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MEMBRANE ULTRAFILTRATION TO TREAT NON-SANITARY MILITARY WASTES

FINAL REPORT

by

Dibakar Bhattacharyya, Ph.D.

and

Robert B. Grieves, Ph.D.

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Ultrafiltration with non-cellulosic membranes is demonstrated to be a feasible process, from both engineering and health standpoints, for the treatment of laundry and shower wastes to enable the use of the recycled ultrafiltrate for non-potable, human contact purposes. Among the various non-cellulosic membranes evaluated, those containing charged groups in the anisotropic skin provide minimum flux drop and maximum rejection of solutes (including 40 to 60% rejection of dissolved solids). Extensive, laboratory-scale

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ultrafiltration data in a thin-channel unit for synthetic laundry wastes and for actual and synthetic shower wastes are utilized to establish optimum values of operational parameters and to determine empirical equations for ultrafiltrate water flux and ultrafiltrate water quality. The equations are used with a computer simulation procedure to establish the optimum multiple module arrangement (tapered mode), membrane area requirements, and predicted water quality at 90% water recovery for the full waste flow. A model of the entire waste treatment-water reuse system predicts the maximum build-up of organic carbon and total dissolved solids in the recycled water at a large number of recycle passes and the predictions are validated experimentally. A thorough toxicity and irritancy (dermal, ocular, and oral) study on mice and rabbits is carried out with various concentrated ultrafiltrates and feed solutions (1000-fold concentration) and shows that the recycle water can be reused for human contact purposes with a large safety factor (200:1), even at a very high number of recycle passes. The animal studies are validated by human skin irritancy tests.

SUMMARY

Ultrafiltration with non-cellulosic membranes is demonstrated to be a feasible process, from both engineering and health standpoints, for the treatment of laundry and shower wastes to enable the use of the recycled ultrafiltrate for non-potable, human contact purposes. Among the various non-cellulosic membranes evaluated, those containing charged groups in the anisotropic skin provide minimum flux drop and maximum rejection of solutes (including 40 to 60% rejection of dissolved solids). Extensive, laboratory-scale ultrafiltration data in a thin-channel unit for synthetic laundry wastes and for actual and synthetic shower wastes are utilized to establish optimum values of operational parameters and to determine empirical equations for ultrafiltrate water flux and ultrafiltrate water quality. The equations are used with a computer simulation procedure to establish the optimum multiple module arrangement (tapered mode), membrane area requirements, and predicted water quality at 90% water recovery for the full waste flow. A model of the entire waste treatment-water reuse system predicts the maximum build-up of organic carbon and total dissolved solids in the recycled water at a large number of recycle passes and the predictions are validated experimentally. A thorough toxicity and irritancy (dermal, ocular, and oral) study on mice and rabbits is carried out with various concentrated ultrafiltrates and

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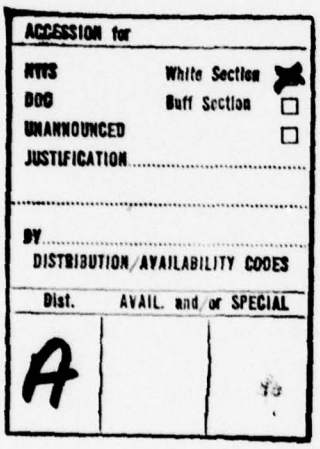

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INTRODUCTION

The overall objective of this investigation is the development of membrane ultrafiltration as a waste treatment and water renovation (multiple-pass reuse) technique for non-sanitary military wastes. Preliminary experiments are carried out to establish concentration polarization effects produced by surfactants and the individual rejection behavior of several laundry waste constituents with various membranes. An extensive experimental investigation is then conducted with two types of wastes: synthetic laundry wastes containing surfactant, polyphosphates, silicates, hypochlorites, clay particulates, and oil; and synthetic and actual shower wastes containing aliphatic acid soaps, toothpaste constituents, hair oil, shampoo, insect repellent, scouring powder/disinfectant containing phenylphenol, and soil. The specific objectives are to develop the necessary design equations (to predict water flux and water quality) for scale-up of ultrafiltration units to multiple-pass water recycle, from extensive laboratory-scale experimental data; to find optimum module arrangements by computer simulation for full waste flow at high water recovery; and to demonstrate thoroughly the safety of the recycled ultrafiltrate by quantitative evaluation of toxicity and irritancy (dermal, ocular, and oral) on mice and rabbits with solutions up to 3000 times the actual ultrafiltrate concentration. The animal studies are further substantiated by quantitative data on mutagenicity in

microbial assays and for irritation to the skin of volunteer human subjects. All toxicity and irritancy studies are conducted by Witherup and Emmett under a separate U.S. Army Medical Research and Development Contract (No. DADA17-76-C-6006) to the University of Cincinnati.

Membrane ultrafiltration with non-cellulosic membranes is an effective process for the separation of various organic compounds and colloidal particulates present in aqueous solution and has been used[1-5] for the treatment of a large number of industrial wastes. Applications include the ultrafiltration of primary sewage,[1] food processing wastes,[2,3,5] shipboard oily wastes,[6] spent sulfite liquors,[7] and latex wastewaters.[8] The ultrafiltration process is appropriate for applications requiring water recycle and reuse and particularly for systems in which the high rejection of low-molecular-weight organic solutes is not warranted. Some of the water reuse applications involving ultrafiltration include color removal from Kraft mill effluents,[9] electrodeposition primers,[3] laundry wastes,[10] and nitrotoluene manufacturing wastes.[11]

Ultrafiltration is a pressure-activated process and is generally carried out with anisotropic membranes at low pressures of 10^5 to 10^6 N/m^2. The solute rejection characteristics of a membrane depend on the pore size distribution and frictional interaction between solute and pore wall in the thin membrane

skin, and on the relative diffusivities and structures of the species of significance. With ultrafiltration membranes containing fixed charged groups (such as sulfonic acid), the simultaneous achievement of moderate rejections of ionic (inorganic) dissolved solids and of high rejections of modest-molecular-weight (size) organic solutes have also been reported.[1,10-13] The Donnan exclusion mechanism is primarily responsible for the rejection of ionic solutes; Bhattacharyya, et al.[14,15] have studied extensively the rejection characteristics of various inorganic systems by charged membranes. In applications involving water reuse, the build-up of low-molecular-weight ionic solutes in the recycled water can be minimized by using charged membranes.[10,11,14]

The treatment of laundry wastes and shower wastes (non-sanitary wastes) by membrane ultrafiltration and post disinfection of the ultrafiltrate for the purpose of multiple-pass water reuse is a very promising application. The use of reverse osmosis[16] and ultrafiltration for laundry wastes[10,12] and of dynamic membrane hyperfiltration of simulated shower water generated in space stations,[17] have been reported in the literature. For successful application of an ultrafiltration process, the unit must be designed to operate at high water recovery levels to reduce the amount of needed fresh make-up water, and, for human-contact applications, must yield water quality acceptable from a toxicity (skin and eye irritation) and comfort standpoint based on chemical (total organic carbon, total solids) and microbial impurities.

WATER FLUX AND MEMBRANE REJECTION

A viscous flow model describes water transport through ultrafiltration membranes, and, in the absence of concentration polarization and osmotic pressure effects, the ultrafiltrate flux, J_w, can be related to the transmembrane pressure difference.

$$J_w = \frac{\Delta p}{R_m} \qquad (1)$$

The Millipore PSAL membrane extensively used in this study had an average resistance $R_m = 2.8 \times 10^8$ N/m^2/cm/sec at 25°C, in the absence of solutes.

The phenomenon of concentration polarization, and particularly gel polarization (water flux invariant with Δp), is a major process limitation. The accumulation of solute(s) on the membrane surface (concentration polarization) is caused by the rapid convection to the surface of rejected solutes. The important variables which affect concentration polarization (and thus water flux) are transmembrane pressure, channel velocity (Reynolds Number), and waste constituent concentrations, and with complex waste systems containing particulates and organic molecules, the observed water flux may be considerably lower than the J_w obtained from Equation 1. Excellent mathematical formulations on concentration polarization have been presented by Michaels, et al.[18] and Porter.[19] Concentration polarization caused by nonionic

surfactant micelles has been investigated by Grieves, et al.[20] In the pre-gel region, an empirical equation must be developed from experimental data, relating J_w to the independent variables Δp, U, and C, the bulk solute concentration.

Below a critical channel velocity gel polarization causes a substantial decline in J_w, and membrane fouling which may necessitate frequent cleaning operations. In the gel polarization region,

$$J_w \propto K_s \tag{2}$$

and in the turbulent flow regime,[10,18,19]

$$K_s \propto \frac{U^{0.8}}{d^{0.1}} \tag{3}$$

With operation in the laminar flow regime, $J_w \propto U^{0.33}$. For waste systems containing suspended solids, charged membranes have been reported[1,13] to be non-fouling in nature.

The extent of separation of solutes by ultrafiltration (at insignificant water recovery) can be defined in terms of a rejection parameter, R,

$$R = 1 - \frac{C_f}{C_i} \tag{4}$$

Solute rejection by a membrane is due to a combination of several factors, such as sieving action, solute-solute interaction at the membrane surface, diffusion rates through membrane pores, and the repulsion of anions (Donnan exclusion) by negatively-charged membranes. The concentration of a particular solute in the ultrafiltrate stream is often a strong function[10,11,14,20] of the feed stream solute concentration, C_i, and a weak function of Δp and U.

ULTRAFILTRATION OF VARIOUS LAUNDRY WASTE CONSTITUENTS

Concentration Polarization with Surfactant

Because the surfactant is the most important constituent of any laundry waste, an extensive ultrafiltration study[21] was conducted with a nonionic surfactant utilizing three different membranes of pore diameters in the range of 15 to 30 A°. The model surfactant selected was isoctyl phenoxy polyethoxy ethanol (Triton X-100), containing 9 to 10 moles ethylene oxide, with an average molecular weight of 625, and a critical micelle concentration of 100 mg/l as carbon. The thin-channel (channel height 0.076 cm), continuous-flow ultrafiltration unit was operated with feed streams containing from 60 to 4000 mg carbon/liter of Triton X-100 over a temperature range of 22 to 50°C and with channel Reynolds numbers from 50 to 1200. The membrane resistances were: 3.9×10^8 N/m^2/cm/sec for Amicon UM2, 1.1×10^8 N/m^2/cm/sec for Amicon UM10, and 0.23×10^8 N/m^2/cm/sec for Amicon PM-10; thus the initial distilled water fluxes varied by a factor of 17:1.

Surfactant rejection increased with increases in the values of R_m and with increases in feed stream concentration (C_i) because of micelle formation. For example, at a feed concentration of 150 mg/l surfactant, the rejections of the three membranes (at 25°C) were,

	$R_m \times 10^{-8}$, $N/m^2/cm/sec$	Rejection
UM-2	3.9	0.87
UM-10	1.1	0.82
PM-10	0.23	0.20

Rejection was also found to decrease with temperature: the surfactant rejection was 0.80 at 45°C with UM-10. Grieves, et al.[20] have reported the effects of all independent variables on ultrafiltrate concentration (and thus rejection) by a stepwise, multiple linear regression analysis.

The loosest membrane, PM10, was subject to extreme gel polarization: J_w was decreased by 81% at C_i = 1140 mg/l. For the same variation, the water flux with the tight UM2 membrane decreased by only 7%. With the intermediate porosity UM-10 membrane, gel polarization occurred at $\Delta p \geq 3.5 \times 10^5$ N/m^2 for $C_i \geq 1200$ mg/l. Typical effects of Δp on J_w are shown in Figure 1. The solute concentration, at which gel formation occurs depends on the type of solute. The present ultrafiltration study showed a gelation concentration ($J_w \approx 0$) of 30,000 mg carbon/l with Triton X-100.

In the laminar flow range, the mass transfer coefficient, K_s, is generally proportional to $U^{0.3 \text{ to } 0.5}$: for the Triton X-100 system, the relationship between J_w and channel velocity, U, is shown in Figure 2, and K_s (thus J_w) was proportional to $U^{0.5}$.

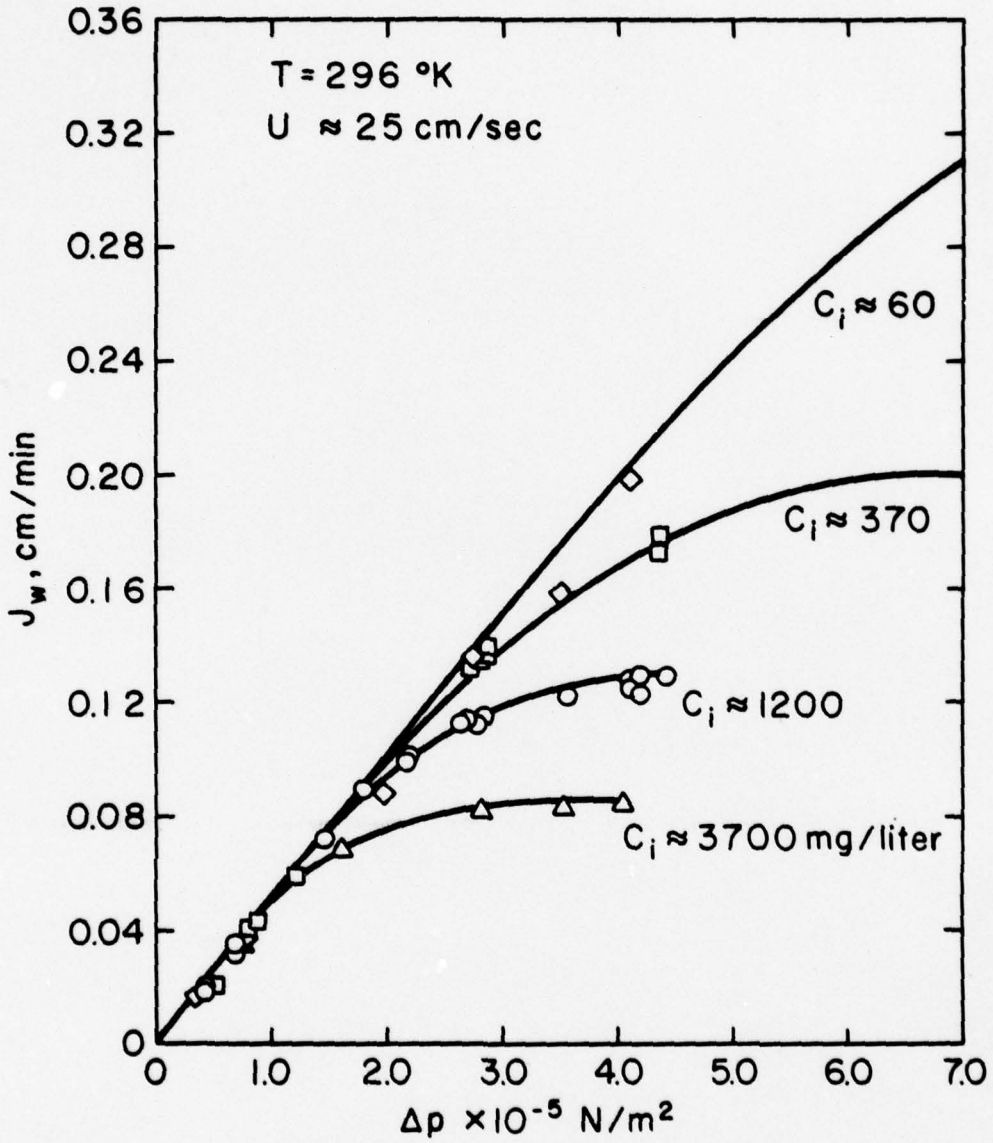

Figure 1. Effect of average transmembrane pressure difference on ultrafiltrate water flux for nonionic surfactant solution.

