Rejection, %	
	Solids, g/l	Color, mg/l		Solids, g/l	Color, mg/l	Solids	Color
0.5	9.31	18,000	30.8	4.22	888	54.7	95.1
1.2			27.5	3.90	792		
1.7			24.8	4.00	748		
2.2	9.57	19,050	23.1	3.87	736	59.6	96.1
2.7			23.1	3.97	720		
3.2			22.8	3.97	736		
3.7			22.1	3.93	776		
4.2	9.54	19,050	21.8	3.95	704	58.6	96.3
<u>Backflushed for 5 min with tap water</u>							
	Wash water			7.07	11,800		
4.2							
4.4			27.7	3.80	820		
4.9	9.08	17,300	25.2	3.76	736	58.6	95.7
5.4			23.7	3.79	736		
5.9			22.4	3.74	804		
6.4	8.99	17,300	22.1	3.70	736	58.8	95.7

*Pressure, 800 kPa; feed rate, 75 l/min.

CONCENTRATION RUN

In this run, permeate was not recycled back to the feed tank. As a result, the concentration in the feed tank steadily increases, as shown by the results of Table 9. These results should be compared with those in Table 4 for the same operating conditions except that permeate was recycled.

As one would expect, the rate of flux decline is slightly greater in the concentration run (Table 9) compared with constant feed run (Fig. 7). The flux decline in 2.7 hr was 31% and 25%, respectively, in the two cases.

The effect of a backflush in this case is to increase the flux from 21.2 to 24.9 l/m² hr, bringing it to about 80% of the original flux value (30.8 l/m² hr). This result is comparable to that reported in the previous run (Table 8), if one notes that concentration of feed is roughly double the original feed in the present case (Table 9).

