Research Report
Textile Research and Implementation

Use of Membrane Filtration for Water Recycling in Fiber Reactive Dyeing

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ABSTRACT

A process was evaluated for the recycling of water and salt from fiber reactive dyebaths. The hydrolyzed dyes, auxiliaries, and other materials in the dyebath and first rinse composite mixture were removed by ultrafiltration followed by nanofiltration. The filtered brine was reused to dye another batch of fabric. Monochromatic red and yellow shades and trichromatic gray colors were dyed with water which had been previously used to dye the same color or other colors. Shade, depth of color and physical properties of the fabrics processed in recycled water were compared to fabric dyed with fresh water. The effluent was analyzed to determine the fate of the dyes and other dyebath additives.

The system studied would allow recovery of up to ninety percent (90%) of the salt used in the dyeing process and at least ninety percent (90%) of the water treated by the filtration process. A case study is presented for a hypothetical mill processing 160,000 pounds of fabric per week which must reduce toxicity by 90% due to salt in the mill wastewater stream. The mass balances for the optimum recycling possibilities are determined. Reduced purchases of salt, water and sewer costs generate a 30% return on investment (ROI).

INTRODUCTION

During the past several years, there has been increasing concern about the environment. Various industries contribute to pollution in the form of air emissions, discharge of wastewater and the disposal of materials in landfills. In 1972, the United States Congress passed the Water Pollution Control Act declaring that the national goal was to eliminate the discharge of pollutants into navigable waters.

The Environmental Protection Agency (EPA) has promulgated rulings since the enactment of this law which have continued to place stricter controls on point source dischargers. Rulings include regulations and limits for biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, oil and grease, toxicity, trace organics and heavy metals, to name the most frequent parameters measured on effluent. Most recently, the EPA has considered color and total dissolved solids to be additional undesirable characteristics in wastewater discharges to the environment either by point sources such as textile plants or publicly owned treatment works (POTW) facilities that may process wastewater from textile dyeing and finishing facilities. Eventually, rulings are likely to include maximum allowable limits for these two parameters in wastewater discharges. Textile mills will need to remove residual color from the effluent or be confronted with surcharges and/or fines or will be forced ultimately to shut down. Some textile dyeing plants are being challenged by some municipal POTW's to reduce salt in wastewater discharges. Currently, a particular mill must balance the use of chloride and sulfate containing electrolytes in order to comply with wastewater permit regulations. In another case, a mill is required to lower the toxicity of the waste stream which means that salt contained in the effluent must be reduced.

Fiber reactive dyes have the lowest average yield and fixation of color of all the dyes used for coloration of cellulosic fiber. In addition to being the most water soluble dyes for cotton, these colors require the most salt for application. Fiber reactive dyes represent the most difficult treatment problem and were chosen for this study based on these characteristics.

Various technologies are available to treat textile mill wastewater. These include flocculation/sedimentation, chlorination, ozonation, electrolysis, UV/peroxide, other chemical treatments, and membrane filtration. This study describes the results obtained using membrane filtration as a treatment technology to remove color from dyebath wastewater and the reuse of the brine obtained from the filtration process for subsequent dyebath make up.

HISTORICAL BACKGROUND

Membrane filtration has been used for recycling processes in the textile industry for a long time. Ultrafiltration was introduced for PVA size recovery in textile processes on a full plant scale nearly twenty years ago [1]. Several large textile mills continue to use membrane filtration techniques successfully today for this type application.

Ultrafiltration has been applied to caustic recovery in the mercerization process [2]. This methodology allows for the repetitive use of recovered alkali, thereby significantly reducing caustic consumption. The recovery of indigo dye by ultrafiltration [3] is another example of an application suitable to the use of membrane technology. A membrane system for the recovery of indigo currently is used by a major denim manufacturer in the United States.

A system for the recovery of hot water, dyes and auxiliary chemicals from textile waste streams was described by Porter and Goodman [4] ten years ago. The system incorporated zirconium oxide-polyacrylate membranes dynamically formed on the interior of sintered stainless steel support tubes.

MEMBRANE TECHNOLOGY

Membrane processes are filtration processes in which the pore size of the membrane is of molecular dimensions (Figure 1). These pore sizes are controlled and determined during the manufacture of the membrane material. Microfiltration (MF) membranes have pore sizes which are capable of separating colloidal particles from dissolved polymers. Ultrafiltration (UF) membranes separate polymers and colloids from soluble low molecular weight molecules. Nanofiltration (NF) membranes allow the partitioning of divalent ions from monovalent ions. Finally, reverse osmosis (RO) membranes pass only water. Most commercial membranes are made with an asymmetric cross section, with the smallest hole facing the feed solution and an open structure downstream. This feature prevents the membrane pores from blocking as would occur in a depth filter.

Unlike ordinary filters, membrane processes are operated with a strong cross flow which is tangential to the membrane surface. The crossflow provides a scrubbing action which controls the buildup of a `filter cake' and maintains a "concentration polarization" layer of a few microns (Figure 2). For this reason, membrane processes can operate for long periods of time without a decrease in the production of clean water or permeate. Membranes can usually be chemically cleaned to a nearly new condition. Typical membrane life is two to five years depending on the application.

Membranes provide a positive barrier between the influent and effluent streams. The quality of the effluent is only nominally dependent on that of the influent stream, making membrane systems insensitive to process upsets.

In wastewater applications, membranes are most advantageously applied as a point source treatment. Point source treatment also provides the best opportunities for internal recycle and the recovery of valuable by-products. Point source treatment also minimizes the capital investment compared to end-of-pipe treatments. The molecular separation characteristics and ease of operation make membranes a reasonable choice for investigation in dyebath reuse.

EXPERIMENTAL

Fabric used in this evaluation was 100% cotton interlock knit from 40/1 ring spun yarn. Fabric was scoured and bleached in sufficient quantity from the same yarn lot in order to make available prepared substrate for multiple dyeings. A conventional scour/bleach procedure was employed in the fabric preparation. Laboratory analysis was run on the fabric to measure pH and alkalinity of the substrate, insuring a neutral pH and an alkalinity level of less than 0.05 percent.

Dyeings were done in a laboratory jet dyeing machine. Standard fabric loading was seven and one quarter pounds at a liquor ratio of 15:1. Liquor hold-up for the fabric in this machine is approximately three pounds of water per pound of fabric. Dyeing procedures were those recommended by the dyestuff supplier.

Dyeings performed with C.I. Reactive Red 184 represent fiber reactive dyes with relatively low fixation rates typical of many used in the industry. Trichromatic gray dyeings were conducted with reactive dyes representative of a new generation of bi-reactive dyes with higher fixation rates. Dyeing procedures are shown in Figures 3 & 4.

The dyebath and first rinse were filtered through a 500 micron bag filter and collected in a 35 gallon plastic container. The purpose of the bag filter was to remove lint and any particulate matter. The mixture was acidified with commercial grade muriatic acid to pH 4 or lower, allowing sufficient time for neutralization, and consequent generation and dissipation of carbon dioxide. Subsequently, caustic soda was added to bring the mixture to pH 6.5 to 7.5 before the solution was filtered through the membrane system. A mass balance equation is shown in Figure 5 for the neutralization reaction.

The neutralized solution was passed through a hollow fiber ultrafilter (HF5-60-PM50, Koch Membranes) in order to remove colloidal material, auxiliaries and other substances which would foul a nanofiltration membrane. The UF permeate was supplied to the nanofiltration pilot containing a membrane (Filmtec NF-2540) having characteristics of retaining color bodies but passing brine. Characteristics of the NF permeate with respect to chloride, carbonate and bicarbonate ion concentration were determined by appropriate titration methods. A simplified flow diagram for the laboratory reuse system is shown in Figure 6.

An independent laboratory was used to measure biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), heavy metals, and pH.