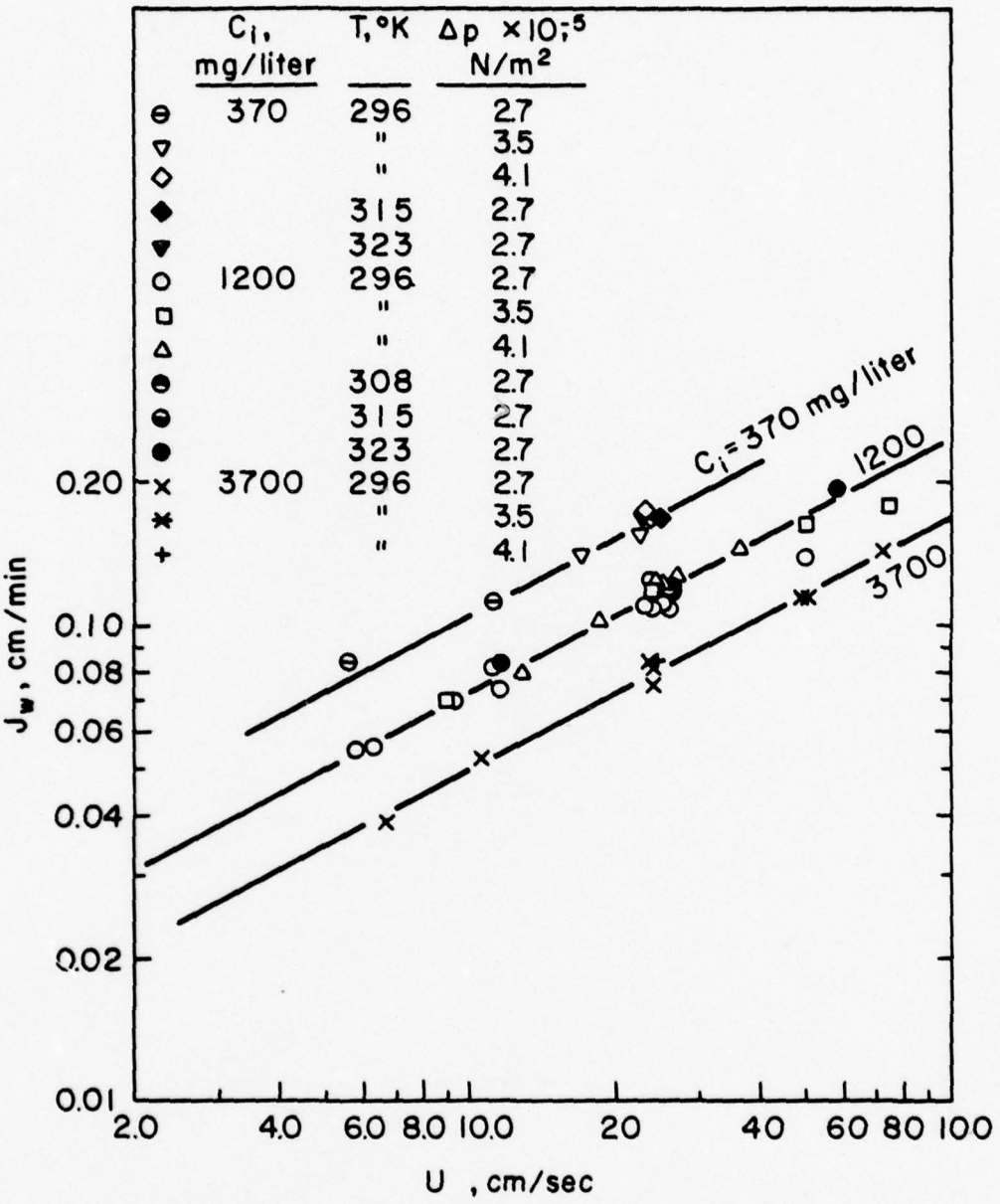

Figure 2. Power dependence of ultrafiltrate water flux on average channel velocity for nonionic surfactant solution.

The predicted water fluxes in the gel region (with diffusive transport of surfactant micelles from the membrane surface limiting) calculated from the heat transfer correlations of Leveque, were about 70% low due to the difficulty of estimating the diffusivity of surfactant micelles. The water flux in the gel region was invariant with temperature, because the micellar weight and micelle size of nonionic surfactants increase with temperature. Concentration polarization was substantially reduced by maintaining U > 50 cm/sec; even at a C_i of 3800 mg/l, a water flux of 18 X 10^{-4} cm/sec (0.11 cm/min) was obtained.

Preliminary Evaluation of Several Cellulosic and Non-cellulosic Membranes

For the treatment of laundry wastes, the membranes must be capable of adequately rejecting surfactants (anionic and/or nonionic) and phosphates. Linear alkylbenzene sulfonate (LAB) was used as the model anionic surfactant and phenolic ethoxylate or primary alcohol ethoxylate was used as the model nonionic surfactant. Table 1 shows the membranes used for the experiments.[22] The same feed stream solute concentrations were used with each membrane.

Figure 3 shows the maximum rejection that could be obtained with each membrane for feed streams containing surfactant, polyphosphate, or both; practically no concentration polarization

TABLE 1. ULTRAFILTRATION MEMBRANES

Membrane	Chemical Composition	$R_m \times 10^{-8}$, $\frac{N/m^2}{cm/sec}$	U, cm/sec
HFA-180 (Abcor)*	Cellulose acetate	1.2	53
Exp. (Calgon-Havens)**	" "	13.0	132
Type 215 (Calgon-Havens)**	" "	5.3	132
F-601 Exp. (Gulf)	" "	3.5	154
UM-2 (Amicon)	Polyelectrolyte complex	3.9	25
PM-10 (Amicon)	" "	0.23	200
PSAC (Millipore)	Cellulose ester	2.1	25
PSAL (Millipore)	Noncellulosic skin on cellulosic backing	3.9	154

* Tubular configuration: 1-2.54 cm I.D. tube, 1000 cm^2 area.

** Tubular configuration: 18-1.27 cm I.D. tubes, 929 cm^2 area.

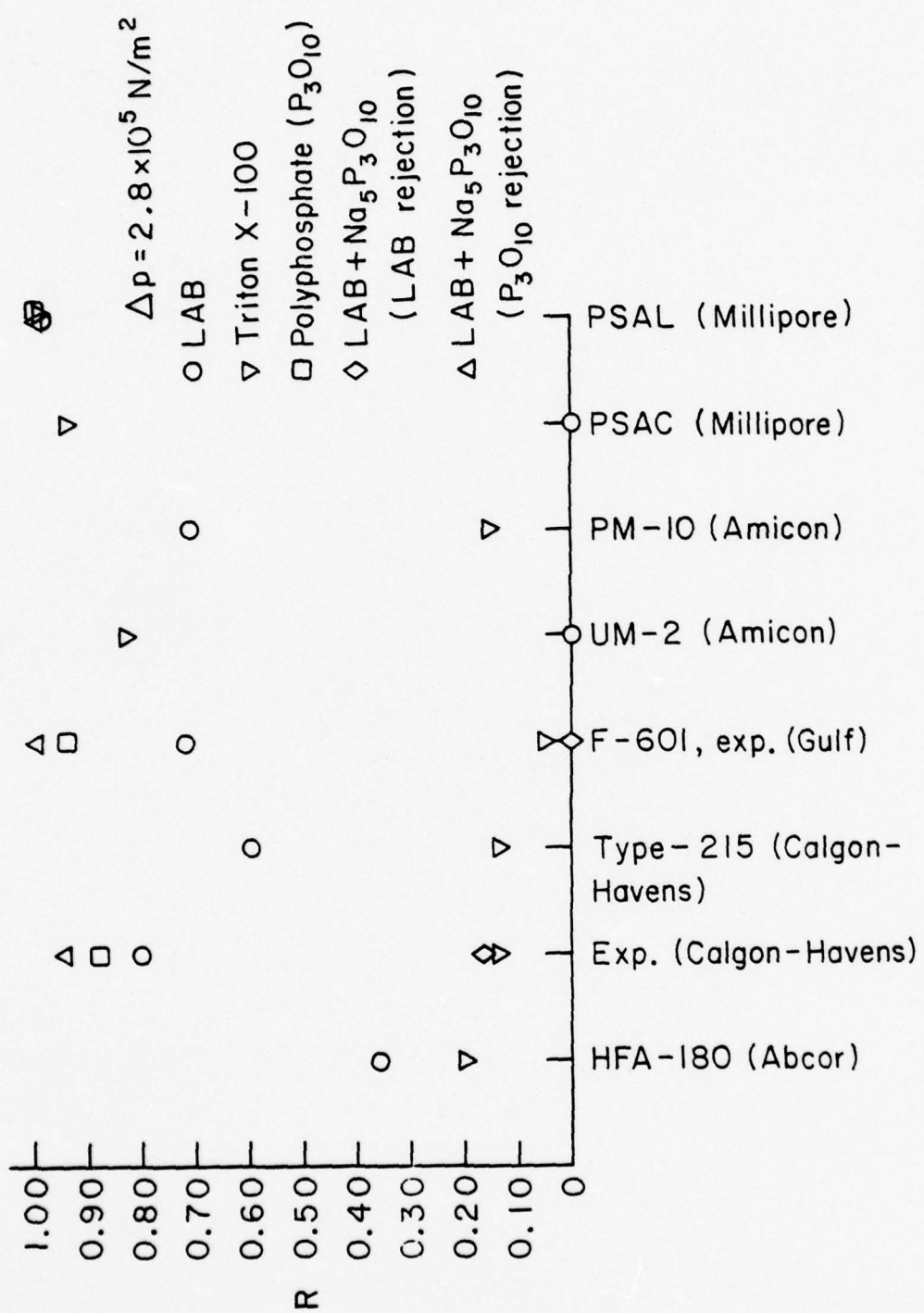

Figure 3. Rejection characteristics of various ultrafiltration membranes.

was observed. The membrane PM-10 had the highest flux and Exp. had the lowest. Figure 3 indicates very poor rejection characteristics ($R < 0.2$) of the nonionic surfactant (Triton X-100) by all cellulose acetate membranes, because of strong membrane sorption. Although both the UM-2 and PSAC membranes rejected Triton X-100 quite efficiently, LAB caused destruction of the membrane skin. The PSAL membrane was the only one that gave $R = 0.98$ for both LAB and Triton X-100. In a mixture of LAB and Triton X-100, the cellulose acetate membranes rejected LAB only. Both Exp. and F-601 cellulose acetate membranes yielded practically no rejection of LAB when present in a mixture with polyphosphate, whereas the rejection of LAB with PSAL was still 0.98. Thus the overall rejection behavior of PSAL was the best among all the membranes tested.

A detailed study with non-cellulosic PSAL was conducted with several laundry waste constituents.[22] Typical effects of feed concentration on ultrafiltrate quality are shown in Figure 4 for solutions containing only LAB. At $U \geq 150$ cm/sec, no concentration polarization was observed. With the nonionic surfactant, C_f practically remained constant (≈ 1.5 mg/l) for variation of C_i in the range of 58 to 300 mg/l. For mixtures of LAB + Triton X-100 + $Na_5P_3O_{10}$, with total feed organic carbon from 60 to 500 mg/l (equal weight ratios of anionic to nonionic)

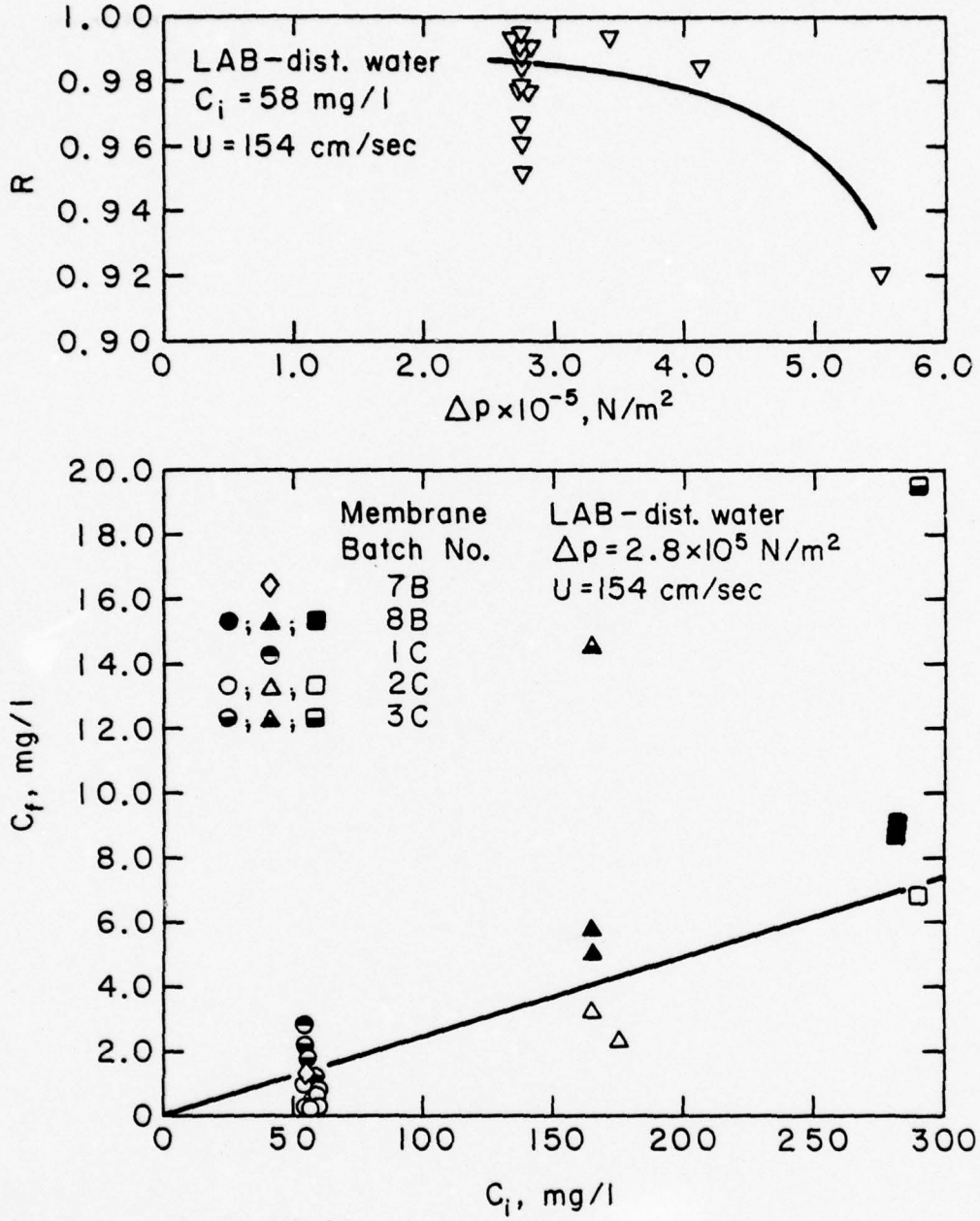

Figure 4. Effects of feed stream concentration and of transmembrane pressure difference on ultrafiltrate water quality for anionic surfactant solution.

and phosphate from 100 to 800 mg/l, C_f ranged from 1 to 7 mg/l, corresponding to surfactant rejection greater than 0.96; phosphate rejection was always greater than 0.97.