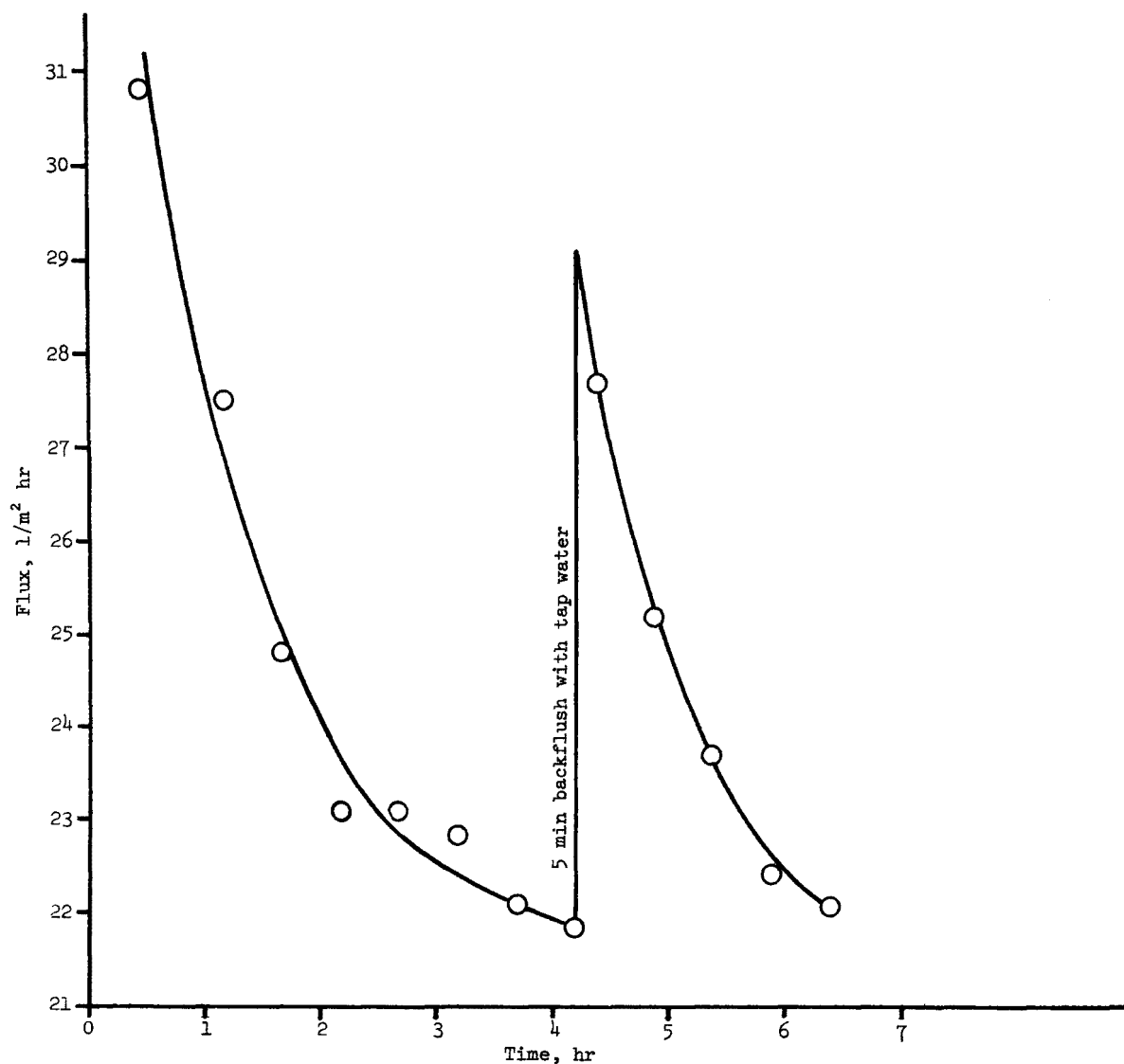


Figure 8. The effect of backwashing.

It can be seen from Table 9 that the concentration of feed (when concentrate was recycled but permeate was not) doubles in about 3 hr. Since in actual practice the concentrate is sent to another membrane module, it would be important to determine the membrane area required to double the concentration.

Let us take the original feed rate to be 100 l/min (i.e., 144,000 l/day). In order to double the concentration we should remove about 50 l/min as permeate. Thus, feed velocity from module to module will vary from 100 l/min to 50 l/min giving an average of 75 l/min. From Table 9, one can say that permeate flux will vary from about 32 to 20 l/m² hr. Since flux declines rapidly, let us assume permeate flux to be about 20 l/m² hr. Membrane area can now be calculated as:

$$\begin{aligned}
 \text{Membrane Area Required} &= \frac{\text{Permeate to be removed}}{\text{Permeate Flux}} \\
 &= \frac{(50 \text{ l/min})(60 \text{ min/hr})}{20 \text{ l/m}^2 \text{ hr}} \\
 &= 150 \text{ m}^2
 \end{aligned}$$

Thus, about 144,000 l/day [38,000 gal/day] of feed can be treated with 150 m² of membrane, giving 72,000 l/day of permeate and 72,000 l/day of concentrate.

TABLE 9. CONCENTRATION RUN*

Hr	Feed		Flux, l/m ² hr	Permeate		Rejection, %	
	Solids, g/l	Color, mg/l		Solids, g/l	Color, mg/l	Solids	Color
0.25	8.87	22,200	30.8	3.69	1270	58.4	94.3
0.75	9.94	27,200	24.6	3.80	1400	61.8	94.9
1.25	10.89	27,500	23.1	4.06	1480	62.7	94.6
1.75	12.11	31,800	22.5	4.33	1550	64.2	95.1
2.25	13.87	40,600	22.1	4.62	1660	66.7	95.9
2.75	15.35	42,400	21.2	4.90	1810	68.1	95.7
<u>Backflushed with tap water</u>							
2.75							
3.25	14.19	46,600	24.9	4.90	2090	65.5	95.5
3.75	14.29	51,100	24.0	4.83	2000	66.2	96.1
4.25	14.24	49,000	22.4	5.22	2090	63.3	95.7
4.75	14.47	48,700	22.1	4.77	1950	67.0	96.0

*Pressure, 800 kPa; feed rate, 75 l/min.

ZERO-RECYCLE RUN

In this run neither concentrate nor permeate was recycled, and the results are presented in Table 10 and Fig. 7. This experiment was carried out for about 8 hours and required roughly 15,000 l [4,000 gal] of feed. These results are to be compared with those obtained by recycling both feed and permeate (Table 5). It can be seen from Fig. 7, Curve 3, that flux decline rates in the two cases are not significantly different and fall on the same curve.