<u>Red Dyeings</u>

Initial testing was designed to determine the reproducibility of our process and our system by studying the repeatability of depth of color. This was achieved by dyeing the same color multiple times. A total of twelve dyeings were conducted with Reactive Red 184. Figure 7 shows a color representation of swatches for the red dyeings. Five dyeings were processed using fresh water and seven dyeings were performed with NF permeate generated from a previous dyeing. All dyeings were done on fabric that had been prewetted.

Titrations were performed for chloride (salt) and carbonate (alkali) in order to verify dye bath concentrations and measure the reproducibility of our weighing and processing techniques. The NF permeate was analyzed to determine if it was acceptable for reuse by performing laboratory swatch dyeings with permeate water before dyeings were conducted in the lab jet.

Color measurements of the fabrics were taken on a Diano Match-Scan spectrophotometer equipped with a Shelyn Sliform software package. The results for CIELab units as well as percent strength and uncorrected and corrected DEcmc units are reported. Titrations for chloride and carbonate were conducted and pH readings taken for each dyebath. The second red dyeing (R-2) was arbitrarily chosen as the target color. Dyeings R-6, R-7, and R-8 were used to develop the procedures for pH adjustment (neutralization) and salt addition to the subsequent dyebath.

Gray Dyeings

Beige and gray shades tend to be colors that are difficult to reproduce. For this reason, a trichromatic gray shade was chosen to continue our evaluation of the feasibility of reusing brine water generated from the pilot membrane filtration unit utilizing a new generation of higher fixation bifunctional reactive dyes.

Three gray dyeings (G1, G2, and G3) were conducted with fresh water in order to establish a baseline for the gray shade. Three additional dyeings were run using recycled brine water (G4, G5, and G6) from gray dyeings, followed by two dyeings using filtered water from six percent navy dyeings (G7, G8) and two with filtered water from six percent red dyeings (G9, G10).

The second gray dyeing (G2) was taken as the reference shade for the first ten dyeings. An `all-in' procedure was used for dyeings G1 through G10. In the case of dyeings G11 through G16, dyes and makeup quantities of salt were added initially with the carbonate added later. Altering the procedure did not appear to interfere with shade reproducibility.

Dyeings G11 to G16 were performed on fabric from a different yarn lot. The fabric in these trials was not prewet. Three new reference dyeings (G11, G12, and G13) were processed with fresh water in order to establish another baseline. G11 was used as the reference dyeing for the second group of gray dyeings. A color representation of the sixteen (16) gray dyeings is shown in Figure 8.

Color measurements were taken on fabric for each test dyeing. Titrations were conducted to determine salt and alkali levels in the individual dyebaths.

Pastel Shade Test - Yellow Dyeings

A final critical test was conducted in the reuse application of permeate water. Six pastel yellow dyeings were processed in order to determine the feasibility of dyeing a light color with permeate water from other colors.

Two dyeings were processed with fresh water (Y5, Y6) in order to establish a reference point. Two dyeings were conducted with NF permeate water from gray dyeings (Y1, Y2) and two with filtered water from dark blue dyeings (Y3, Y4). Color measurements were taken on the dyed fabrics and titrations conducted to generate analytical data for dyebath parameters. The yellow dyeings are shown in Figure 9.

RESULTS AND DISCUSSION

Three areas will be reviewed. These include shade reproducibility, fabric quality, and fate of chemicals and impact on pollution minimization. Factors that may contribute to error will be discussed.

Shade Reproducibility

Color measurements taken on the red dyeings are shown in Table 1. Color strength measurements on the fabric for the dyeings with fresh water (R1, R2, R3, R4, and R5) indicate excellent reproducibility. The color difference represented by DEcmc (adj) shows a tight tolerance of 0.3 units.

As indicated in the experimental section, dyeings R6, R7, and R8 were used to determine the best approach for pH adjustment and to establish a standard procedure for achieving thorough neutralization reaction. The lower strength values for dyeings R6, R7, and R8 may be a result of lower salt concentration and/or low pH. The lower pH can be attributed to excess bicarbonate that was not fully neutralized. For example, the pH of the dyebath/first rinse feed to the filtration system from dyeing R5 was lowered only to pH 7. A significant amount of bicarbonate remained in the system. It was determined that excess bicarbonate (>1 g/L) created a buffering action that tends to reduce the pH of the recycled brine thereby interfering with color production in a subsequent dyeing. Measures were taken to minimize residual bicarbonate in permeate water by insuring complete or nearly complete neutralization.

Shade reproducibility for dyeings R9 through R12 show more consistent results with respect to strength in comparison to the R6 through R8 trials. Overall, there appears to be good consistency among the dyeings within the group dyed with fresh water and within the trials dyed in recycled water.

Color measurements for trichromatic gray dyeings processed are shown in Table 2 and Table 2A. The strength and color difference values indicate good reproducibility. With the exception of G4 and G10 in the first series of dyeings, and G14 in the second series of dyeings, the color difference measurement (DEcmc) gave better than a 0.6 unit tolerance to the standard and would be expected to fall within specifications of most dyers. Titration results for salt and alkali as well as pH readings indicate a high level of reproducibility for chemical additions in the gray dyeings.

Data for the color measurements on the pastel yellow shade are shown in Table 3. Shade reproducibility was acceptable regardless of the color of the dyeing wastewater used in the filtration to produce NF permeate for reuse in the yellow dyeings.

Fabric Quality

Fabric physical properties were measured for the red fabrics dyed in this study. Physical measurements taken included percent shrinkage, Mullen burst, course and wale count, 2A wash and lightfastness. Results are shown in Table 4 and indicate no significant change or loss of fabric physical properties as a result of using recycled brine for dyeing purposes. These measurements were taken in order to verify that no detrimental effects occurred when using recycled brine.

Laboratory dyeings performed with NF permeate containing some slight color resulted in no significant permanent staining on multifiber strips or prepared undyed fabric. Superficial staining caused by residual color, when present in recycled brine, did not cause an impairment of shade when used for dyeing fabric in the lab jet.

Pollution Minimization

The blue dye in the trichromatic shade was a copper bearing color. In order to verify the fate of copper in the effluent, analyses were performed by an independent laboratory on samples obtained from the various steps of the gray dyeing procedure. Results of the analyses are shown in Table 5. The copper is accumulated in the NF concentrate which is expected, particularly if the copper is still in the bound state in the dye molecule. Although analysis for copper in the UF concentrate was not performed, one would expect to find a portion of the copper in the UF concentrate as well. These results have a positive implication in terms of separating metal containing dyestuffs and compounds from recycled water.

No significant amount of copper was found in the NF permeate. As a matter of fact, the amount of copper in the NF permeate sample is essentially the same value as that determined for the background level of incoming water to the plant.

Table 5A shows the contribution of each step of the dyeing process to COD, TOC, TDS, and copper levels in the wastewater. It is evident that the dyebath drop, first rinse, acid rinse, and soap-off steps contribute to both copper and organic material loading in the wastewater stream. Unfixed and hydrolyzed dye contribute to the copper levels. Dye and auxiliary chemicals affect the organic material loading in the effluent.

Control of Process Variables

Control of salt concentration and pH are critical for shade reproducibility in any type of reactive exhaust dyeing. Errors in weighing of chemicals, dyes, fabric and liquor level variation in the process can cause variation in shade.

As described earlier, the analytical methods employed in these experiments to determine chloride (salt) and carbonate/bicarbonate levels in the NF permeate were key measurements in order to be able to adjust the salt level in the subsequent dyeing. The titrations were important to verify the nearly complete neutralization of the carbonate from the previous dyeing. Presence of excessive amounts (>1 g/L) of bicarbonate in the NF permeate tended to suppress the pH for the dyebath which followed. This condition results in difficulty in reproducing pH levels and shade.