Table 2 summarizes the rejection characteristics of PSAL membranes for several laundry waste constituents. High rejections of various inorganic compounds are due to Donnan exclusion by charged (negative) sites on the PSAL membrane skin. All compounds (except LAB at high concentration and severe polarization condition) produced no membrane-solute interaction or membrane swelling.

TABLE 2. REJECTION CHARACTERISTICS OF PSAL MEMBRANES

System	Concentration, mg/l	Rejection
Anionic surfactant (LAB)	58 as carbon	0.98
Nonionic surfactant (Triton X-100)	58 as carbon	0.98
Nonionic surfactant (Neodol 25-9)	60 as carbon	0.92
$Na_5P_3O_{10}$	100 as phosphorous	0.99
Na_2HPO_4	100 as phosphorous	0.96
$Na_2B_4O_7$	107 as boron	0.92
Na_2SO_4	200 as sodium	0.97
Urea	25 as carbon	0.00
LAB + $Na_5P_3O_{10}$	58 as carbon, 30 as phosphorous	0.97C, 0.99P
LAB + Triton X-100	60 as carbon	0.98

ULTRAFILTRATION OF LAUNDRY AND SHOWER WASTES

Experimental

All ultrafiltration experiments were conducted under continuous-flow conditions as shown in a schematic diagram of the experimental unit in Figure 5. Various membrane systems and operating ranges used are shown in Table 3. All experiments were carried out until steady-state was reached; this generally required from 6 to 10 hr, and in a few experiments the ultrafiltration time was extended to 30-80 hr. For those experiments which were conducted under negligible water recovery conditions, the feed solute(s) concentration was maintained constant by recycling both the concentrate and the ultrafiltrate stream to the feed tank. For experiments involving water recovery, only the concentrate stream was recycled back to the feed tank. At the termination of each run, the membrane was thoroughly flushed with tap water or chlorine solution (for some systems) at high flow rate and low pressure.

Synthetic Laundry Wastes. The composition of a normal laundry waste (designated as 1 X) used as the feed stream in the ultrafiltration experiments was:

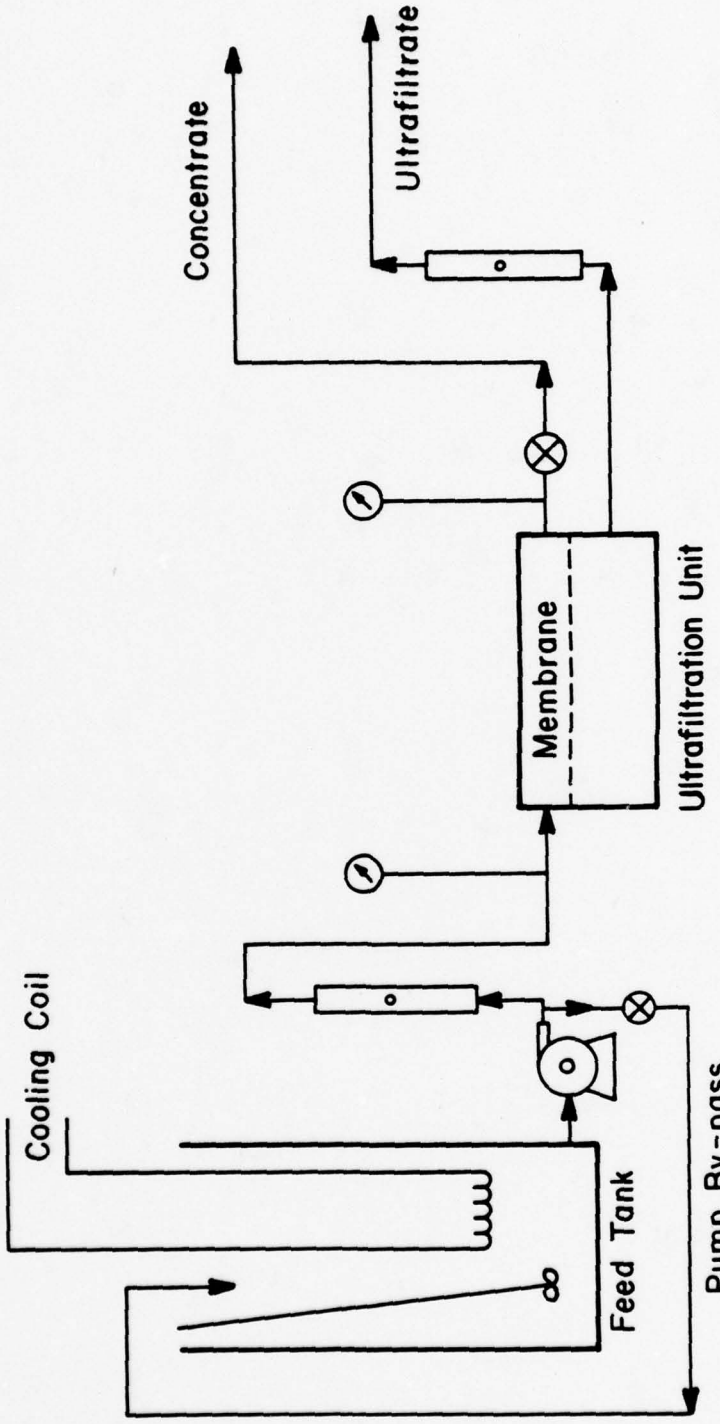

Figure 5. Schematic diagram of experimental ultrafiltration unit.

TABLE 3. ULTRAFILTRATION MEMBRANE SYSTEM OPERATIONS

Membrane	System	Membrane Area, cm^2	$\Delta p \times 10^{-5}$, N/m^2	U, cm/sec	Re
PSAL	thin-channel	51.2	2.8 - 7.0	86 - 1300	2416 - 36000
PSAL	cassette	4645	2.8 - 5.6	12	-
FLUXO	thin-channel	51.2	2.8 - 5.6	170 - 427	4777 - 12000
UOP-225	mini-module (tubular)	980	2.8 - 7.0	157 - 204	20000 - 26000
UOP-225	commercial-module* (tubular)	15514	2.8 - 7.0	146 - 241	3720 - 6140
UOP-X117	single tube	900	5.6	197	25000
HF20-PM5	hollow fiber cartridge	1672	1.1 - 1.3	47 - 132	239 - 671
HF43-AM2	hollow fiber cartridge	929	1.0	295	3215

*with volume displacement rods

	Concentration, mg/l	Organic Carbon Concentration, mg/l
Nonionic surfactant	100	60
CMC	5	2
Vegetable oil	200	124
Ca^{2+} ($CaCl_2 \cdot 2H_2O$)	50	-
P ($Na_5P_3O_{10}$)	100	-
SiO_3^{2-} ($Na_2SiO_3 \cdot 9H_2O$)	100	-
Bleach (NaOCl-5% solution)	10	-
Soil (kaolinite; 0.2 μm)	100	-

The nonionic surfactant selected here is typically used in various commercial laundry detergents and military detergents (Type I). The surfactant was linear, C_{12}-C_{15} primary alcohol ethoxylate containing nine moles of ethylene oxide.

Synthetic Shower Wastes. The composition of a normal shower waste (1 X) used as the feed stream was:

	Concentration, mg/l	Organic Carbon Concentration, mg/l
Soap (Dial)	70	38
Shampoo (Prell)	40	9
Hair tonic (Vitalis)	25	6
Toothpaste (Crest)	40	5
Shower-lavoratory cleaner (Ajax)	100	4
Disinfectant (sodium ortho-phenylphenolate)	20	10
Insect-repellent (50% diethyl-toluamide, 50% ethanol)	20	14
Soil (kaolinite; 0.2 μm)	20	-

It should be noted that commercial trade names are shown only for the purpose of identification.

Actual Shower Wastes. The volunteers were asked to use Dial soap, Prell shampoo, and Crest toothpaste. After the collection of shower water, proper amounts of shower cleaner, disinfectant, and insect repellent were added to obtain "normal" concentrations of these constituents the same as those in the 1 X synthetic waste. Prior to all ultrafiltration runs, prefiltration

(with a fine screen) was used to remove most of the hair.

Analytical. The concentrations of total organic carbon, phosphate, total solids, and total dissolved solids (and conductivity) in the feed stream and in the ultrafiltrate were monitored. Organic carbon (total carbon minus inorganic carbon) concentrations were measured by a Beckman, Model 915 Carbon Analyzer, and the reproducibility of the carbon analysis was $\pm$ 5% of full scale. Phosphate (expressed as mg P/l) concentrations were measured by vanadomolybdophosphoric acid colorimetric method.[23] The tap water used to prepare the feed solutions was of conductivity approximately 240 μmho/cm and contained organic carbon ranging from 2 to 6 mg/l.

Evaluation of Various Ultrafiltration Systems

The commercially available ultrafiltration modules (containing non-cellulosic membranes) evaluated in this study are shown in Table 3. Tubular, plate and frame, and hollow fiber cartridges were evaluated with the wastes. The results of the Millipore PSAL in a thin-channel system will be discussed in detail in the next section. Table 4 shows the temperature, pressure, and pH tolerance limits along with the resistances of the various membranes in solute-free water. Initial water fluxes (with no solutes) were highest for the hollow fiber systems as indicated by the low R_m. With both cassette (plate and frame) and hollow fiber systems, all waste streams were prefiltered with a 400 mesh screen.

The flux behavior with the wastes and flux recovery after each flushing and/or cleaning are shown in Figures 6-9 for the tubular and hollow fiber systems. A hollow fiber cartridge can be considered to be micro-tubular system. With the UOP-225 (Figure 6) tubular system, the flux loss was quite drastic, and the flux recovery was negligible even after cleaning by chlorine and enzyme detergent. The irreversible flux loss was probably due to membrane-surfactant interaction. With the UOP-X117 tubular system (Figure 7) containing a different non-cellulosic membrane, the membrane flux recovery after each run was considerably better. With hollow fiber cartridges, both backflushing and normal flushing

TABLE 4. MEMBRANE CHARACTERISTICS

Membrane	Manufacturer	Configuration	Maximum Pressure, X 10^{-5}, N/m^2	Maximum Temperature, °C	pH range	R_m X 10^{-8}, $N/m^2/cm/sec$
PSAL	Millipore	0.152 cm channel or 0.076 cm spacer cassette	9.0	37	2.5 - 11	2.0 - 4.0
FLUXO	Millipore	0.152 cm channel	9.0	45	2 - 12	0.5 - 0.6
UOP-225	Universal Oil Products	tubular (1.27 cm dia. tubes)	14.0	45	2 - 11	7.0 - 8.0
UOP-X117	Universal Oil Products	tubular (1.27 cm dia. tubes)	8.4	35	2 - 13	7.0 - 9.0
HF20-PM5	Romicon	hollow fiber (0.051 cm dia. fibers)	1.8	65	1.5 - 13	0.6
HF43-AM2	Romicon	hollow fiber (0.109 cm dia. fibers)	1.8	65	1.5 - 9	0.8

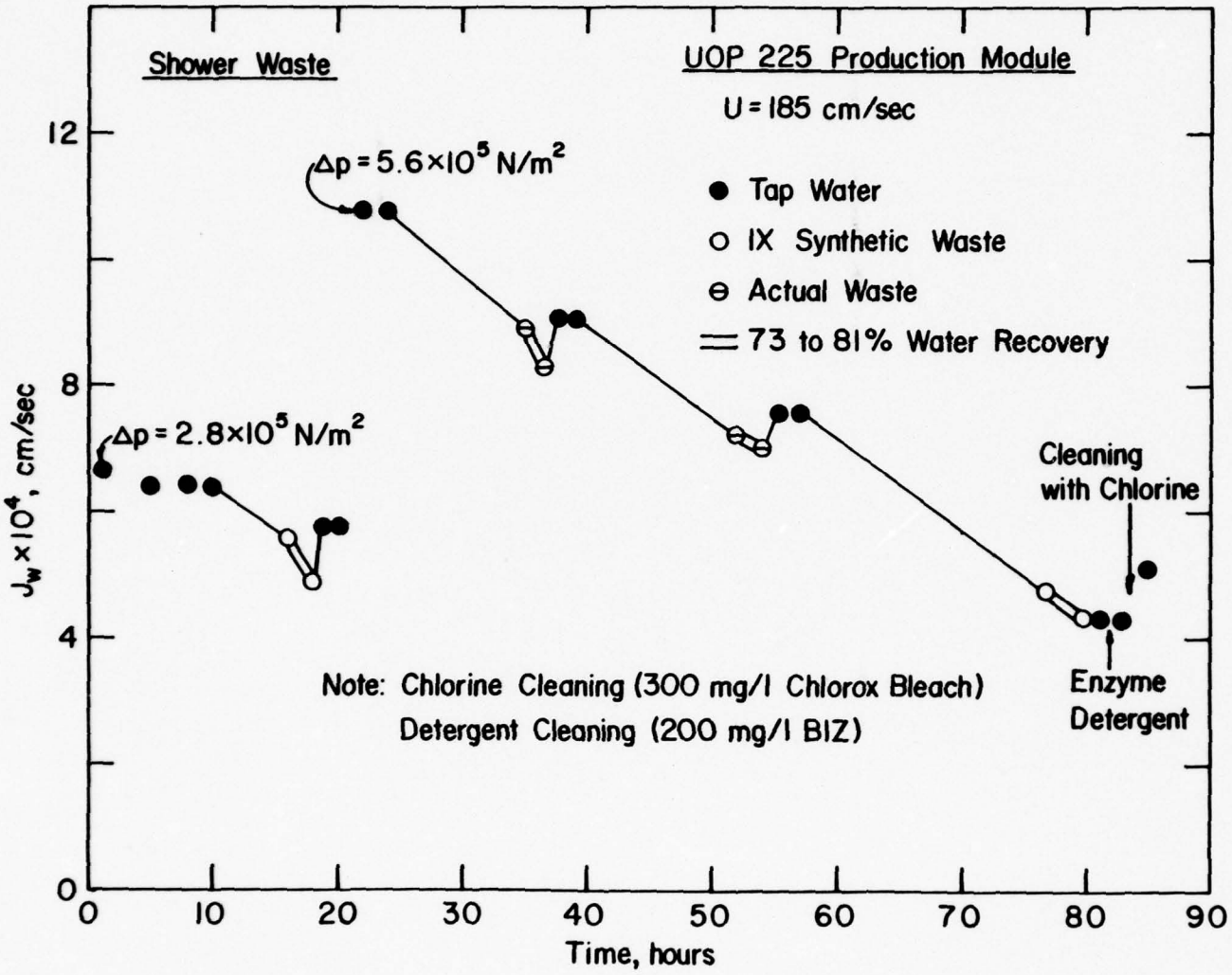

Figure 6. Long term ultrafiltrate water flux behavior for UOP-225 tubular module.