TABLE 10. ZERO-RECYCLE RUN

Pressure, kPa	Feed			Permeate			Rejection, %	
	Rate, l/min	Solids, g/l	Color, mg/l	Flux, l/m ² hr	Solids, g/l	Color, mg/l	Solids	Color
445	30							
<u>Time</u>								
0								
0.5		8.72	16,250	19.1	4.80	2040	45.0	87.4
1.0		8.76	18,500	15.7	4.76	1850	45.7	90.0
1.5		8.76	18,500	15.4	4.63	1850	47.1	90.0
2.0		9.02		14.1	4.80		46.8	
2.5		8.61	17,750	13.5	4.69	1775	45.5	90.0
3.0		8.72	16,250	12.9	4.68	1640	46.3	89.9
3.5		8.80	19,750	12.3	4.71	1335	46.5	93.2
4.0		8.54	19,000	12.0	4.70	1825	45.0	90.4
4.75		8.83		11.7	4.70		46.8	
5.25		8.85	17,600	11.5	4.68	1560	47.1	91.1
5.75		8.78		11.1	4.65		47.0	
6.25		8.71	17,750	10.8	4.73	1865	45.7	89.5
6.75		8.83		10.5	4.74		46.3	
7.25		8.82	19,400	10.2	4.68	1590	46.9	91.8
7.75		8.99	17,600	9.8	4.60	1560	48.8	91.1

SECTION 8

RESULTS OF LIME TREATMENT

Lime treatment is one of the commonly used methods for color removal. Therefore, feed, permeate and concentrate samples from ultrafiltration studies were subjected to lime treatment. Results are given in Table 11.

TABLE 11. RESULTS OF LIME TREATMENT BEFORE AND AFTER UF

(a) Feed color = 9320 mg/l						
Lime dosage, mg/l	Feed		Concentrate		Permeate	
	Color, mg/l	Removal, %	Color, mg/l	Removal, %	Color, mg/l	Removal, %
0	9320	0	18,420	0	735	0
1000	7080	24	18,800	-2	698	5
2000	3340	64	15,220	17	828	-13
5000	2310	75	5,220	72	466	37
(b) Feed color = 6425 mg/l						
Lime dosage, mg/l	Feed		Permeate			
	Color, mg/l	Removal, %	Color, mg/l	Removal, %		
0	6425	0	641		0	
1000	6425	0	463		28	
2000	4290	33	414		35	
3000	3810	41	429		33	
4000	3730	42	410		36	
5000	3280	49	336		48	
(c) Feed color = 18,750 mg/l						
0	18,750	0	1406		0	
1000	17,250	9	862		39	
2000	8,812	53	881		37	
5000	4,125	78	600		57	

Color removal from feed or concentrate was 75% or lower when lime dosage was as high as 5,000 mg/l. In the case of permeate, color removed was less than 60%. One may argue that low molecular weight organics may be responsible for the lower amount of color removed from permeate. If this is true, lime treatment of concentrate should give higher color removal compared to that of feed. However, this is not the case, as can be seen from the results of Table 11a.

EFFECT OF CARBOHYDRATES ON COLOR REMOVAL BY LIME

Color removals by lime treatment of NSSC effluents is much lower than that of kraft. NSSC color bodies are hard to remove by this flocculation technique. Also, when NSSC and kraft effluents are mixed, the total color removal efficiency of kraft drops from about 80% down to 65% or lower.

One of the reasons for lower color removals from NSSC effluents was thought to be carbohydrates. We believed that carbohydrates helped stabilize lignin salts in solution and/or in colloidal forms. The separation of these carbohydrates could, therefore, enable the highly colored lignin compounds to be easily precipitated from solution.

The role of carbohydrates in color removal by lime treatment was followed by running detailed carbohydrate analysis of the UF-feed, -permeate and -concentrates before and after acid hydrolysis and lime treatment. Results are given in Tables 12-14.

Table 12 shows carbohydrate data before and after acid hydrolysis on the three UF-fractions: feed, concentrate and permeate. All fractions show a substantial increase (see ratio) in monomer sugar content after acid hydrolysis indicating that the major portion of the sugars existed in the polymeric form. The ratios of after acid hydrolysis to before acid hydrolysis data are lowest in the permeate, indicating membrane rejection of the polymeric sugars.

A portion of the NSSC effluent was first acid hydrolyzed and then ultra-filtered. Results are given in Table 13. Results show a marked increase in sugar content after acid hydrolysis (compare Feed columns), confirming earlier observations. The data further show that sugar concentrations remain almost the same in all three UF-fractions. We think the sugars behave like water and pass through the membrane in the same proportions. In other words, the monomeric sugars are not preferentially passed through or rejected. The data indicate that this technique is not good enough for recovering sugar-free NSSC color bodies.