To insure good color reproducibility and pH control, the carbonate was removed by acidification to pH 4 or slightly lower. Following the dissipation of carbon dioxide, the adjustment of the pH to 7 was achieved by the addition of caustic soda prior to the membrane filtration step (Figure 5).

Membrane Operation

The UF and NF modules ran at consistently high flux rates during the filtration of the eighty liters of the combined dyebath and first rinse. The concentration factors were approximately 15X in each case. The overall water recovery was 88%. The water recovery was determined by measuring the volume of fluid in the piping and modules. No cleaning was necessary between runs indicating that fouling was not a factor in these experiments.

The UF system shows rejection of heavy metals (divalent) and some organic materials. Metal rejection may be due to the presence of insoluble metal hydroxides and organically complexed metal. The apparent low rejection of BOD, COD, and TOC are due to the fact that these numbers are overwhelmed by the high levels of dye passed by the UF membrane. The nanofilter shows 98.6%, 99.5% and 99.8% rejection of TOC, color and copper respectively.

APPLICATION FOR A FIBER REACTIVE DYEHOUSE

An individual mill will have specific requirements which drive the application. Membranes can be applied as a point source technique to maximize the benefits of the technology and minimize capital costs. Some mills are concerned with color only and may not have a problem with toxicity. In this case, the dyebath and rinses can be combined and treated for color removal. The recovery of salt may or may not be economically advantageous. Other mills may have acute color and salt toxicity problems. A mill in this particular situation has better economic benefit by treating the dyebath as one stream and the rinses as another stream.

Finally, a mill may have a minor color problem but a major salt problem. In this case, the dyebath and first rinse are combined and treated, recovering the salt water (brine) for reuse. A plant which has only minor color and salt toxicity problems may wish to treat only the dyebath thereby obtaining the economic benefit of salt reuse. In all cases, the scouring water would be treated if BOD and COD are the driving issues. If water and sewer costs are the issue, then possibly all streams would be treated.

The case study taken here is a knitted cotton dyeing facility with a major toxicity problem due to salt and a lesser problem with color. An example of such a situation is a plant located on a small stream. The mill has sixteen four port jets with an average loading capacity of one thousand pounds per machine. Production is one hundred sixty-five thousand pounds of dyed knit fabric in a six day week (14 hr/scour, dye, rinse cycle) operation using fiber reactive dyes. The average salt concentration in the dyebath is sixty grams per liter (60 g/L). Dye consumption averages four percent dye on the weight of fabric at a liquor ratio of 10:1. The holdup ratio of water in the fabric is 2:1. Dyeing cycles incorporate six fill and drop steps in each run. Each cycle of the dyeing process generates 960 gallons per batch, or 26,400 gal./day. Dyeing and rinsing generates 158,000 gallons per day of wastewater which contains 16,400 pounds of salt.

The majority of the salt is removed from the fabric in the dye bath and first rinse. Combining these two streams recovers approximately 95% of the salt which can be reused. However, the salt concentration in the combined streams after a neutralization step will be approximately two thirds of the initial concentration assuming a 2:1 holdup of liquor in the fabric. Combination of these two drops for recycling will reduce the color released from the plant by sixty percent.

<u>Salt Recovery System</u>

The dyebath and first rinse are combined and sent to a UF/NF/RO system producing 22,400 gallons per day of brine with 14,000 pounds per day of salt (75 gm/L). Material balances for this concept are shown in Figure 10. Total salt losses are approximately 100 lbs./day in the other rinses, 800 lbs./day or less in the combined UF/NF concentrates, and 500 lbs./day in the RO permeate. This analysis assumes a 97.5% recycling of water in each of the UF and NF operations. Losses of salt in the UF and NF permeate drop to 2% if 99% recovery is attained in the UF and NF operations. The RO will maintain a constant concentration of brine in the water to be reused in the dyebath.

The UF minimizes fouling of the NF membrane system by removing organic polymeric, colloidal materials, and oil. The NF removes the dye producing a clear brine at approximately sixty percent of the salt concentration used in the dyebath. The RO system is used to concentrate the brine to 75 gm/L to compensate for the dilution by the incorporation of the first rinse in the recycle system. The RO permeate can be mixed with process water.

The existing facilities will need several modifications. Effluent from the dyeing machines must be segregated into two streams which include dyebath and first rinse water and other rinse waters. This may be accomplished using the jet pump to drain the dyebath and first rinse into an overhead piping manifold or by a segregated sewer. Heat may or may not be recovered as appropriate. A brine storage and surge tank will need to be added. Salt addition to the jet will have to be recalculated based on the salt concentration of the brine makeup tank.

Process Economics

The capital cost for the membrane system is $369,000 for the recovery of salt and water from the recovered dyebath and first rinse. Recovery economics are shown in Table 6. The payback period is 1.12 years. Additional costs for installation, tank storage and any plant modifications would be roughly the same order of magnitude and would depend on the physical layout of the plant. These additional costs are not accounted for in the payback calculation.

The basis for the operating economics were $2.50/K gal for water which includes purchase and disposal, $0.06/KW for electricity, 250 operating days/year, $160/ton for salt, membrane life of three years, fully burdened labor of 3 hr/day at $25/hr., and maintenance at 4% of capital investment. Capital costs are based on the membrane systems and do not include installation and tank storage.

CONCLUSIONS

Membrane filtration technology can be used to reduce or eliminate salt toxicity and color from dyehouse effluent containing fiber reactive dyes. Recovery of the salt and water can pay for the membrane installation. Recycling of water reduces the impact of water and sewer charges and can serve as a mechanism to approach a `zero wastewater discharge' plant. The problem of salt toxicity can be eliminated without major changes in dyeing procedures.

The water produced by UF/NF/RO membranes from dyebath and first rinse recovery can be reused as dyebath water. The physical properties and dyeing quality of fabrics dyed with fresh water or recycled brine are virtually the same. Slight modification or alterations in procedures may be necessary for measurement of brine concentration and salt makeup for dyebaths.

Heavy metals which are present in some dyes (i.e. copper) are effectively removed from the recycle streams and concentrated into the NF concentrate stream. This includes both bound metal and free divalent ions.

It is anticipated that other dyestuffs can be removed and the filtered water reused. Fiber reactive dyes represent the worst case scenario in terms of high tinctorial value.

It is expected, by inference, that rinse water can be treated by an appropriate system and reused. This application would further support the pursuit of a zero wastewater discharge plant [5].

Membrane filtration can be implemented in a modular fashion, thereby incrementally treating the waste stream as regulations change and treating and filtering dyeing cycle wastewater in a selected fashion, as necessary, in order to comply with wastewater effluent guidelines. This incremental approach would also be associated with water and sewer charges which can make water recovery a viable option as these costs continue to increase.

The issue of concentrate disposal or use has not been addressed. Several options have been or are being investigated with respect to disposal, recycle or reuse of the concentrate. This topic is a critical issue which may be addressed in conjunction with the application of other technologies and is beyond the scope of this paper.

ACKNOWLEDGMENT

The authors wish to express our thanks and appreciation to Birgit Schwartz-Andersen for performing innumerable laboratory titrations in support of this work. Her efforts were invaluable in order to verify pH, alkali and salt parameters of individual dyeings and permeate samples which were critical ingredients in demonstrating the applicability of membrane filtration in water reuse applications.

NOTE: Mention of specific equipment used in this study is not intended to be an endorsement of these products.