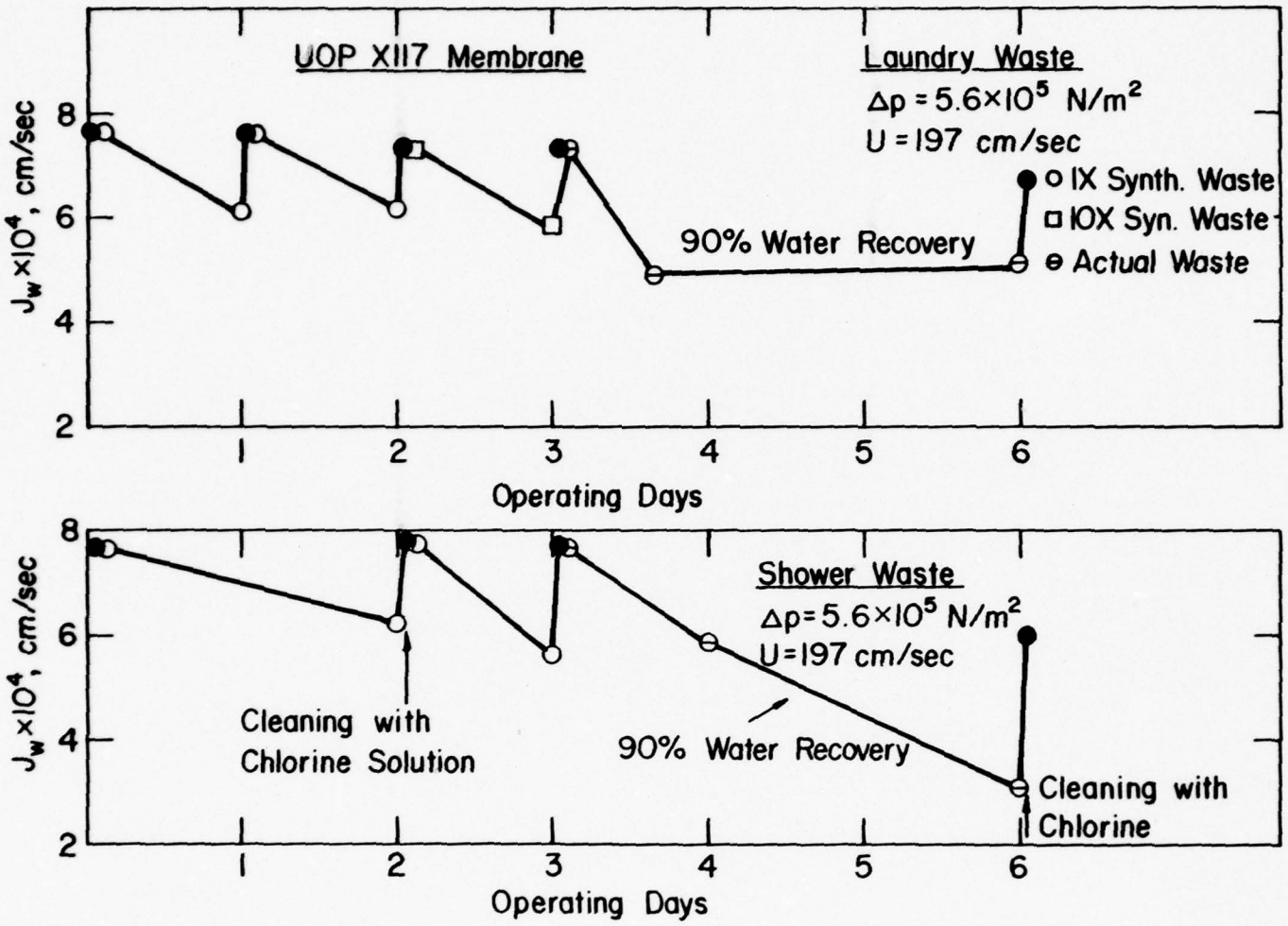

Figure 7. Long term ultrafiltrate water flux behavior for UOP-X117 tubular membranes.

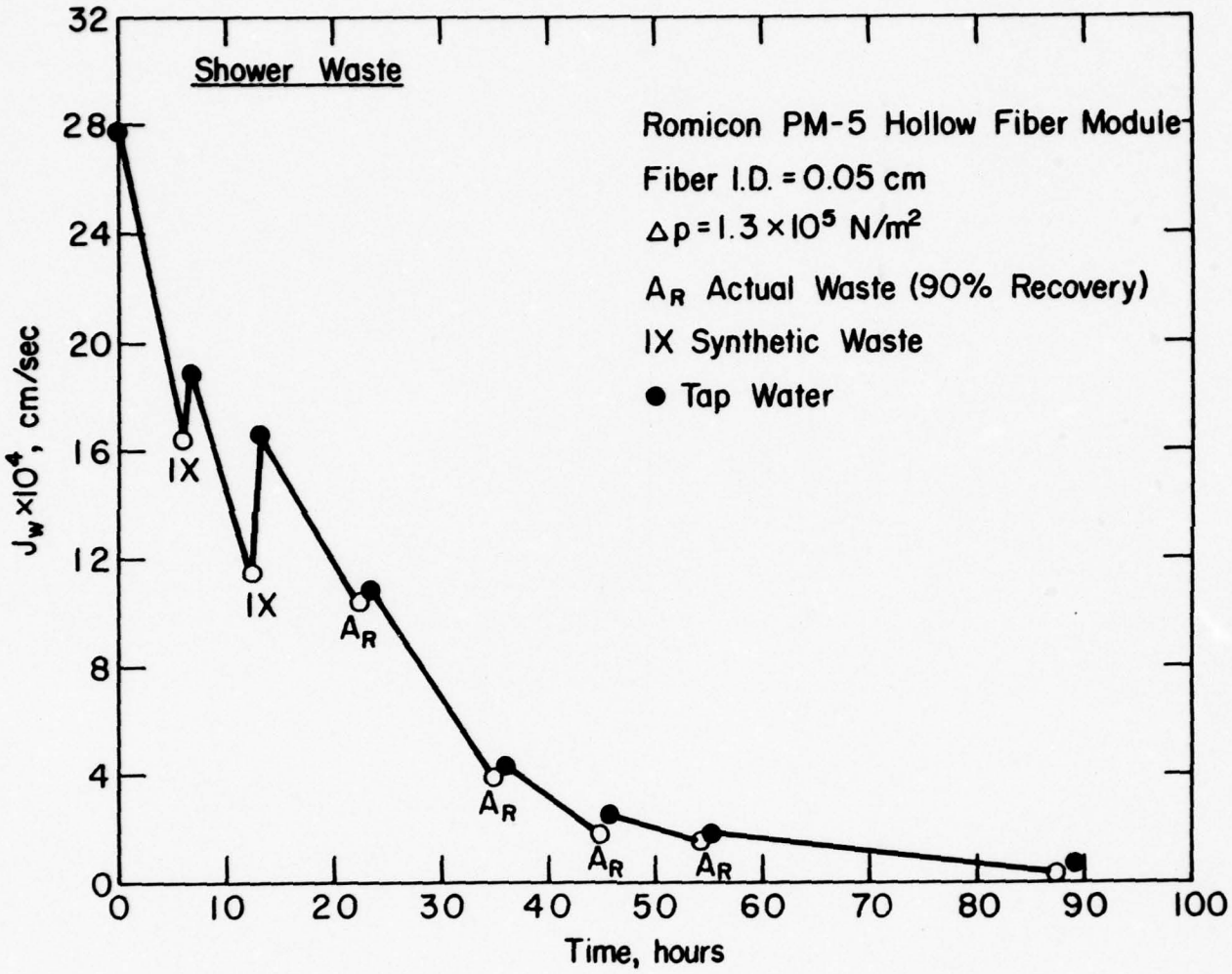

Figure 8. Long term ultrafiltrate water flux behavior for Romicon HF 20 - PM 5 hollow fiber cartridges.

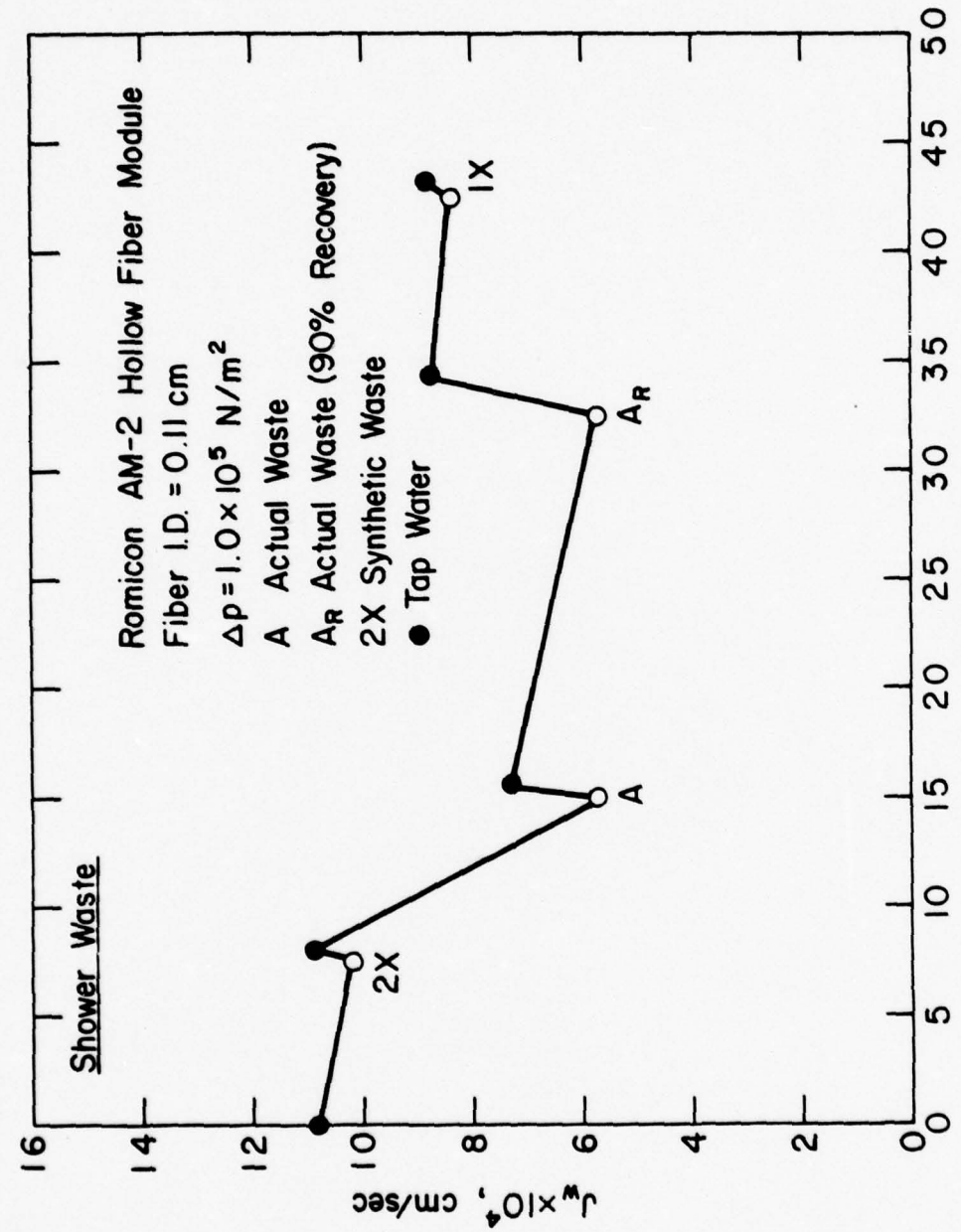

Figure 9. Long term ultrafiltrate water flux behavior for Romicon HF 43 - AM 2 hollow fiber cartridge..

sequences were utilized. Fibers of 0.05 cm diameter (HF 20-PM 5) showed (Figure 8) a severe flux drop problem and at the end of 80 hr. operation with frequent membrane flushing (shown by solid circles), the water flux was less than 0.5×10^{-4} cm/sec (1.1 gal/ft^2 day). The Romicon HF 43-AM 2, with a fiber diameter twice as large as that of the PM 5, showed considerably better performance (Figure 9). Four typical runs with actual shower wastes (both with and without water recovery) are shown in Figure 10 for tubular and hollow fiber membranes. The flux drop was 50% with the tubular membranes, 75% with the PM 5 hollow fibers, and 50% with the AM 2 hollow fibers. It should be noted that from the point of view of design, both minimization of flux drop and maximization of flux recovery after each successive use must be achieved.