Although not completely sugar free, the above UF fractions were used for color removal experiments with lime. The data are given in Table 14 and plotted in Fig. 9. Data from Table 11 and 14 are further plotted in Fig. 10 and 11. Figures 9 and 10 show that at lower concentrations of lime (less than 4000 ppm) the acid hydrolyzed samples (containing more monomeric sugars) show lower color removals. The presence of sugars does seem to retard color removal. At higher dosages of lime approximately the same color removals are obtained in all cases except permeate. The difference in color removal of

TABLE 12. CARBOHYDRATE ANALYSIS OF ULTRAFILTERED NSSC EFFLUENT BEFORE AND AFTER ACID HYDROLYSIS

Carbohydrate	Feed			Concentrate			Permeate		
	Before, mg/l	After, mg/l	Ratio, (after/ before)	Before, mg/l	After, mg/l	Ratio, (after/ before)	Before, mg/l	After, mg/l	Ratio, (after/ before)
Arabinose	6	54	9.0	4	54	13.5	3	22	7.3
Xylose	11	136	12.4	6	136	12.4	10	62	6.2
Mannose	7	27	3.9	6	27	4.5	5	12	2.4
Galactose	9	64	7.1	10	67	6.7	6	24	4.0
Glucose	18	121	6.7	22	114	5.2	15	69	4.6
Rhamnose	0	20	--	0	20	--	0	7	--

unhydrolyzed and acid hydrolyzed permeates seems to continue throughout the lime additions range (Fig 11). Maximum removals for these NSSC effluents are still below those reached for kraft effluents.

TABLE 13. ULTRAFILTRATION OF ACID-HYDROLYZED NSSC EFFLUENT

Carbohydrate	Untreated feed, mg/l	Ultrafiltered after acid hydrolysis		
		Feed, mg/l	Concentrate, mg/l	Permeate, mg/l
Arabinose	2	49	49	46
Xylose	20	233	236	219
Mannose	13	28	28	27
Galactose	13	64	63	63
Glucose	16	361	367	346
Rhamnose	0	16	14	21

TABLE 14. % COLOR REMOVAL BY LIME TREATMENT OF ULTRAFILTERED NSSC EFFLUENT BEFORE AND AFTER ACID HYDROLYSIS

Lime addition, ppm	Before acid hydrolysis Feed	After acid hydrolysis		
		UF Feed	UF Concentrate	UF Permeate
0	0	0	0	0
1000	11.1	2.5	1.9	21.4
2000	61.9	26.0	40.8	29.6
3000	72.6	52.4	58.6	35.7
4000	73.9	67.4	64.1	40.4
5000	76.9	72.5	68.6	45.3

Thus, we can conclude that the presence of carbohydrates is not the main cause of poor color removal from NSSC effluent by lime treatment. The nature of the chromophore-containing molecule must be the major reason for the differences in color removal by lime addition between kraft and NSSC effluents.