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Figure 1

MEMBRANE FILTRATION CONCEPTS

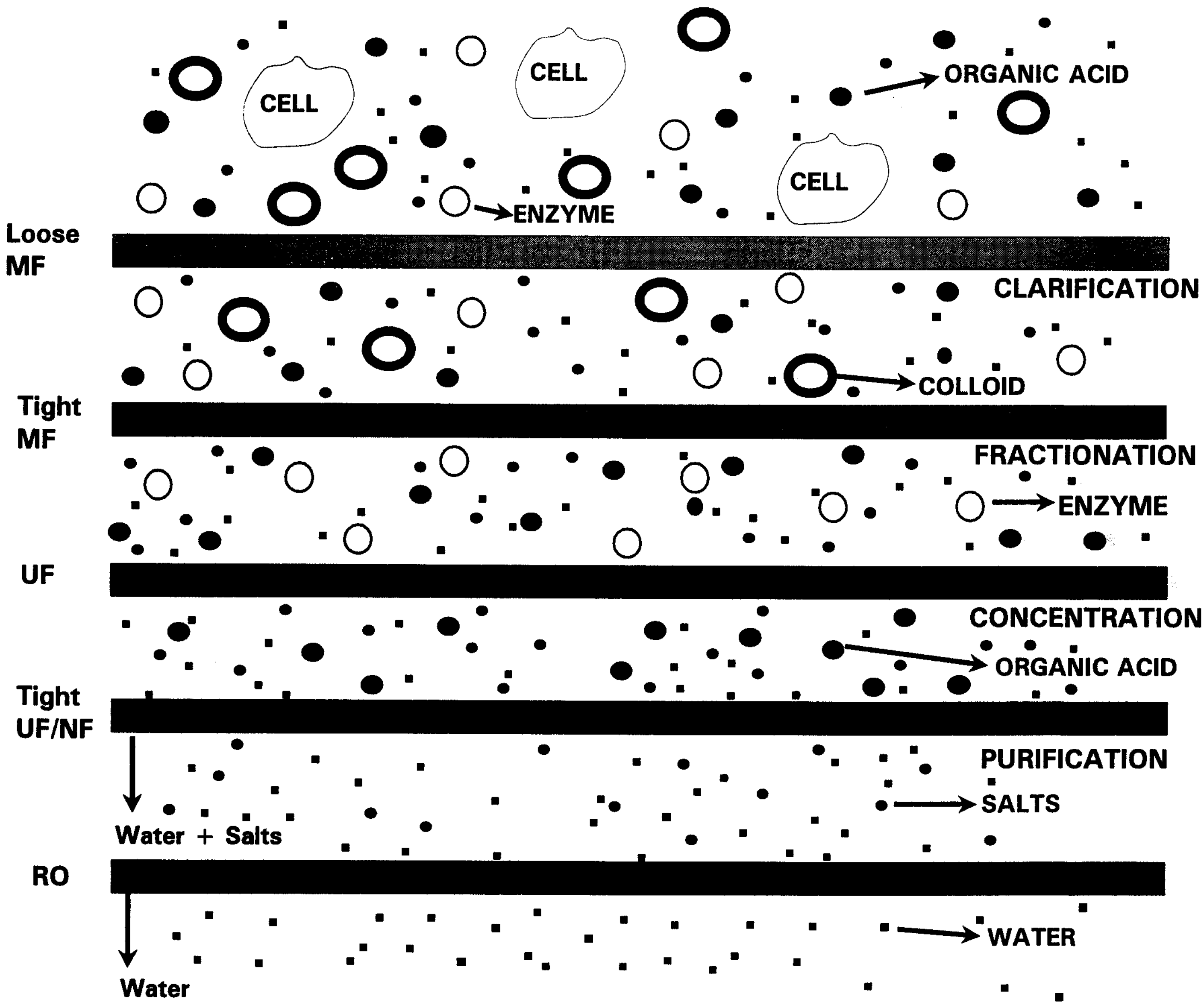

Figure 2

COMPARISON OF FLOW PATTERNS

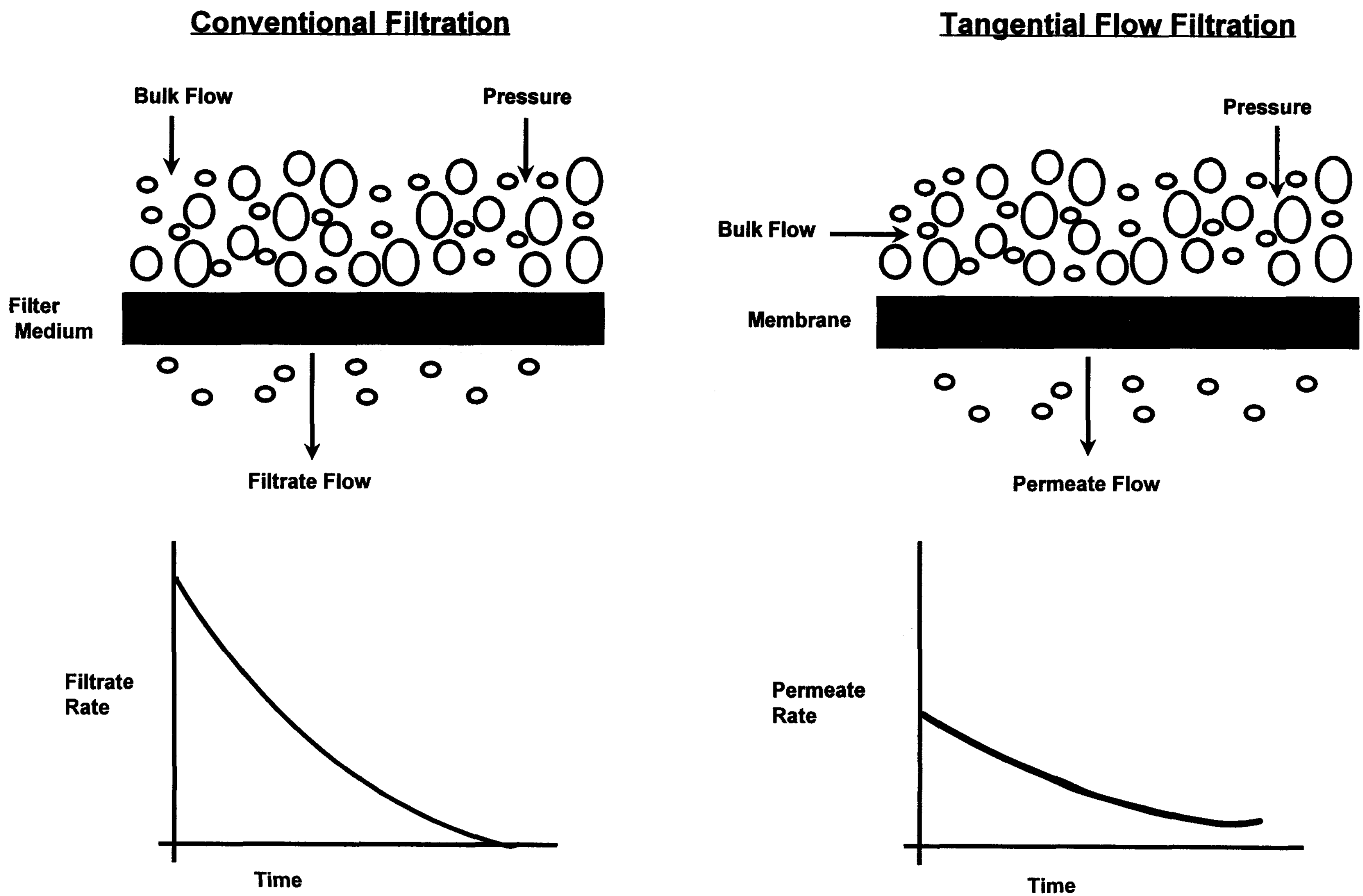

Figure 3

Red Dyeings

Exhaust Dyeing System

* Set bath at 100° F (38° C)
  Add:

	%
Albatex FFC	0.20
Irgasol CO-NF	0.50
Reserve Salt Flake	1.00

* Circulate five (5) minutes at 100° F (38° C).

* Add predissolved reactive dyes over ten (10) minutes.
  Circulate five (5) minutes.

* Add prescribed amount of common salt over fifteen (15) minutes.
  Circulate five (5) minutes.