The flux behavior of a plate and frame type cassette module (Millipore PSAL) with 0.076 cm spacers is shown in Figures 11 and 12. The cassette contained ten parallel feed channels of 15.2 cm width. Because of the geometry it was not possible to use a channel velocity > 12.0 cm/sec. The overall flux behavior was considerably better than tubular or 0.05 cm diameter hollow fiber membranes. Physical fouling from particulates could be substantially reduced with channel spacing greater than 0.13 cm, as evidenced by the PSAL thin channel experiments described below. Because of the low channel velocity used, the flux drop (Figure 12) was less at the

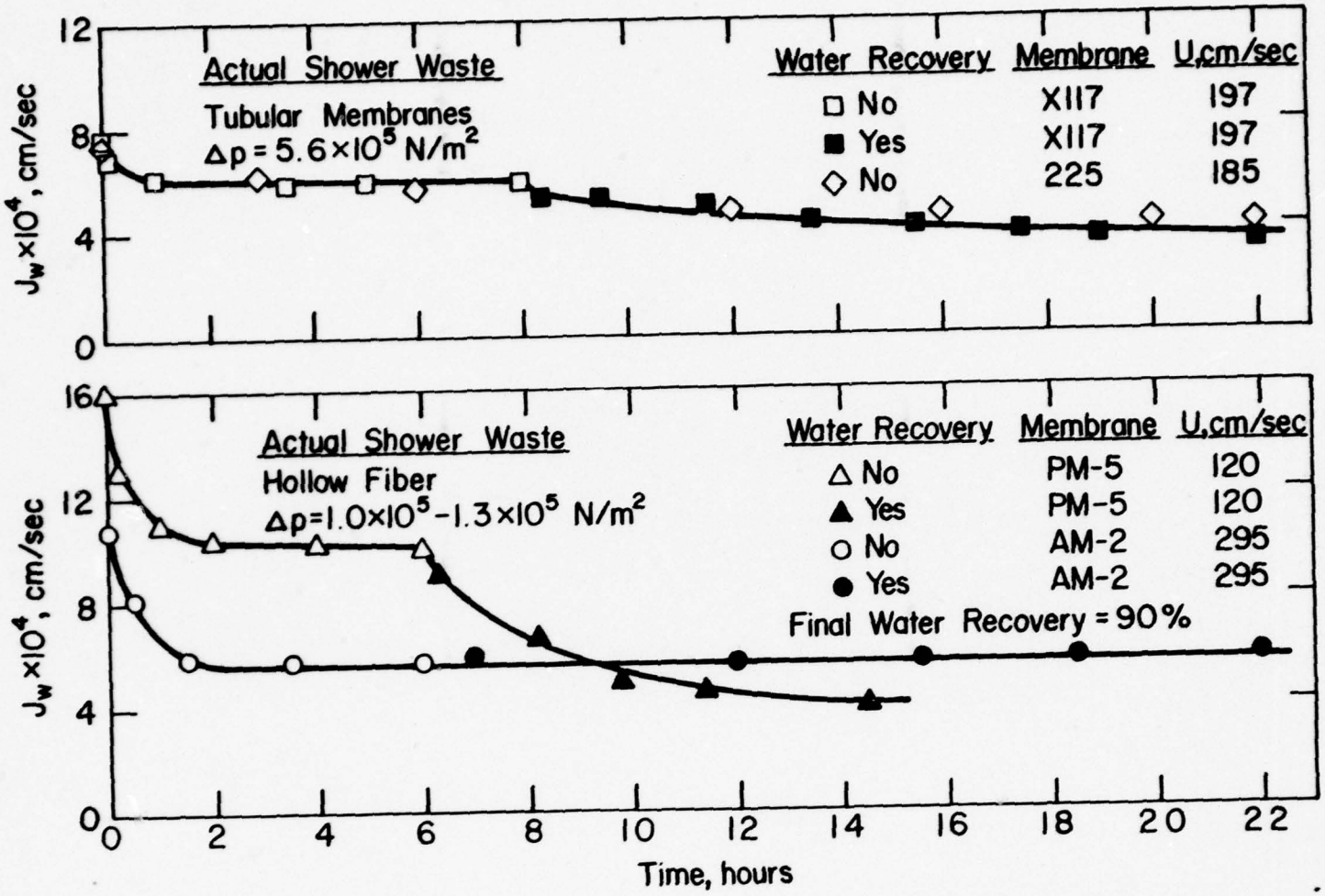

Figure 10. Typical ultrafiltrate water flux behavior for tubular and hollow fiber membrane systems.

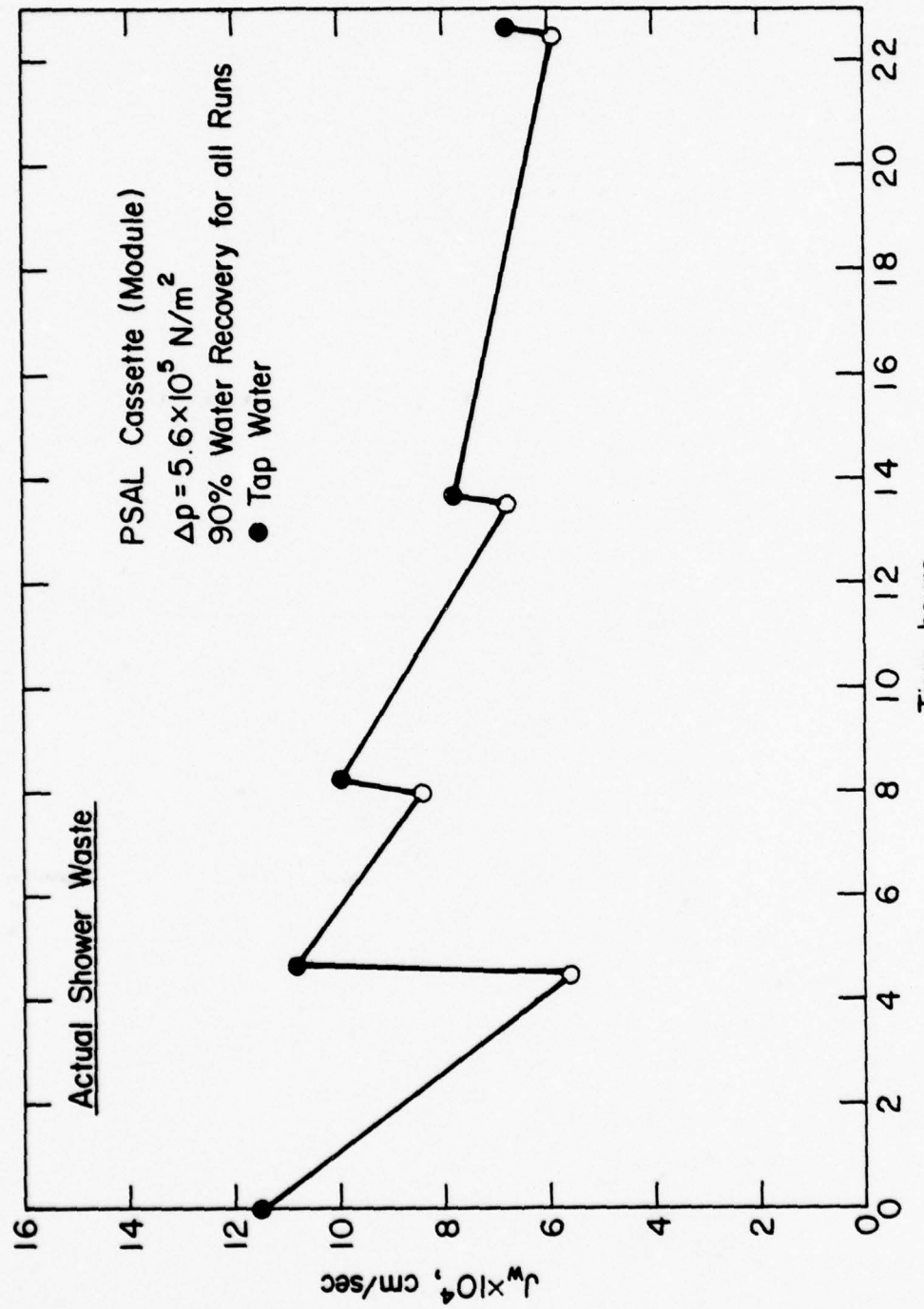

Figure 11. Long term ultrafiltrate water flux behavior for Millipore PSAL cassette module.

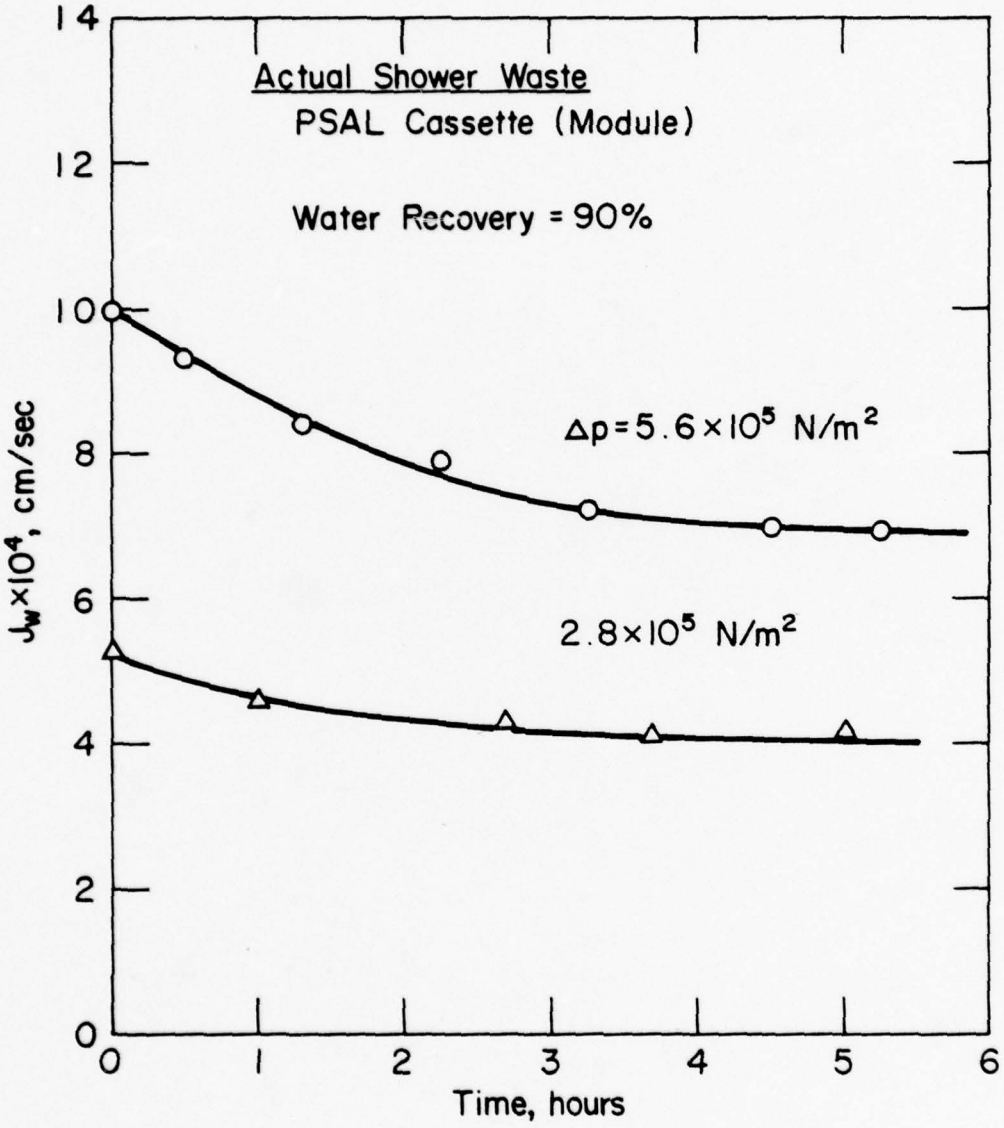

Figure 12. Typical ultrafiltrate water flux behavior for Millipore PSAL cassette module.

lower Δp, and the flux recovery with water flushing was greater than 80%.

Various studies with laundry and shower wastes were conducted with the comparatively-porous Millipore FLUXO (initial water flux = 50×10^{-4} cm/sec at 2.8×10^{5} N/m^2). Figure 13 shows the flux decline and flux recovery after each flushing operation. With shower wastes, extensive fouling was observed; with laundry wastes, the flux recovery behavior after each flushing was excellent.

The ultrafiltrate quality (as organic carbon) obtained with actual shower wastes utilizing various membrane systems is shown in Figure 14. The behavior of PSAL, UOP–225, and UOP–X117 was quite similar and the ultrafiltrate concentrations ranged between 20 and 30 mg/l. Hollow fiber cartridges gave considerably poorer ultrafiltrate quality, and C_f values were greater than 45 mg/l. Conductivity rejections for all membranes, except PSAL, were less than 0.15. With laundry wastes, organic carbon rejections with all membranes were greater than 0.90 and conductivity rejections were less than 0.30 (except PSAL). Poor conductivity (and dissolved solids) rejections by all membranes except PSAL indicate that dissolved solids build-up could be a problem during multiple-pass water reuse involving low fresh water make-up.

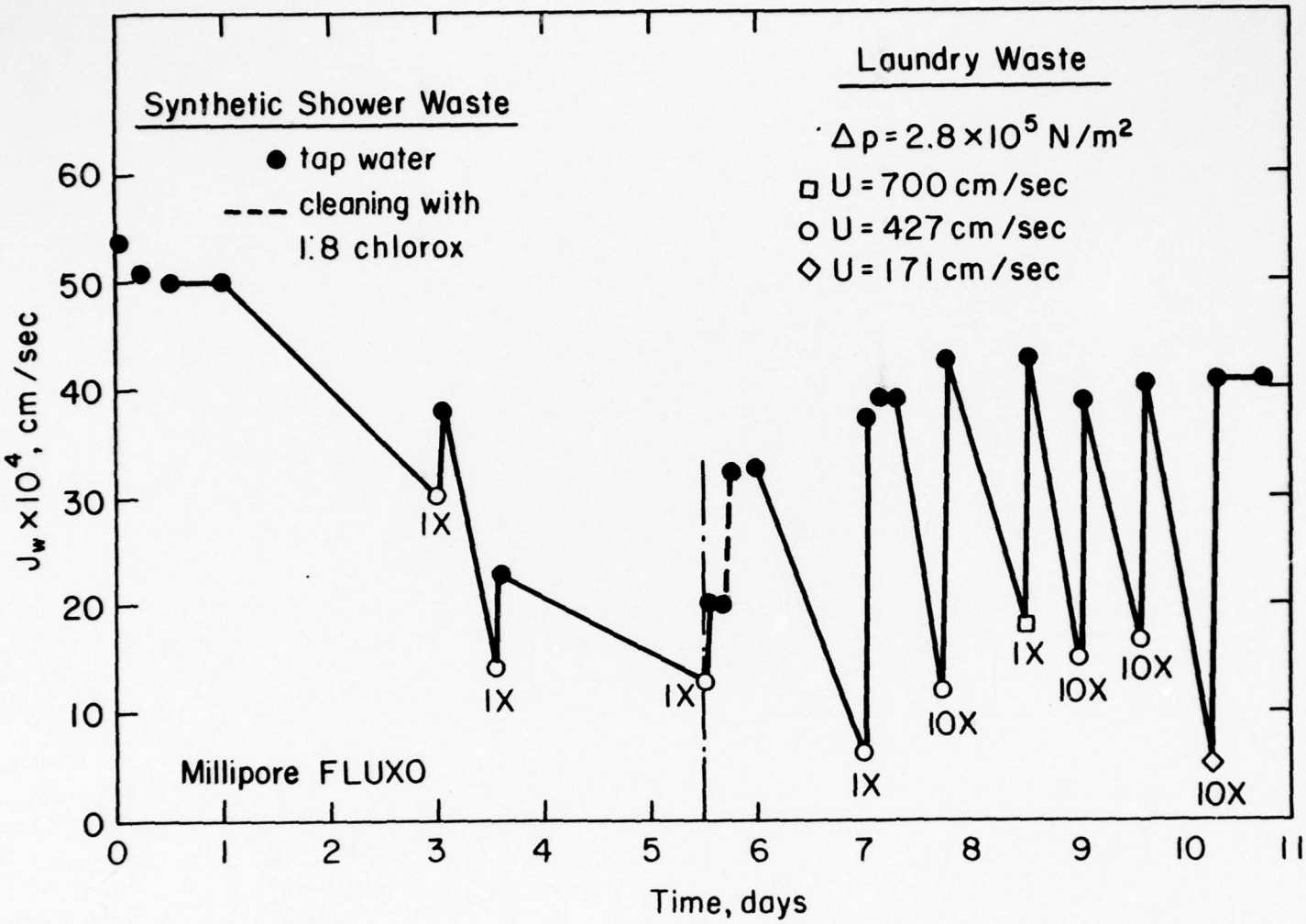

Figure 13. Long term ultrafiltrate water flux behavior for a comparatively open, Millipore FLUXO membrane.