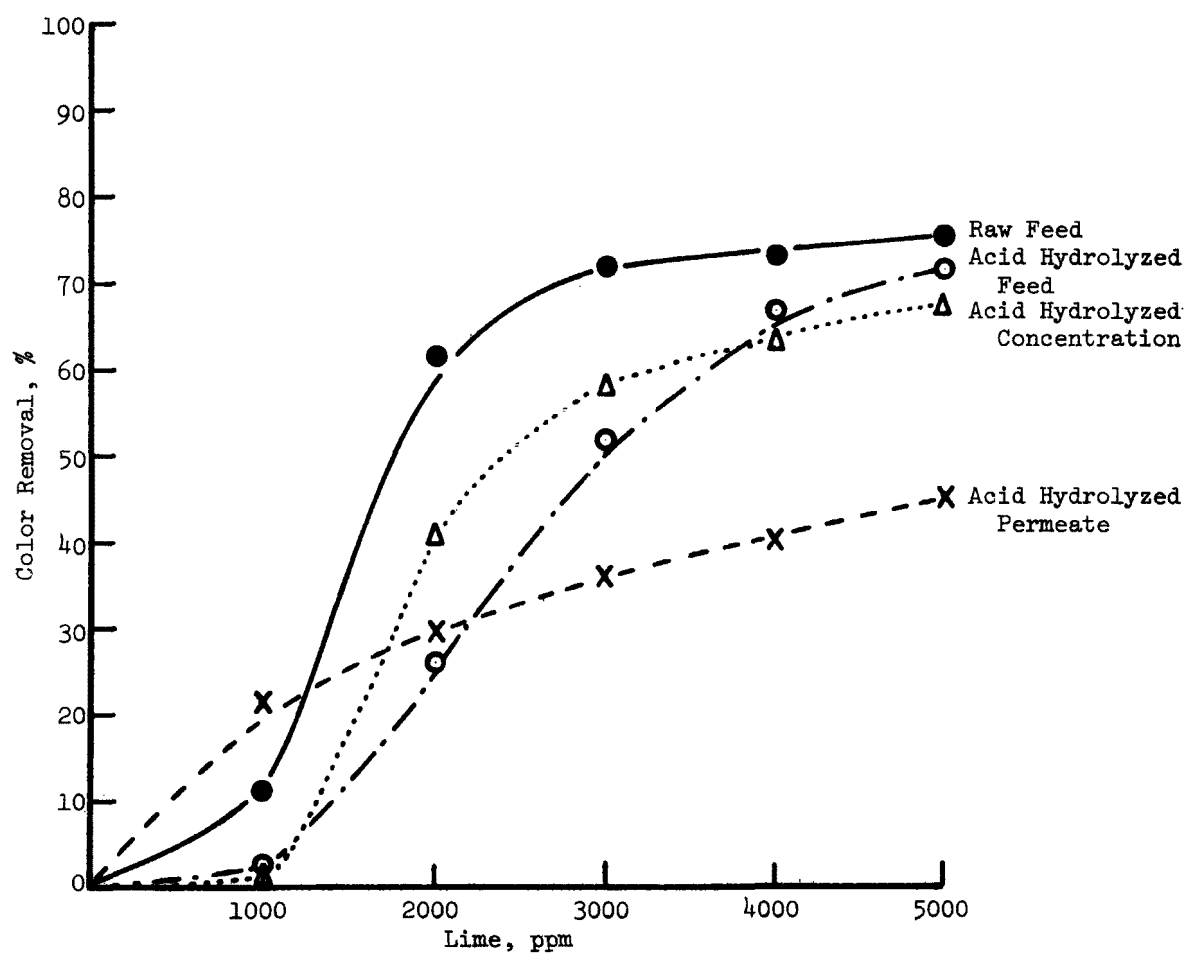


Figure 9. Color removal of UF fractions by lime treatment.

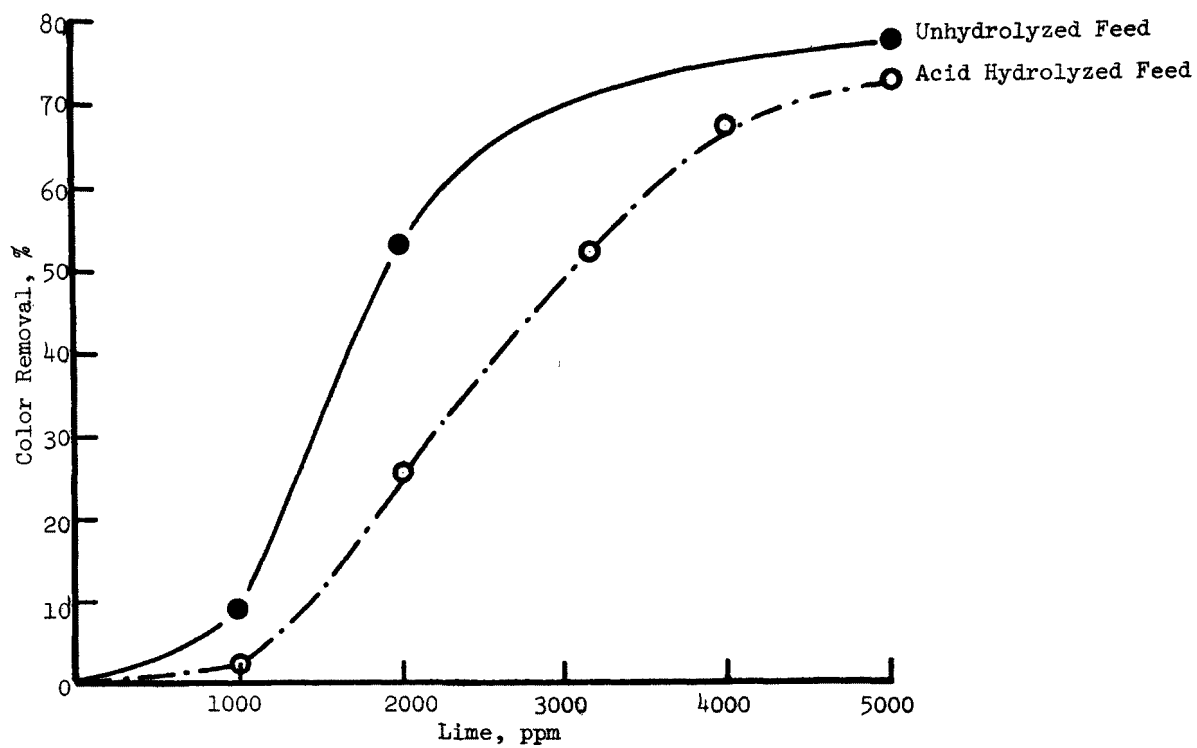


Figure 10. Color removal of feeds by lime treatment.