* Add x g/L soda ash over five (5) minutes.
  Circulate fifteen (15) minutes.

* Heat to 140° F (60° C) over twenty-five (25) minutes.
  Run at 140° F (60° C), thirty (30) minutes.

* Sample / Drain

* Rinse at 120° F (49° C), five (5) minutes / Drain (Repeat).

* Soap at 200° F (93° C), ten (10) minutes with 0.5% Silvatol ASN Conc. / Drain.

* Rinse at 160° F (71° C), five (5) minutes / Drain.

* Rinse clear.

Figure 4

Gray Dyeings

Exhaust Dyeing System

* Set bath at 100° F (38° C).
  Add:

	%
Albatex FFC	0.2
Irgasol CO-NF	1.0
Common Salt	x (g/L)
Dissolved Dye	y
Soda Ash	z (g/L)

* Circulate five (5) minutes at 100° F (38° C).
* Heat to 140° F (60° C) at 2° F per minute.
  Run at 140° F (60° C), for forty-five (45) minutes.
* Sample / Drain.
* Rinse at 120° F (49° C), five (5) minutes / Drain.
* Rinse at 120° F (49° C) with 0.5% acetic acid, five (5) minutes / Drain.
* Soap at 180° F (82° C) with 0.5% Irgasol CO-NF, ten (10) minutes / Drain.
* Rinse at 140° F (60° C) five (5) minutes / Drain.
* Rinse cold, five (5) minutes.

Figure 5

NEUTRALIZATION REACTION

Step 1:

$$Na_2CO_3 + HCl \dashrightarrow NaHCO_3 + NaCl$$

Step 2:

$$NaHCO_3 + HCl \dashrightarrow NaCl + H_2CO_3$$

$$H_2CO_3 \rightleftarrows H_2O + CO_2\uparrow$$

Overall Mass Balance Reaction:

$$Na_2CO_3 + 2HCl \dashrightarrow 2NaCl + H_2O + CO_2\uparrow$$

Figure 6

DYE BATH REUSE SYSTEM

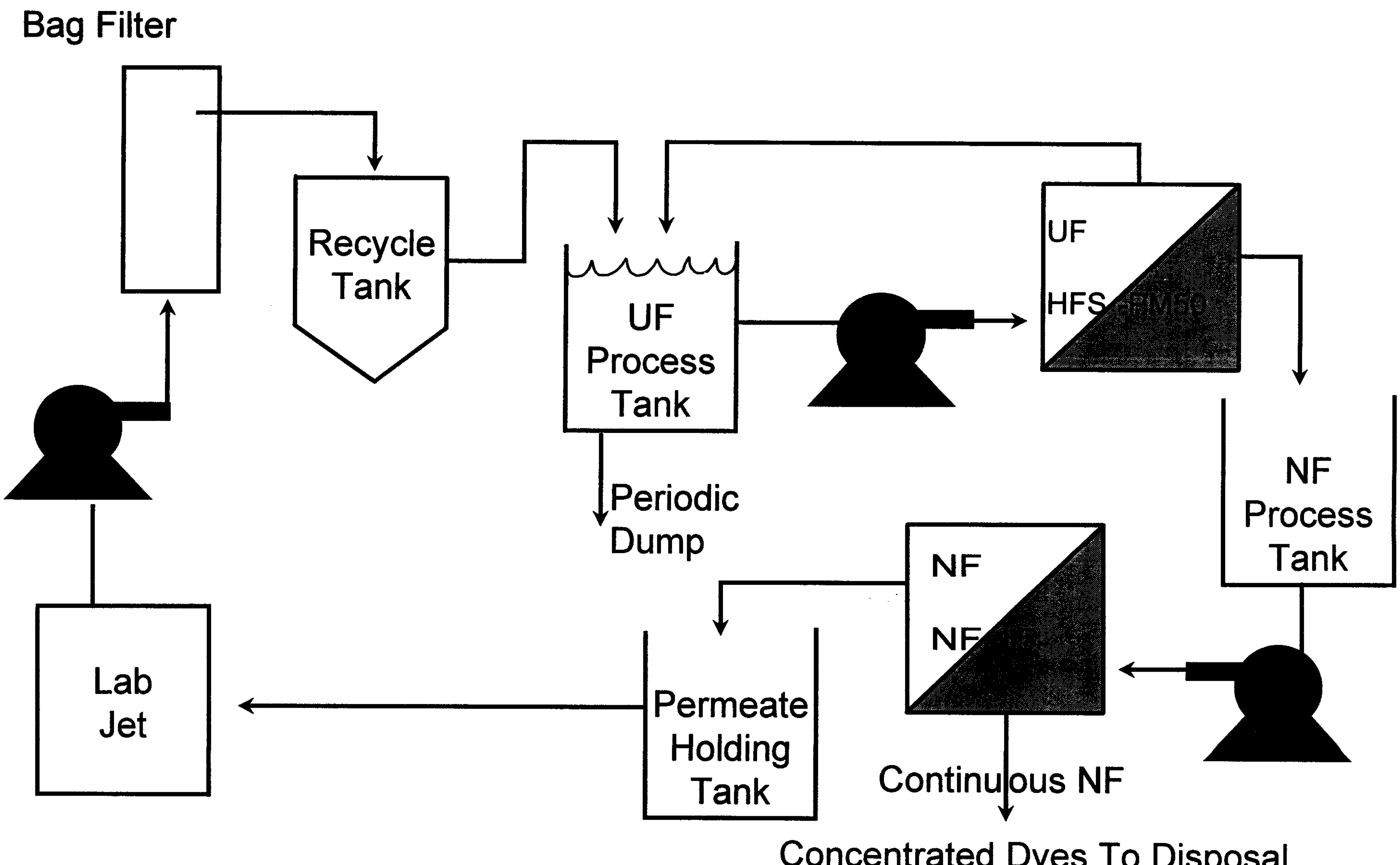

Figure 7

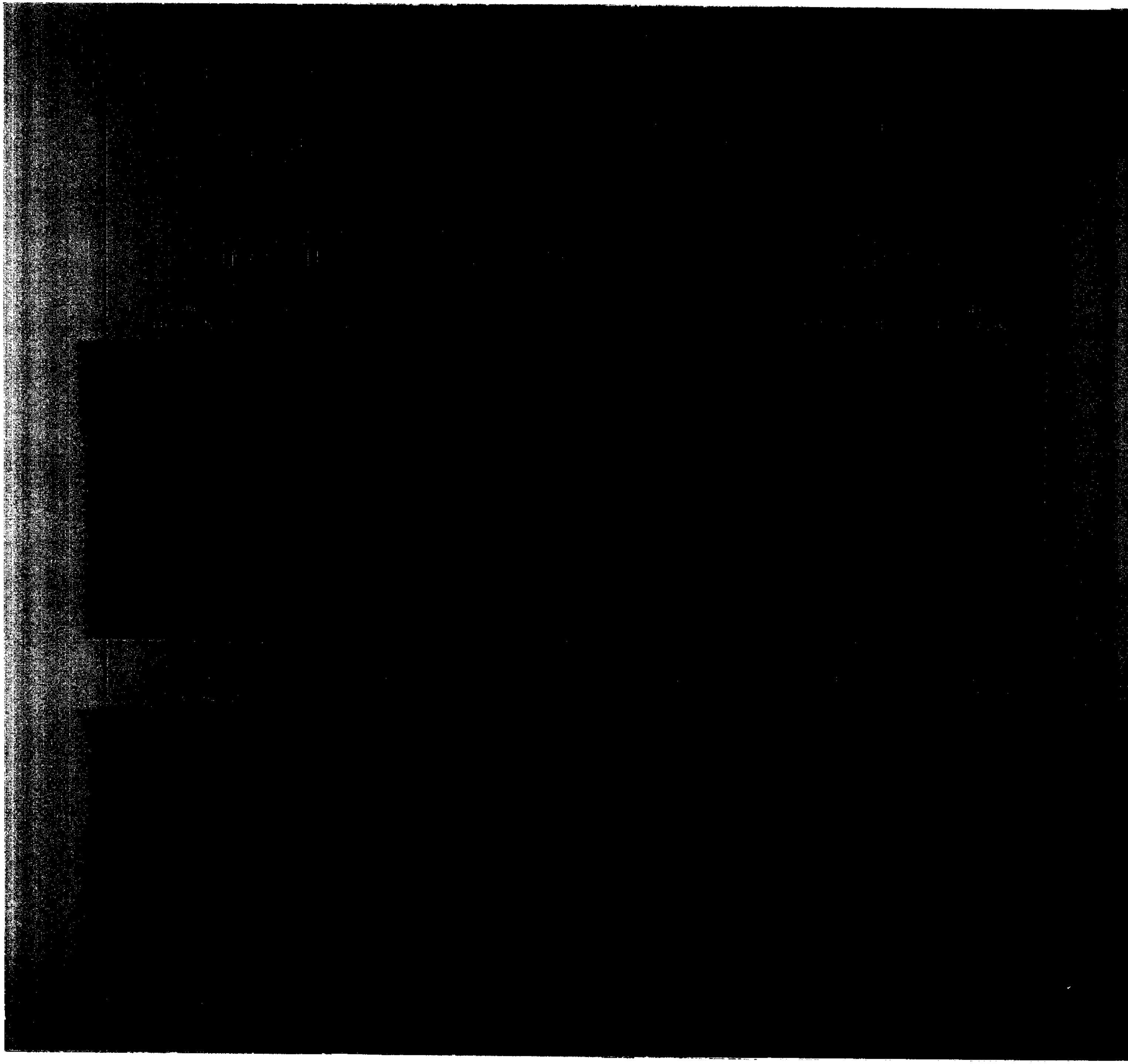

Figure 6

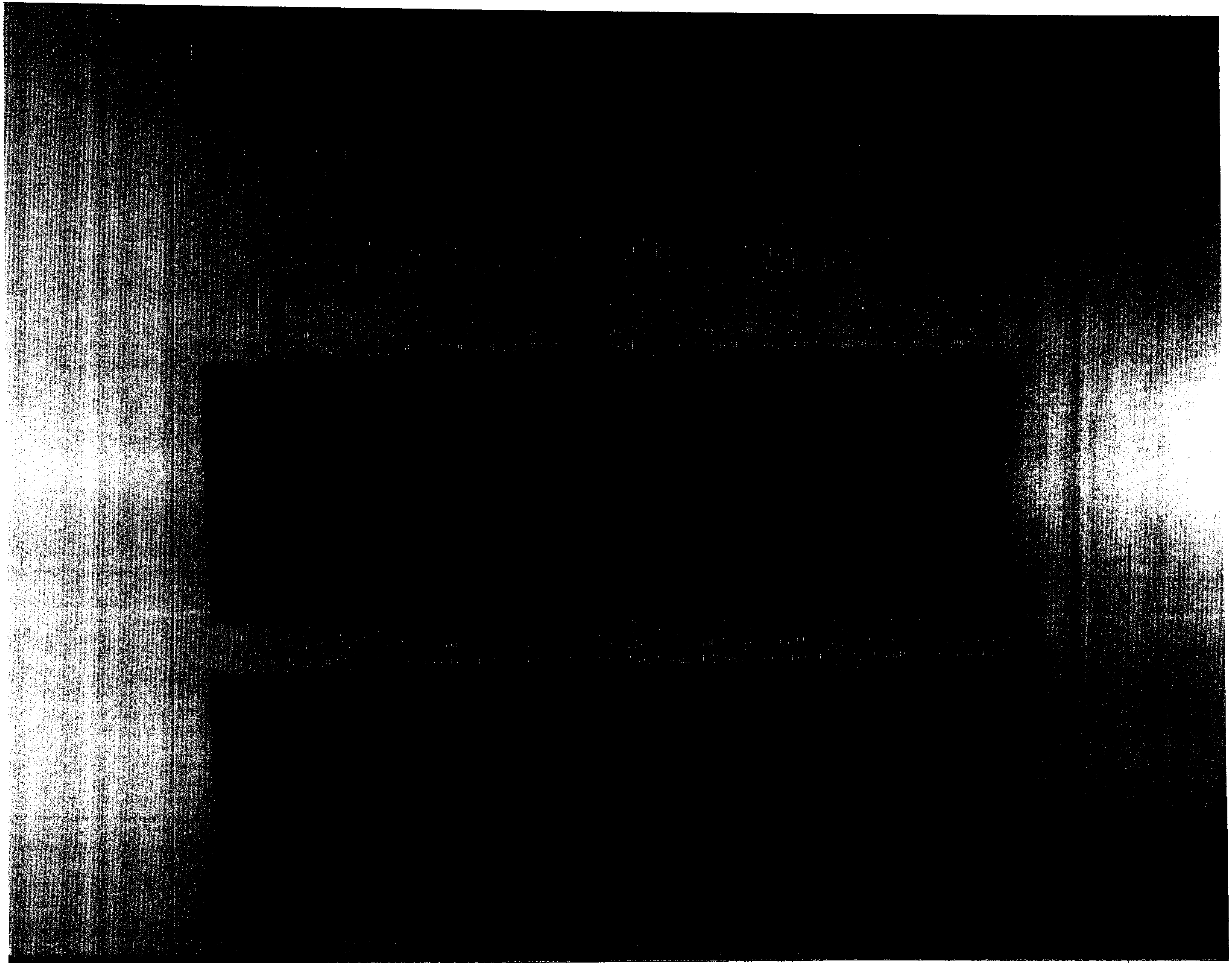

Figure 9

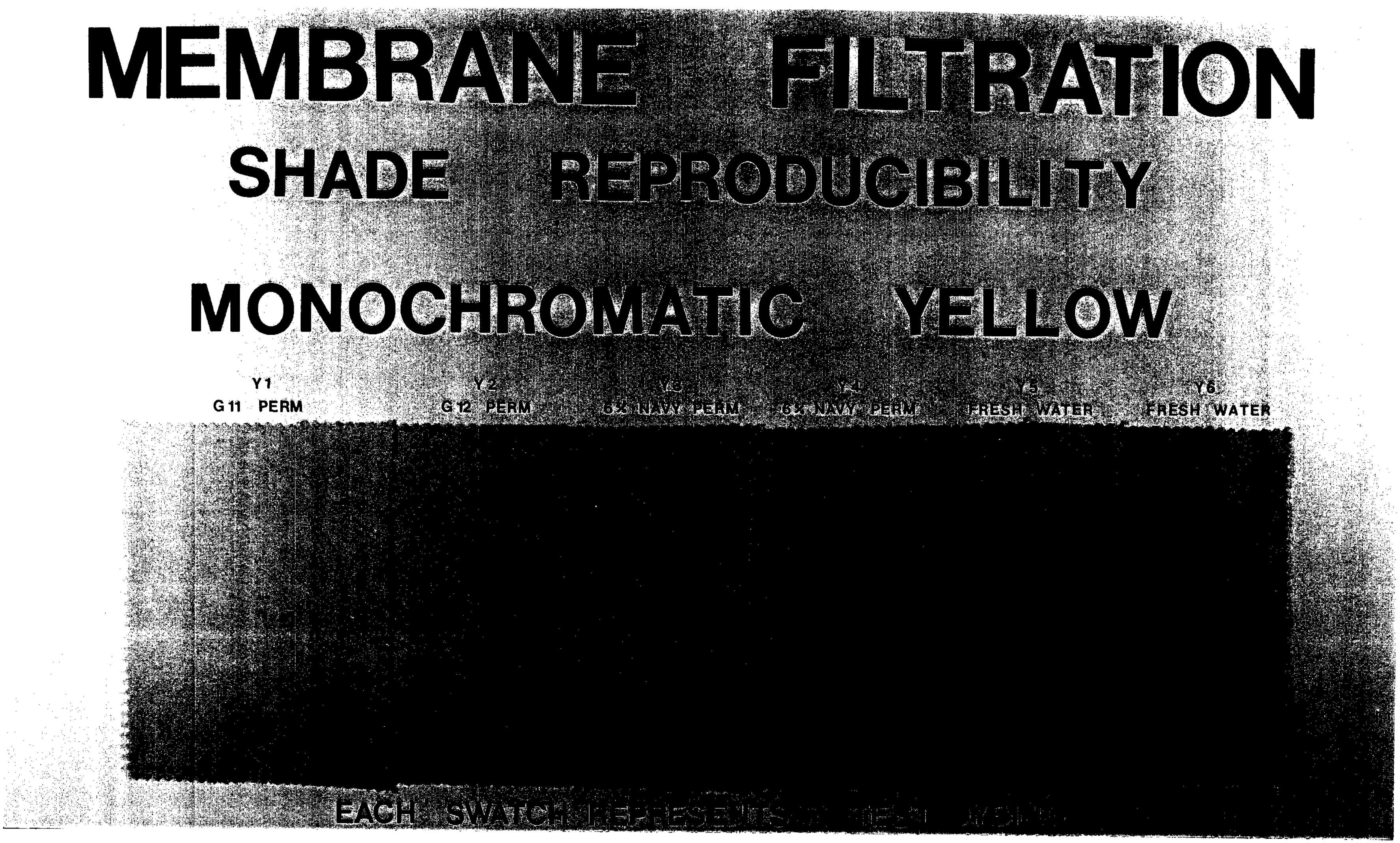
MEMBRANE FILTRATION
SHADE REPRODUCIBILITY
MONOCHROMATIC YELLOW
Y1
G11 PERM
Y2
G12 PERM
NAVY PERM
NAVY PERM
Y5
FRESH WATER
Y6
FRESH WATER
EACH SWATCH REPRESENTS

Figure 10

Material Balances
Dye Bath and First Rinse System

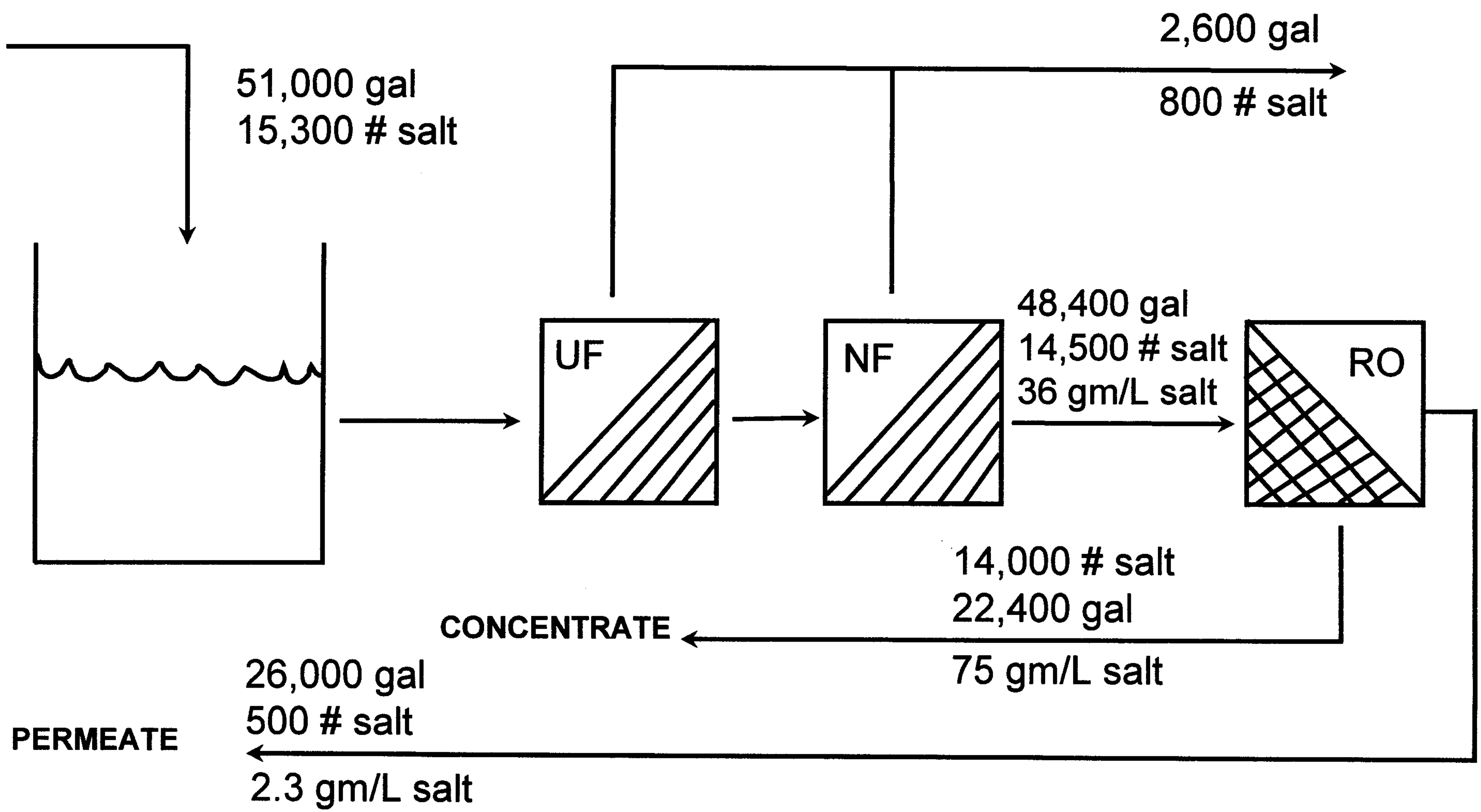

Table 1

2% Reactive Red 184
60 g/L NaCl[a] 6.0 g/L Na_2CO_3[a]

Dyeing #	Water Source	Percent Strength	DL* Adj	Da* Adj	Db* Adj	DEcmc As-Is	DEcmc Adj	NaCl g/L	Na_2CO_3 g/L	pH
R-1	Fresh	102.5	-0.09	-0.31	-0.15	0.20	0.14	58	5.7	10.5