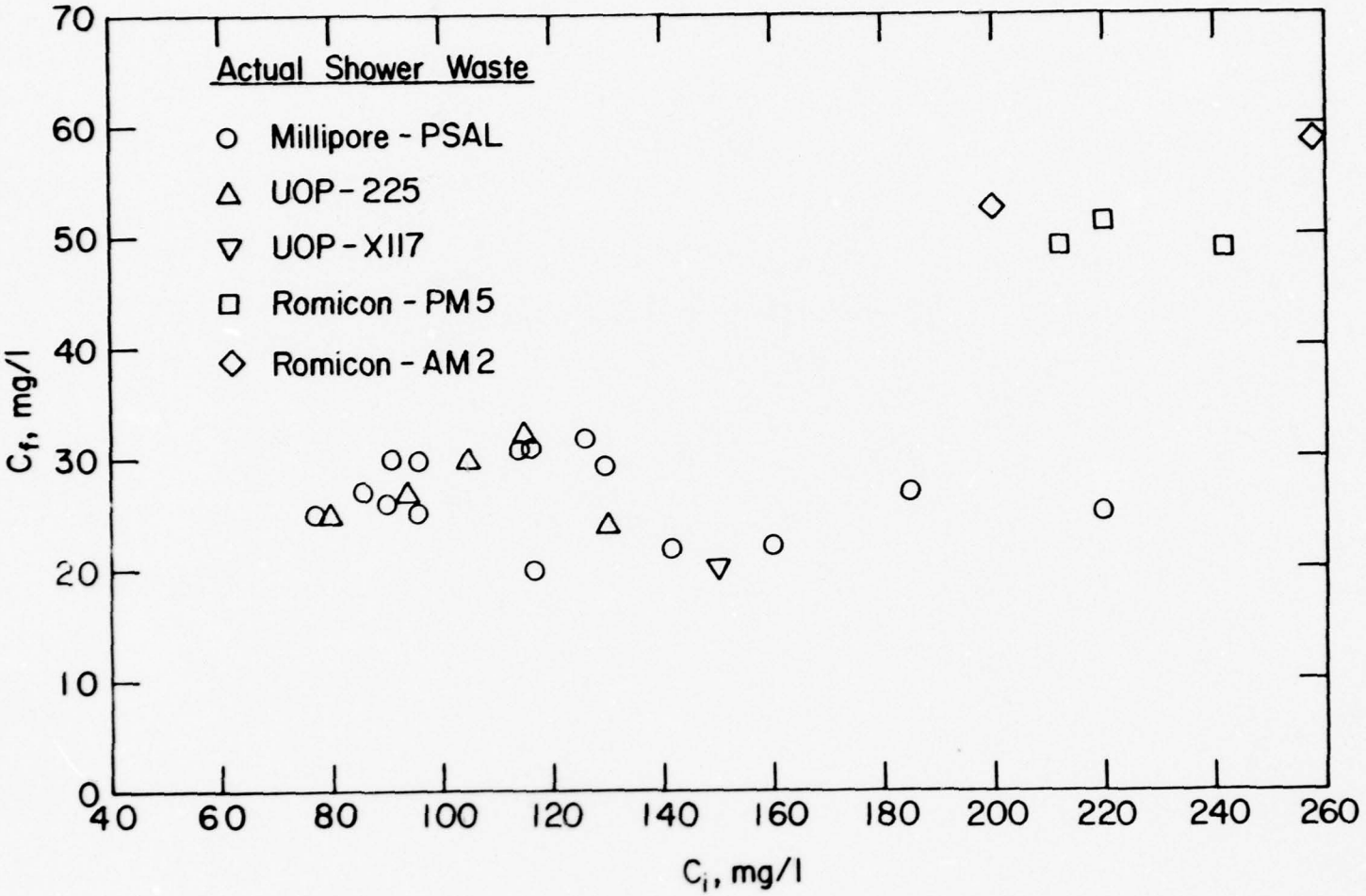

Figure 14. Ultrafiltrate organic carbon concentrations achievable with various membrane systems.

Ultrafiltration with PSAL Membranes

For an ultrafiltration process to be feasible in treating laundry wastes and shower wastes, the membranes must be capable of adequately rejecting total organic carbon, surfactants and soaps, dissolved solids, and phosphates, and in particular any irreversible flux decline with time must be avoided. Millipore PSAL provided minimum flux drop and maximum solute(s) rejection and is thus extensively studied in a thin channel (0.152 cm) configuration. In addition, PSAL membranes also provide high rejections (> 0.9) of anionic surfactants present in various commercial detergents. The height, width, and length of the thin channel cell used were 0.152, 1.28 and 40.0 cm, respectively. The effective membrane area was 51.2 cm^2. The typical tap water (no waste constituents) flux of PSAL at 5.6×10^5 N/m^2 (5.6 atmospheres) transmembrane pressure was 20×10^{-4} cm/sec (42 gal/ft^2 day).

Ultrafiltration of Laundry Wastes. Normal 1 X laundry waste feed streams used for the experiments contained a total organic carbon concentration, C_i = 186 mg/l, phosphate, P_i = 100 mg/l, total solids = 1130 mg/l, total dissolved solids = 700 mg/l conductivity = 910 μmho/cm, and pH = 8.1 - 8.5. In order to simulate the effects of high water recovery, studies were conducted over a twenty-fold (1 X to 20 X) feed stream concentration range. The experimental ranges of the variables Δp and U were: $2.5 \times 10^5 \leq \Delta p \leq 6.9 \times 10^5$ and $170 \leq U \leq 1300$.

The effect of channel velocity, U, on water flux, J_w, must be known for the satisfactory design of a unit. The occurrence of extensive flux decline below a critical threshold velocity is shown in Figure 15 for the PSAL membrane at two feed stream concentrations and $\Delta p = 5.6 \times 10^5$ N/m^2. The magnitude of the critical threshold velocity was a function of Δp; this would be expected because convective transfer to the membrane surface increases with Δp, whereas the mass transfer coefficient, K_s (Equation 3), is a function only of U:

Δp, N/m^2	Critical Threshold Velocity, cm/sec
2.8×10^5	300
5.6×10^5	400
6.9×10^5	800

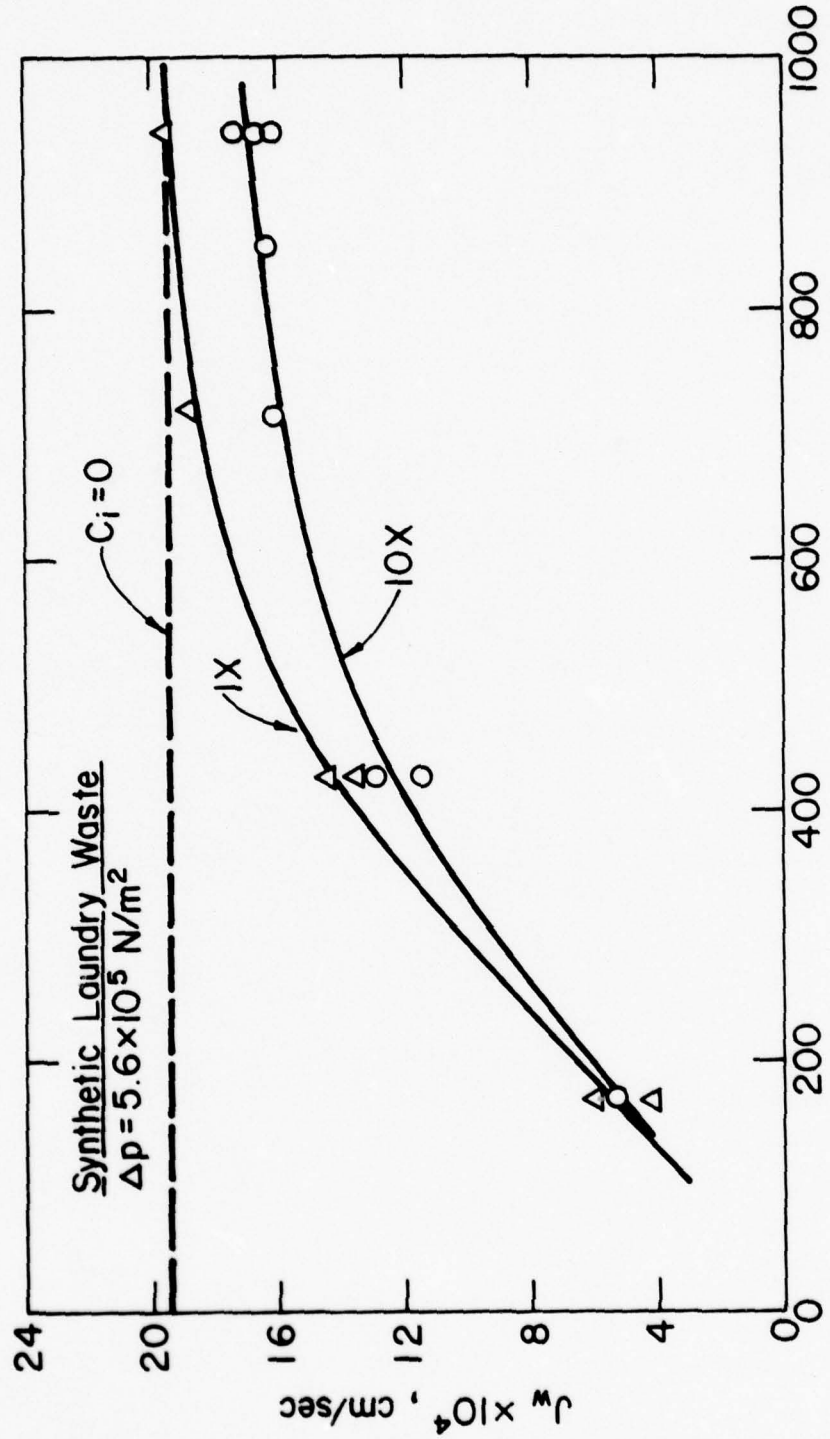

Figure 15. Effect of average channel velocity on ultrafiltrate water flux for laundry waste.

The effect of U on J_w for a comparatively open (R_m = 6.8 X 10^7 N/m^2/cm/sec) membrane, the Millipore FLUXO, is shown in Figure 16, and the behavior is contrasted with the tight (R_m = 2.8 X 10^8) PSAL membrane, both at Δp = 2.8 X 10^5 N/m^2. In the mass transfer limiting region (U < 500 cm/sec), the flux drop was more than 80%, showing that membranes with initial high flux (such as Millipore FLUXO of J_w = 41 X 10^{-4} cm/sec) often are extensively fouled and require frequent cleaning operation. With both membranes, J_w was approximately proportional to $U^{0.8}$ below the critical velocity and agreed reasonably well with the gel polarization model.

In the pre-gel region, the empirical equation obtained from the laboratory data by a multiple linear regression analysis is,[10]

$$J_w = 2.5 \times 10^{-9} \Delta p^{0.81} C^{-0.04} U^{0.44} \qquad (5)$$

The multiple regression coefficient, which is defined as,

$$\frac{\Sigma(J_{w\ calculated} - J_{w\ mean})^2}{\Sigma(J_{w\ experimental} - J_{w\ mean})^2}$$

was 0.8. The concentrations of total organic carbon, C_f, and total phosphate, P_f, in the ultrafiltrate stream were correlated with the respective bulk solute concentrations, C and P, and Δp, and the regression

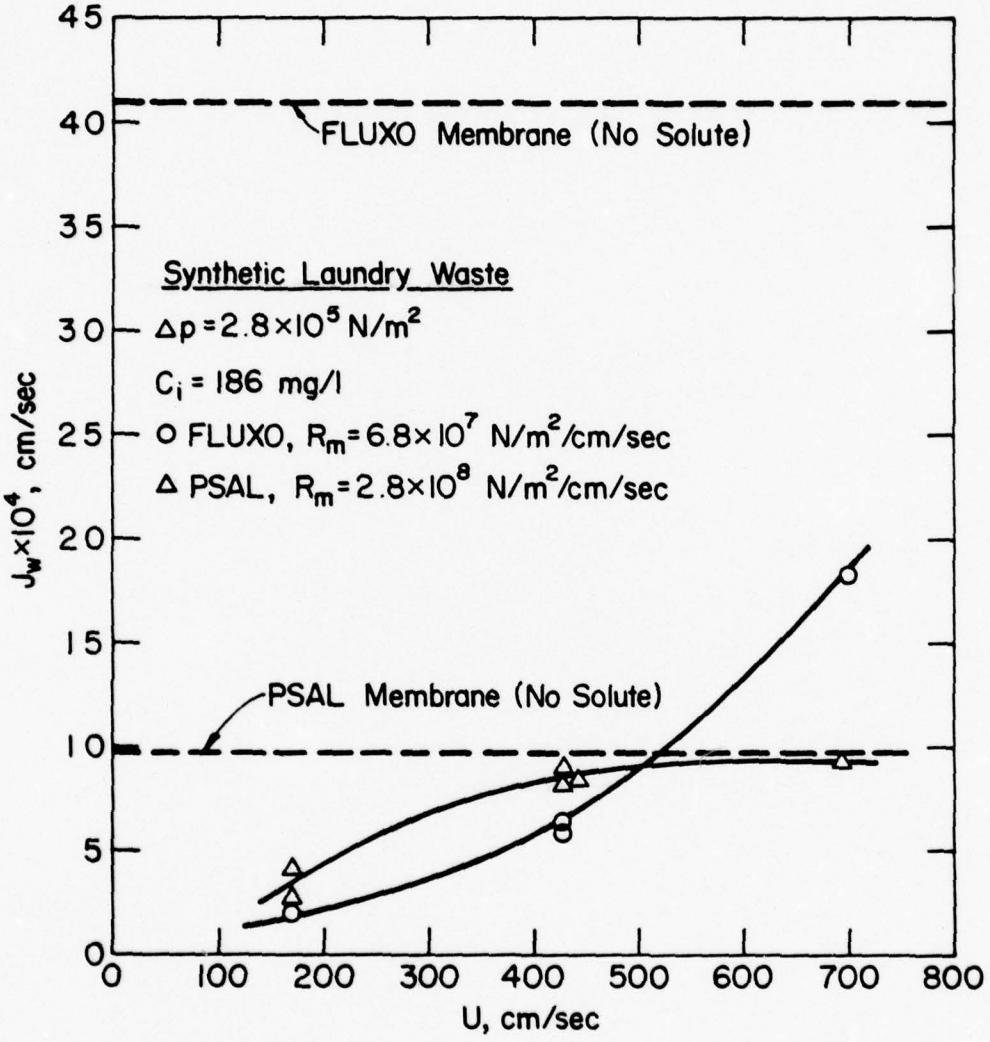

Figure 16. Effect of average channel velocity on ultrafiltrate water flux for laundry waste with two types of membranes.

equations are,

$$C_f = 7.2\ C^{0.45}\ \Delta p^{-0.21} \tag{6}$$

$$P_f = 0.092\ P^{1.2}\ \Delta p^{-0.14} \tag{7}$$

The multiple regression coefficients for Equations 6 and 7 were 0.68 and 0.82. Channel velocity, U, had no effect on C_f and P_f.

Typical concentration and flux data for two long-time runs are shown in Figure 17.