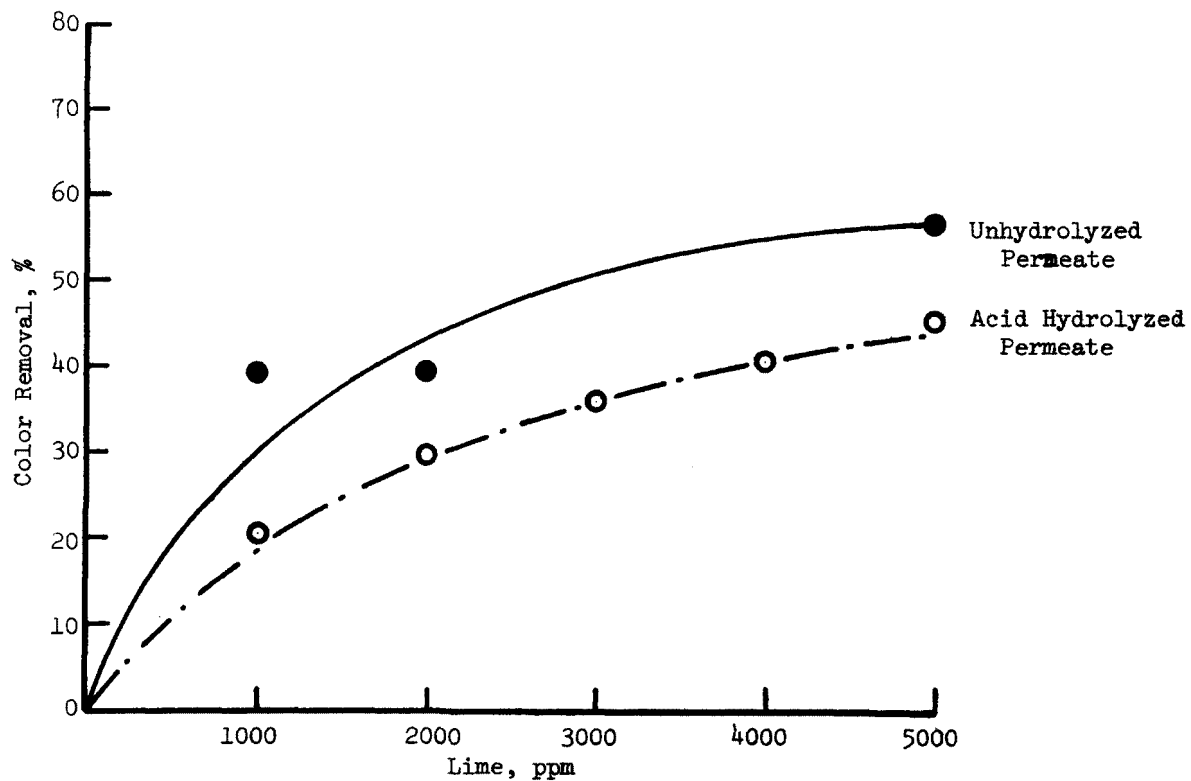


Figure 11. Color removal of permeates by lime treatment.

SECTION 9

TOXIC CHEMICALS ANALYSIS

The Clean Water Act of 1977 (H.R. 1977) as well as the Toxic Substances Control Act of 1976 (P.L. 94-469) put restrictions on the discharge of toxic or potentially toxic compounds. Thirteen compounds have initially been identified as being suspect compounds discharged by the pulp and paper industry. These compounds are listed in Table 15.

TABLE 15. TOXIC CHEMICALS ANALYSIS

Compound	Feed, mg/l	Concentrate, mg/l	Permeate, mg/l	Rejection, % [§]
Oleic acid*	2.27	1.14	0.07	94
Linoleic acid	5.27	2.27	0.10	96
Linolenic acid	0.66	0.17	<0.02	>88
Isopimaric acid (+ palustric)	4.67	1.63	0.02	99
Abietic acid	0.83	0.41	<0.02	>95
Dehydroabietic acid	2.91	1.33	0.09	93
9-10 Epoxidic acid	ND [†]	ND	ND	--
Dichlorostearic acid [†]	ND	ND	ND	--
Monochlorodehydroabietic acid	ND	ND	ND	--
Dichlorodehydroabietic acid	ND	ND	ND	--
Trichloroguaiacol	ND	ND	ND	--
Tetrachloroguaiacol	ND	ND	ND	--
Chloroform	ND	ND	ND	--

*Rosin and fatty acid analyzed by GLC.