R-3	Fresh	100.1	-0.07	-0.06	-0.09	0.13	0.13	59	5.9	10.6
R-4	Fresh	97.2	-0.13	-0.33	-0.11	0.51	0.37	61	6.0	--
R-5	Fresh	98.0	0	-0.02	0.11	0.11	0.06	NA	NA	--
R-6	#4 Permeate	94.2	-0.12	-0.28	-0.04	0.79	0.30	56	6.1	--
R-7	#5 Permeate	90.0	-0.10	-0.29	0.07	0.66	0.13	46	6.4	10.1
R-8	#4/5 Permeate	93.7	-0.15	-0.24	-0.04	0.42	0.11	47	5.9	10.5
R-9	#8 Permeate	96.4	-0.18	-0.35	0.03	0.22	0.16	59	6.5	11.1
R-10	#9 Permeate	95.4	-0.16	-0.28	-0.10	0.33	0.14	58	6.2	10.5
R-11	#10 Permeate	94.6	-0.27	-0.54	-0.13	0.40	0.24	59	6.1	--
R-12	#11 Permeate	93.7	-0.25	-0.53	0.06	0.38	0.23	58	6.3	--
Standard (R-2)	Fresh	100.0	--	--	--	--	--	61	6.1	10.5

[a] Target Values
NA = Not Analyzed

Note: DEcmc (adj) = DEcmc (as is) adjusted for % strength change.