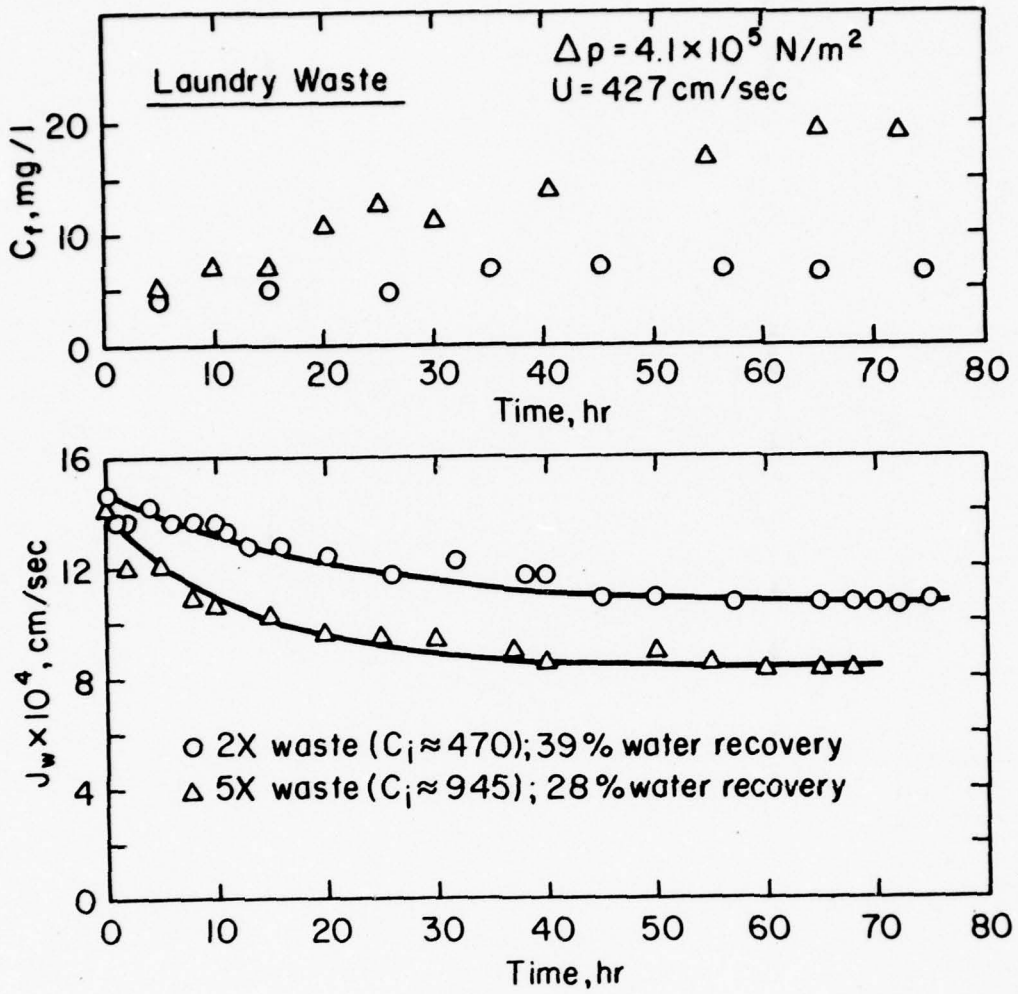

Figure 17. Typical ultrafiltrate organic carbon concentration and water flux behavior with laundry wastes.

Ultrafiltration of Shower Wastes. In the present study, both synthetic and actual shower wastes were used. Shower wastes may contain a variety of constituents: aliphatic acid soaps, toothpaste (containing stannous fluoride, stannous pyrophosphate, anionic surfactants, etc.), hair oil (containing ethyl alcohol, polyalkalene glycol, benzyl benzoate, etc.), shampoo (containing surfactants, methyl cellulose, ethyl alcohol, etc.), shower cleaner (containing phosphates, anionic surfactants, silica, hypochlorite, etc.), disinfectant (sodium orthophenylphenolate, etc.), insect repellent (diethyltoluamide, ethyl alcohol), and soil. Although individual organic compounds were not monitored in the ultrafiltrates, the rejection behaviors of some constituents from the single component systems were determined:

Constituent	Organic Carbon Rejection	Total Dissolved Solids Rejection
Soap	0.89	0.68
Hair oil	0.50	0.45
Disinfectant (sodium-orthophenylphenolate)	0.55	-
Insect repellent (diethyltoluamide)	0.45	-

In the synthetic shower waste experiments, the normal 1 X feed streams had a total organic carbon concentration, C_i = 86 mg/l, phosphate = 10 mg/l, total solids = 390 mg/l, total dissolved solids = 250 mg/l, conductivity = 295 μmho/cm, and pH = 7.8 - 8.2. The solute concentrations were varied over a twenty-fold range. The experimental ranges of other variables studied were: $2.8 \times 10^5 \leq \Delta p \leq 5.6 \times 10^5$ and $86 \leq U \leq 450$.

Figure 18 shows the effect of channel velocity U on J_w for a normal 1 X feed stream and a concentrated feed stream, at $\Delta p = 5.6 \times 10^5$ N/m^2. By comparing Figure 18 with the results for the laundry waste (Figure 15), it can be observed that the critical threshold velocity was considerably lower for the shower waste (< 100 cm/sec) and at U > 300 cm/sec, no significant increase in flux was observed. The effect of transmembrane pressure at U = 171 cm/sec (Re = 4,800) is shown in Figure 19 for two feed stream concentrations. For both concentrations the flux drop (concentration polarization) was negligible below $\Delta p = 2.8 \times 10^5$. At $\Delta p = 5.6 \times 10^5$ N/m^2, a 26% flux drop was observed at the 1 X feed concentration level; this can be compared with a 68% flux drop in the case of the laundry waste.

Using seventy-five continuous-flow, steady-state experiments, the water flux J_w was correlated with C, Δp, and U by stepwise, multiple linear regression analysis,

$$J_w = 4.6 \times 10^{-7} \Delta p^{0.54} C^{-0.06} U^{0.22} \qquad (8)$$

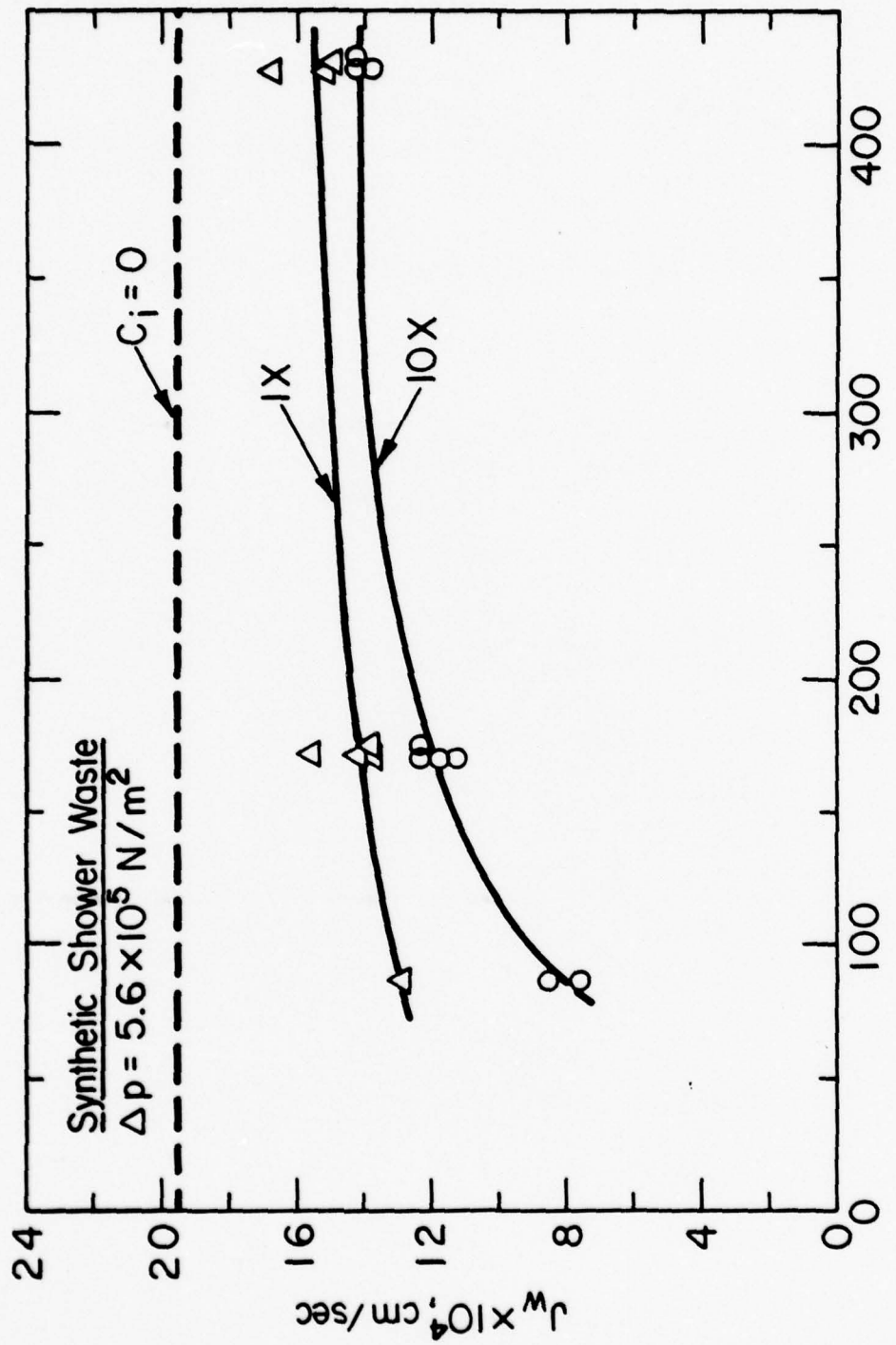

Figure 18. Effect of average channel velocity on ultrafiltrate water flux for synthetic shower waste.

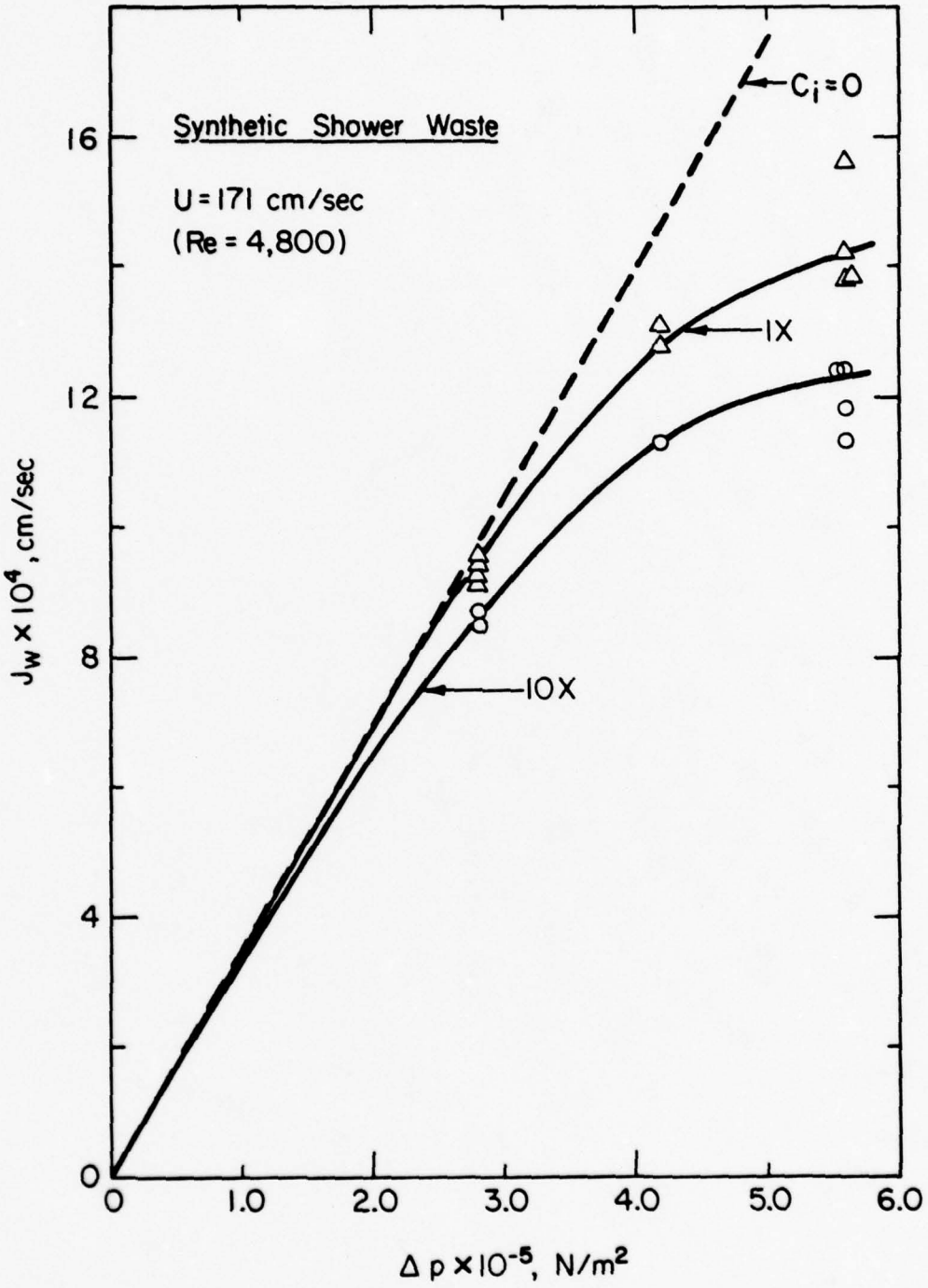

Figure 19. Effect of average transmembrane pressure difference on ultrafiltrate water flux for synthetic shower waste.

The multiple regression coefficient was 0.78 and the average percent deviation of the calculated values from the experimental values was 21.2%. Equation 8 is valid for U > 100 cm/sec; the power on Δp and that on U are considerably lower than for laundry wastes (Equation 5). The power on U would have been higher than 0.22 only if most of the experiments were carried out in the gel polarization region at velocities less than 100 cm/sec.