[†]Chloro-organic compounds analyzed by GC/MS.

[‡]ND - not detectable. Limits of detection were 10 ppb or lower.

[§]Percent rejection is defined on the basis of concentrate concentration.

Feed to and permeate and concentrate from an ultrafiltration run were analyzed for toxic compounds. Results presented in Table 15 show that the chlorinated toxic compounds were not detectable, while some toxic acids were present in small concentrations.

The first seven compounds are normal components of wood and should be found in an effluent. The last six compounds are not normal wood components and should not be found in the effluent of a mill that does not use a chlorine bleach sequence. These theoretical conclusions are confirmed by the data of Table 15.

The feed and concentrate concentrations should be nearly identical, as very little permeate is removed in a single pass through the UF module. A consistent analytical error is possible. Time and budget constraints did not permit the analyses to be duplicated. The permeate concentrations were consistently low, indicating good rejection of the detectable compounds by the membrane. A consistent analytical error would not change the magnitude of the permeate concentration to concentrate concentration ratio.

The membrane performed quite well in rejecting the measured toxic compounds. With one exception (linolenic acid), the potentially toxic compounds were all rejected at levels in excess of 93%. These rejections are based on the concentrate concentration. If the feed concentrations were used, rejection would be in excess of 96%.

The concentrate still contains the toxic compounds and must be treated. Further studies will be needed to determine how best to remove these compounds, if necessary.

SECTION 10

ECONOMICS

As pointed out in an earlier part of this report, the effluents tested in this program were obtained from a highly closed mill. These effluents were highly concentrated and not typical of less highly closed mills. Based on conversations and mill visits, these effluents were then diluted to more typical conditions.

The experimental program was to test the feasibility of using UF to concentrate typical NSSC effluents and to test hypotheses concerning the influence of carbohydrates on the lime precipitation of color. Thus, the extensive experiments necessary to optimize the UF color removal process were not undertaken. The following economic analysis is not an optimum economic design; rather it is a rough estimate of the cost of color concentration by ultrafiltration. Because of the large variety of methods for costing capital, no "cost of capital" has been included in the economic analyses.

The design mill for economic analysis is a moderately closed mill producing about 275 tpd of product by the NSSC process. The major color-containing effluent from this hypothetical mill is overflow from the "white water" chest. This flow amounts to about $0.0315 \text{ m}^3/\text{sec}$ with approximately 13,000 mg/l total color and 15,000 mg/l total solids. The ultrafiltration unit is designed to remove 75% of the influent with approximately 93% color rejection and 50% solids rejection. Thus, the concentrate from the process is a flow of $0.0073 \text{ m}^3/\text{sec}$ with a color load of 48,360 mg/l and solids level of 30,000 mg/l. The permeate flow is $0.0237 \text{ m}^3/\text{sec}$ with color and solids levels of 1,400 mg/l and 10,000 mg/l, respectively. The solids in the permeate are dissolved solids, and thus the permeate could be recycled to the mill, whenever the process could stand the organic and inorganic load. There might be some problems with slime growth, increase in chemical consumption, or corrosion due to these dissolved solids. The permeate should be useable on showers, as there is virtually no suspended material to plug the nozzles.

The economic analysis of ultrafiltration is based on the design parameters outlined in Table 16. Note that a constant flux rate is used for design purposes. The selection of this constant flux is based on the data in Tables 4 and 9. The backwashing experiments show that a high flux can be maintained by a periodic, short term backwash. The flux rate used for economic analysis is based on integrated flux rate between washing cycles.

Table 17 gives the necessary design factors. The membrane and pressure vessel costs are based on the manufacturer's estimate for a plant of the

required size*. Piping and other capital costs are based on typical percentages of major equipment for fluid processing plants (10).

TABLE 16. DESIGN BASIS FOR ULTRAFILTRATION UNIT

Flow	0.0315 m ³ /sec, 2721 m ³ /day
Color level	13,000 mg/l
Solids level	15,000 mg/l
Operating pressure (main)	445 kPa
Flux rate	25 l/m ² hr
Pressure drop/module	35 kPa
Feed removed	75%
Color rejection	93%
Solids rejection	50%
Operates	330 days/yr, 24 hr/day

TABLE 17. DESIGN FACTORS FOR UF UNITS

Membrane cost	\$161.00/m ²
Pressure vessels	\$187.00/m ²
Electric power	\$0.03/kw
Installation	47% of major equipment
Instrumentation	18% of major equipment
Electrical wiring	11% of major equipment
Piping	66% of major equipment
Maintenance	5% of capital
Depreciation	10 yr - straight line
Labor	1 man/shift @ \$20,000/yr

Table 18 summarizes the capital and operating costs for the design facility. The operating cost of \$0.87/m³ of feed solution greatly exceeds that estimated for lime treatment (3), but is about 80% of that for evaporation.