Table 2

Trichromatic Gray Dyeings[a]
D65 Source
55 g/L NaCl[b] 9.0 g/L Na_2CO_3[b]

Dyeing #	Water Source	Percent Strength	DL[a] adj.	Da[a] adj.	Db[a] adj.	DEcmc as is	DEcmc adj.	NaCl g/L	Na_2CO_3 g/L	pH
G-1	Fresh	100.4	0.02	-0.20	-0.09	0.26	0.27	56	9.2	--
G-2 (STD)	Fresh	100.0	--	--	--	--	--	57	9.4	10.7
G-3	Fresh	101.4	0.04	-0.25	0.03	0.33	0.33	55	7.9	10.5
G-4	G-3 Permeate	99.5	0.15	-0.98	0.19	1.28	1.28	53	9.7	10.4
G-5	G-4 Permeate	99.3	0.04	-0.31	0.07	0.42	0.41	55	9.5	10.4
G-6	G-5 Permeate	99.8	0.05	-0.42	-0.09	0.54	0.54	52	9.5	10.4
G-7	6% Navy Permeate[c]	99.1	0.03	-0.20	0.05	0.28	0.26	58	9.6	10.5
G-8	6% Navy Permeate[c]	104.6	0.02	-0.10	0.09	0.37	0.15	58	9.7	--
G-9	6% Red Permeate[d]	103.8	0.05	-0.29	0.14	0.46	0.39	58	9.7	--
G-10	6% Red Permeate[d]	116.1	0.02	-0.20	0.11	1.15	0.27	59	9.6	--

[a] Reactive Yellow 0.18%
Reactive Red 0.14%
Reactive Blue 0.60%
[b] Target Values
[c] Permeates From 6% Reactive Navy Dyeings
[d] Permeates From 6% Reactive Red 184 Dyeings

Note: DEcmc(adj) = DEcmc (as is) adjusted for % strength change.

Table 2A

Trichromatic Gray Dyeings[a]
D65 Source
55 g/L NaCl[b] 9.0 g/L Na_2CO_3[b]

Dyeing #	Water Source	Percent Strength	DL[a] adj.	Da[a] adj.	Db[a] adj.	DEcmc as is	DEcmc adj.	NaCl g/L	Na_2CO_3 g/L	pH
G-11 (STD)	Fresh	100.0	--	--	--	--	--	58	9.4	10.6
G-12	Fresh	99.3	-0.02	-0.03	-0.28	0.24	0.24	56	9.1	10.7
G-13	Fresh	99.9	-0.01	-0.01	-0.21	0.18	0.18	57	9.3	10.7
G-14	G-13 Permeate	92.0	0.10	-0.72	0.05	1.16	0.89	50	9.1	10.3
G-15	G-14 Permeate	97.2	0.05	-0.35	0.02	0.51	0.43	51	9.1	10.7
G-16	G-15 Permeate	97.2	0.06	-0.40	0.12	0.59	0.52	54	9.1	10.5

[a] Reactive Yellow 0.18%
Reactive Red 0.14%
Reactive Blue 0.60%
[b] Target Values

Note: DEcmc(adj) = DEcmc (as is) adjusted for % strength change.

Table 3

Yellow Dyeings[a]

40 g/L NaCl[b] 5.0 g/L Na_2CO_3[b]

Dyeing #	Water Source	Percent Strength	DL[a] adj.	Da[a] adj.	Db[a] adj.	DEcmc as is	DEcmc adj.	NaCl g/L	Na_2CO_3 g/L	pH
Y-1	G-11 Permeate[c]	106.8	-1.08	-0.42	-1.67	0.57	0.71	40	5.3	---
Y-2	G-12 Permeate[c]	111.2	-0.94	-0.41	-1.49	0.52	0.64	36	5.4	10.1
Y-3	6% Navy Permeate[d]	105.5	-1.31	-0.47	-1.96	0.71	0.84	39	5.4	10.2
Y-4	6% Navy Permeate[d]	108.5	-1.33	-0.52	-2.04	0.71	0.88	40	5.4	10.1
Y-5	Fresh Water	108.0	0.12	0.13	0.31	0.54	0.13	40	5.0	---
Y-6 (STD)	Fresh Water	100.0	---	---	---	---	---	40	4.9	---

[a] Reactive Yellow 143, 2%
[b] Target Values
[c] Permeates from Gray Dyeings
[d] Permeates from 6% Reactive Navy Dyeings

Note: DEcmc(adj) = DEcmc (as is) adjusted for % strength change.

Table 4

Fabric Physical Properties

	% Shrinkage		Mullen Burst	Wales	Courses	Color Fastness to Light		2A Wash	
	L	W				20 hr	40 hr	Strength	Shade Change
Greige	17.5	13.5	122	35	39	--	--	--	--
Bleached	7.3	5.3	120	37	43	--	--	--	--
Red 1	9.1	7.0	112	35	41	4	3	4	4-5
Red 2	9.4	5.4	115	36	41	4	3	4	4-5
Red 3	10.5	5.6	117	36	41	4	3	4	4-5
Red 4	9.5	4.4	118	36	40	3-4	3	3-4	4-5
Red 5	10.5	4.7	113	36	40	4	3	4	4-5
Red 6	9.1	5.5	113	35	42	4	3	3-4	4-5
Red 7	4.4	6.9	112	35	42	4	3	3-4	4-5
Red 8	8.5	4.5	111	36	41	4	3	3-4	4-5
Red 9	7.8	5.8	111	36	42	4	3	4	4-5
Red 10	10.5	2.2	115	36	41	4	3	3-4	4-5
Red 11	7.5	4.7	112	36	42	4	3	3-4	4-5
Red 12	6.9	5.3	109	35	41	4	3	3-4	4-5

Table 5

Chemical Analysis of Effluent

Trichromatic Grey G-16

	COD (ppm)	TDS (ppm)	TOC (ppm)	Cu (ppm)	Cu* (ppm)
Dye Bath	1,760	56,700	171	1.320	2.780
Rinse 1	703	16,900	87	0.945	1.200
Rinse 2	193	4,790	33	0.048	0.846
Acid Rinse	210	1,490	75	0.465	0.635
Soap Off	199	555	64	0.499	0.887
Rinse 4	68	250	22	0.160	0.250
Rinse 5	29	146	8	0.045	0.091
Rinse 6	18	143	6	0.018	0.031
Water	<10	119	3	0.020	
UF Concentrate	827	39,000	95		
NF Concentrate	3,960	50,400	671		10.800
NF Permeate (end of run)	3,920	33,800	9		0.022

*Grey dyeing with slightly different procedure on dye and alkali addition. Alkali added after dye addition.

Table 5A

CHEMICAL ANALYSIS OF EFFLUENT

	Percent Contribution				
	COD	TDS	TOC	Cu	Cu*
Dye Bath	55.3	70.0	36.7	37.7	41.4
Rinse 1	22.1	20.9	18.7	27.0	17.9
Rinse 2	6.1	5.9	7.1	1.4	12.6
Acid Rinse	6.6	1.8	16.1	13.3	9.4
Soap Off	6.3	0.7	13.7	14.2	13.2
Rinse 4	2.1	0.3	4.7	4.6	3.7
Rinse 5	1.0	0.2	1.7	1.3	1.3
Rinse 6	0.5	0.2	1.3	0.5	0.5

*Grey dyeing with slightly different procedure on dye and alkali addition. Alkali added after dye addition.

Table 6

Dye Bath and First Rinse Recovery Economics Capital Cost, UF/NF/RO = $369,000

Annual Operating Savings		$395,000
-- Water and sewer charges	$ 46,000	
-- Salt recovery	$349,000 @ $160/ton	
Annual Operation Costs		$ 67,000
-- Electricity, Membrane, Labor, Maintenance		
Net Savings from Operations		$328,000
Payback		**1.12 Years**