Table 19 considers the sensitivity of the economics to various factors. If membrane life can be extended by a factor of two, costs drop considerably. If flux rates and membrane life were doubled, the cost of ultrafiltering the effluent drops to costs similar to lime treatment (3). According to the manufacturer, these changes are not outside the realm of possibility, and they are researching a design which is expected to lead to a doubled flux rate.

*McLendon, Dr. H., Western Dynetics, Personal Communication.

TABLE 18. COST OF UF UNIT

Capital costs:	
Pressure vessels	\$579,600
Pumps and drivers	<u>81,800</u>
Total direct cost	\$661,400
Other direct costs (piping, instr., elect.)	\$939,100
Total direct costs	\$1,600,500
Indirect costs (50%) (buildings, land, etc.)	<u>800,000</u>
Total direct and indirect	\$2,400,500
Contingency at 10%	<u>240,000</u>
Total capital costs	<u>\$2,640,500</u>
Operating cost	
Membranes (2-yr life)	\$310,500
Power	75,000
Depreciation	160,000
Labor	100,000
Maintenance	<u>132,000</u>
Total operating cost	\$777,500
Cost/m ³ of feed	\$0.87
Cost/m ³ of permeate	\$1.15

TABLE 19. SENSITIVITY OF COSTS

Flux rate = 25 l/m² hr and
4-Year membrane life:

Capital costs	\$2,640,000
Operating costs	621,750
Operating costs/m ³ of feed	0.692

Flux rate = 50 l/m² hr and
Membrane life = 4 years

Capital costs	\$1,320,000
Operating costs	271,650
Operating costs/m ³ of feed	0.30

The concentrate from the UF unit must still be treated. These costs are not included in the above analysis. Our experimental work indicates that lime treatment is still feasible, but on a greatly reduced volume of effluent.

REFERENCES

1. Rush, R. J., and E. E. Shannon. Review of Color Removal Technology in the Pulp and Paper Industry. Environmental Protection Services, Canada, Report EPS 3-WP-76-5, April 1976.
2. Dugal, H. S., R. M. Leekley, and J. W. Swanson. Color Characterization Before and After Lime Treatment. Environmental Protection Technology Series, Report No. EPA-660/2-74-029, April 1974.
3. Rock, S. L., D. C. Kennedy, and A. Bruner. Decolorization of Kraft Mill Effluent with Polymeric Adsorbents. Tappi 57(9):87-92, 1974.
4. Lindberg, S. Decolorization of Bleach Plant Effluent and Chloride Handling. Paper Trade J. 12:36-37, 1973.
5. Fremont, H. A., D. C. Tate, and R. L. Goldsmith. Color Removal from Kraft Mill Effluents by Ultrafiltration. Environmental Protection Technology Series, EPA-660/2-73-019, Dec. 1973.
6. Maples, G., and E. W. Lang. Studies of Membrane Processes for Pulp Mill Pollution Control. TAPPI Envir. Conf. Proc., April, 1978:71-82.
7. Bansal, I. K., and A. J. Wiley. Application of Reverse Osmosis in the Pulp and Paper Industry. In: Reverse Osmosis and Synthetic Membranes, S. Sourirajan, editor. pp. 459-475. National Research Council, Canada, 1977.
8. Collins, J. W., L. A. Boggs, A. A. Webb, and A. J. Wiley. Spent Sulfite Liquor Reducing Sugar Purification by Ultrafiltration. Tappi 56(6):121-124, 1973.
9. Bansal, I. K., and A. J. Wiley. Membrane Processes for Fractionation and Concentration of Spent Sulfite Liquors. Tappi 58(1):125-130, 1975.
10. Peters, M. S., and K. D. Timmerhaus. Plant Design and Economics for Chemical Engineers. 2nd ed. p. 9. McGraw-Hill, NY, 1960.
11. Wiley, A. J., L. E. Dambruch, P. E. Parker, and H. S. Dugal. Combined Reverse Osmosis and Freeze Concentration of Bleach Plant Effluents. EPA-600/2-78-132, June 1978.
12. Easty, D., L. Borchardt, and B. Wabers. Removal of Wood Derived Toxics from Pulping and Bleaching Wastes. EPA-600/2-78-031.

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