Transmembrane pressure and channel velocity had no significant effects on ultrafiltrate organic carbon concentration. The regression analysis showed that bulk solute concentration ($C = C_i$ for insignificant water recovery) is the important variable and the resultant equation is,

$$C_f = 1.2\ C^{0.69} \qquad (9)$$

The correlation coefficient, defined as,

$$\left[1 - \frac{\Sigma(C_{f\ \text{calculated}} - C_{f\ \text{experimental}})^2}{\Sigma(C_{f\ \text{experimental}} - C_{f\ \text{mean}})^2}\right]^{1/2}$$

was 0.91 and the average percent deviation was 24.8%. Experimental values of C_f vs C and the calculated line are shown in Figure 20. The poorer organic carbon rejection (higher C_f) with shower wastes (Equation 9) compared to laundry wastes (Equation 6) was produced

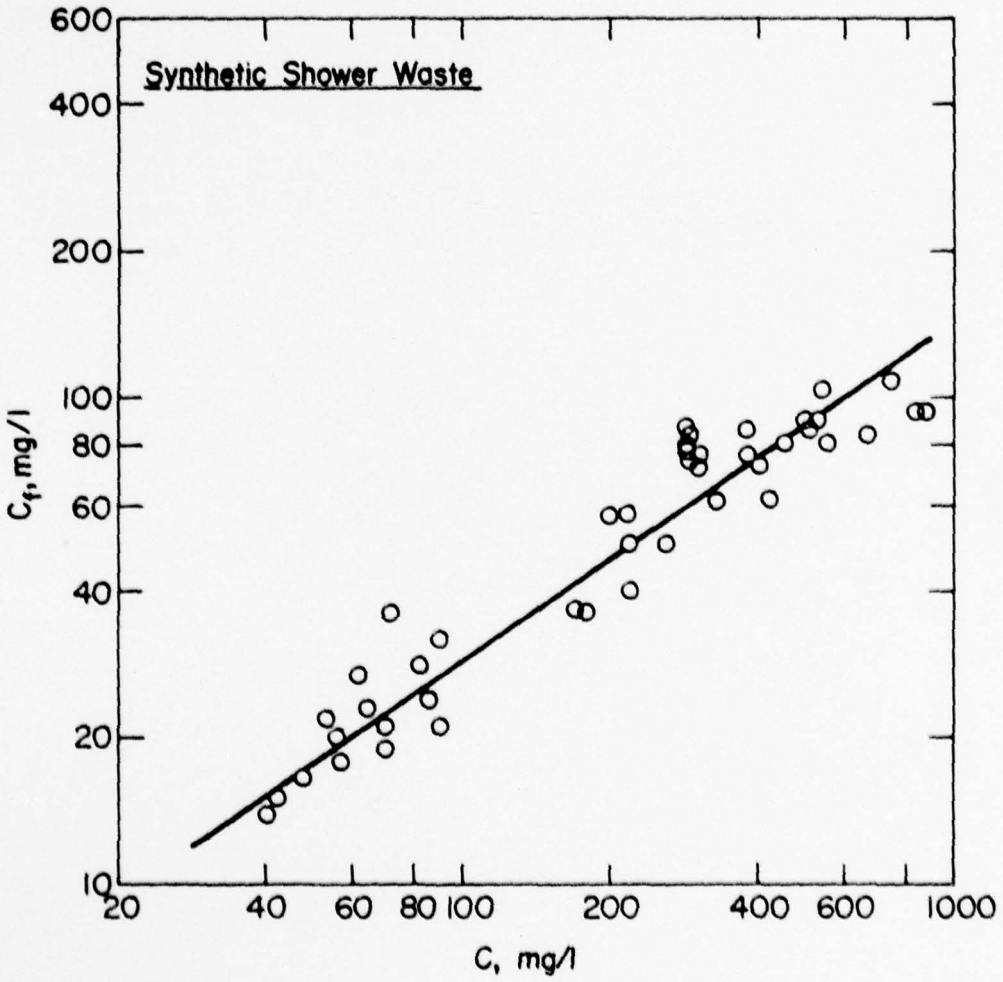

Figure 20. Relation between organic carbon concentration in ultrafiltrate stream and in feed stream for synthetic shower waste.

by the presence of low-molecular-weight (such as ethyl alcohol) organic compounds in the shower waste feed streams. A few laboratory experiments were also performed with mixtures of shower and laundry wastes, and no synergistic effects were observed.

A total of thirty-five different, actual shower wastes were utilized for the next series of ultrafiltration experiments. Analysis of the various feed streams gave the following results:

Total organic carbon, C_i	=	75 - 220 mg/l
Total solids	=	380 -1100 mg/l
Total dissolved solids	=	260 - 650 mg/l
Conductivity	=	350 - 840 μmho/cm
pH	=	7.2 - 8.3

The feed streams prior to ultrafiltration were prechlorinated with 2 - 5 mg/l Cl_2 to prevent biodegradation during the runs.

The water flux behavior was similar to that observed with the synthetic shower wastes. For example, at $\Delta p = 5.6 \times 10^5$ N/m^2 and U = 171 cm/sec, the water flux with all actual shower wastes was between 13.8×10^{-4} to 15.5×10^{-4} cm/sec, compared to an average of 14.0×10^{-4} cm/sec with the synthetic shower wastes. Comparison of experimental water flux results with the values predicted from Equation 8 for synthetic wastes, shows good agreement:

C_i, mg/l	Δp, N/m^2	U, cm/sec	J_w expt'l., cm/sec	J_w calc., cm/sec
96	$5.6X10^5$	171	$14.6X10^{-4}$	$13.8X10^{-4}$
96	$5.6X10^5$	86	$12.5X10^{-4}$	$11.8X10^{-4}$
96	$4.1X10^5$	171	$12.0X10^{-4}$	$11.6X10^{-4}$

An ultrafiltration run with moderate water recovery and long operational time is shown in Figure 21. A flux drop of 33% was observed after 50 hr operation. The long term flux behavior of a single membrane treating several actual and synthetic shower wastes is shown in Figure 22. No chemical cleaning was employed in the forty day operational period; the flux recovery with 5-15 minutes tap water flushing after each run is shown as solid circles. Excellent flux stability was observed after twenty days of operation. The flux recovery could have been improved by occasional membrane cleaning with dilute chlorine cleaning solution.

With all actual shower wastes, the ultrafiltrate organic carbon concentration was in the range of 20 to 30 mg/l, indicating somewhat better rejection than with the synthetic wastes. Table 5 summarizes the rejection characteristics for three actual shower wastes, two synthetic shower wastes, and two synthetic laundry wastes. The rejection of turbidity (suspended solids) was always 1.0.

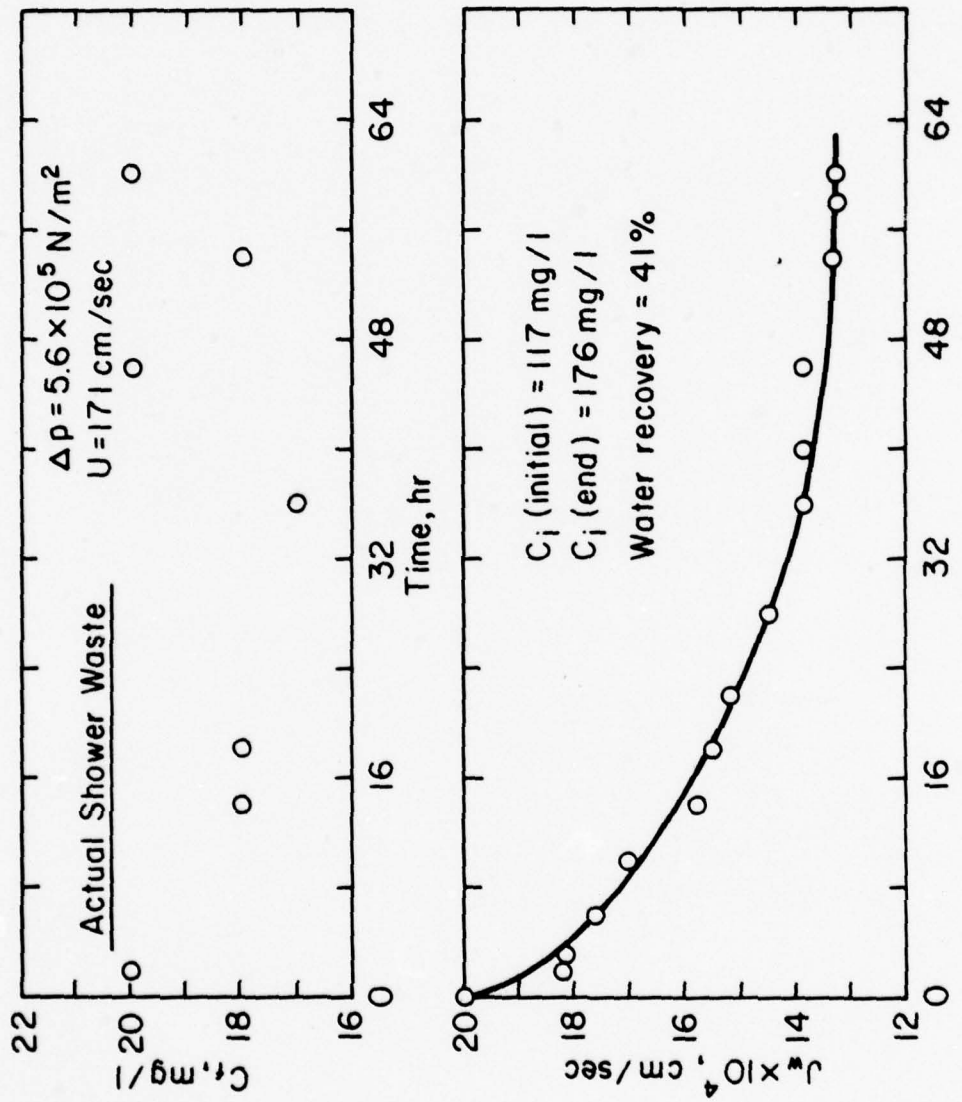

Figure 21. Dependence of ultrafiltrate water flux and ultrafiltrate organic carbon concentration on operational time for an actual shower waste.

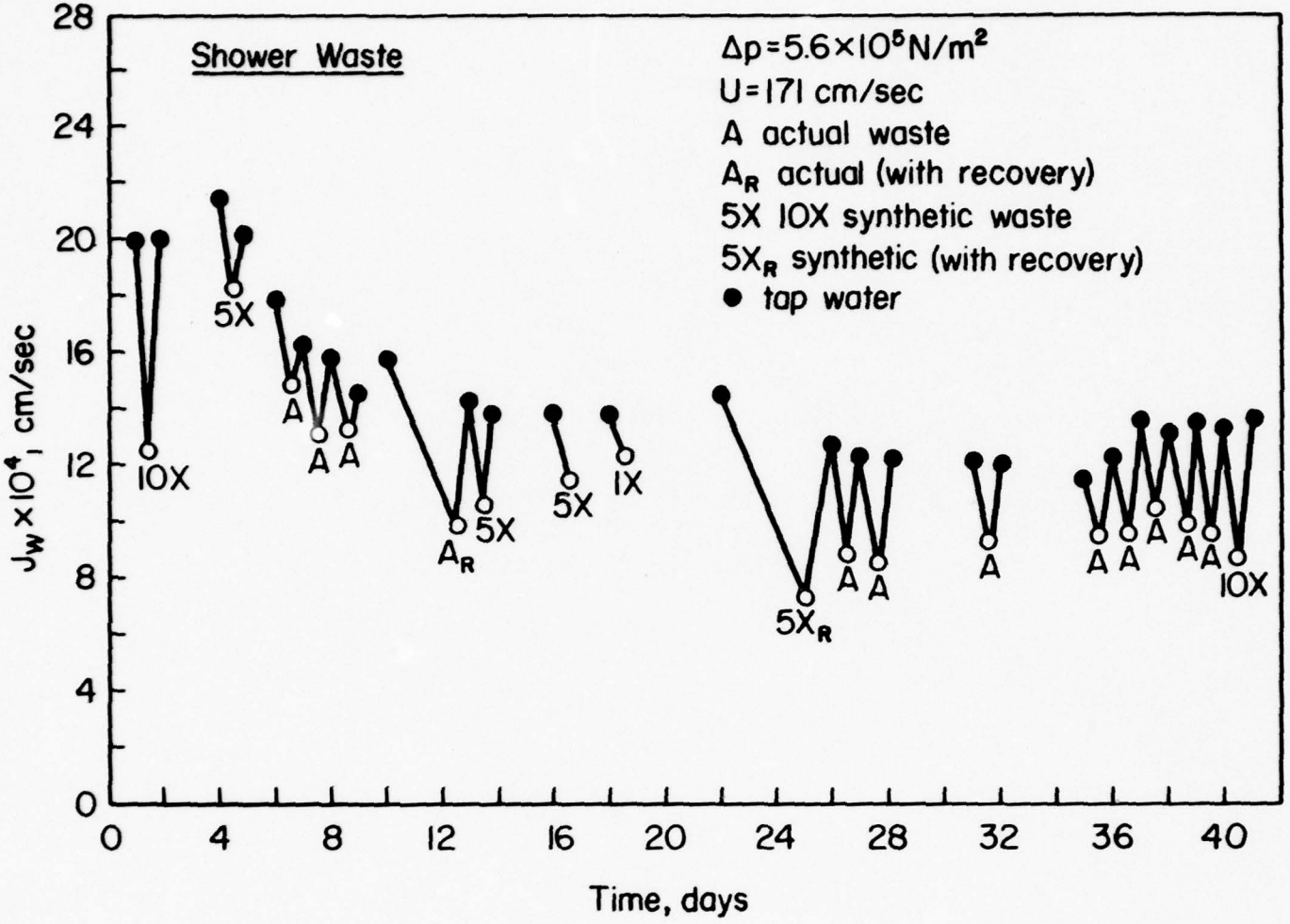

Figure 22. Long term ultrafiltrate water flux behavior with various shower wastes.

TABLE 5. REJECTION CHARACTERISTICS FOR SHOWER AND LAUNDRY WASTES BY PSAL MEMBRANES

Waste	Feed Stream Organic Carbon Concentration, C_i, mg/l	REJECTION			
		Organic Carbon	Phosphate	Conductivity	Dissolved solids
Actual Shower	220	0.86	-	0.45	0.48
Actual Shower	130	0.77	0.77	0.41	0.39
Actual Shower	90	0.70	-	0.35	0.42
Synthetic 1 X Shower	86	0.69	0.78	0.40	0.45
Synthetic 10 X Shower	730	0.85	-	0.55	0.62
Synthetic 1 X Laundry	186	0.97	0.98	0.50	0.72
Synthetic 10 X Laundry	2000	0.99+	0.95	0.56	0.80

Ultrafiltration Process Design: Scale-up. For membrane ultrafiltration to be an effective treatment method directed to laundry and shower water reuse for bathing and/or for laundering, fractional water recoveries of the order of 0.9 to 0.95 (with fresh water make-up), and an adequate degree of solute(s) separation with minimum membrane fouling must be achieved, even at a high number of recycle passes. A process schematic involving waste treatment and ultrafiltrate recycle and reuse is shown in Figure 23. Prechlorination (about 2 - 5 mg/l Cl_2) of the feed stream to the ultrafiltration unit should be practiced to prevent an odor problem and/or bacterial fouling of the membrane surface.

For the design of the full-scale ultrafiltration unit in Figure 23, empirical equations (Equations 5-9) obtained from the laboratory-scale data (at very low water recovery) to compute ultrafiltrate water flux and ultrafiltrate solute(s) concentration can be used readily to predict (by computer simulation) overall solute removal and membrane area requirements at high water recoveries. The fractional water recovery, r, defined as the total ultrafiltrate stream flow rate, rF_i, divided by the feed stream flow rate, F_i, can be increased by means of multiple ultrafiltration module arrangements in series, in parallel, or in series-parallel (tapered) combinations. Bhattacharyya, et al.[10,14] have detailed a computer simulation technique to predict solute removals and membrane area

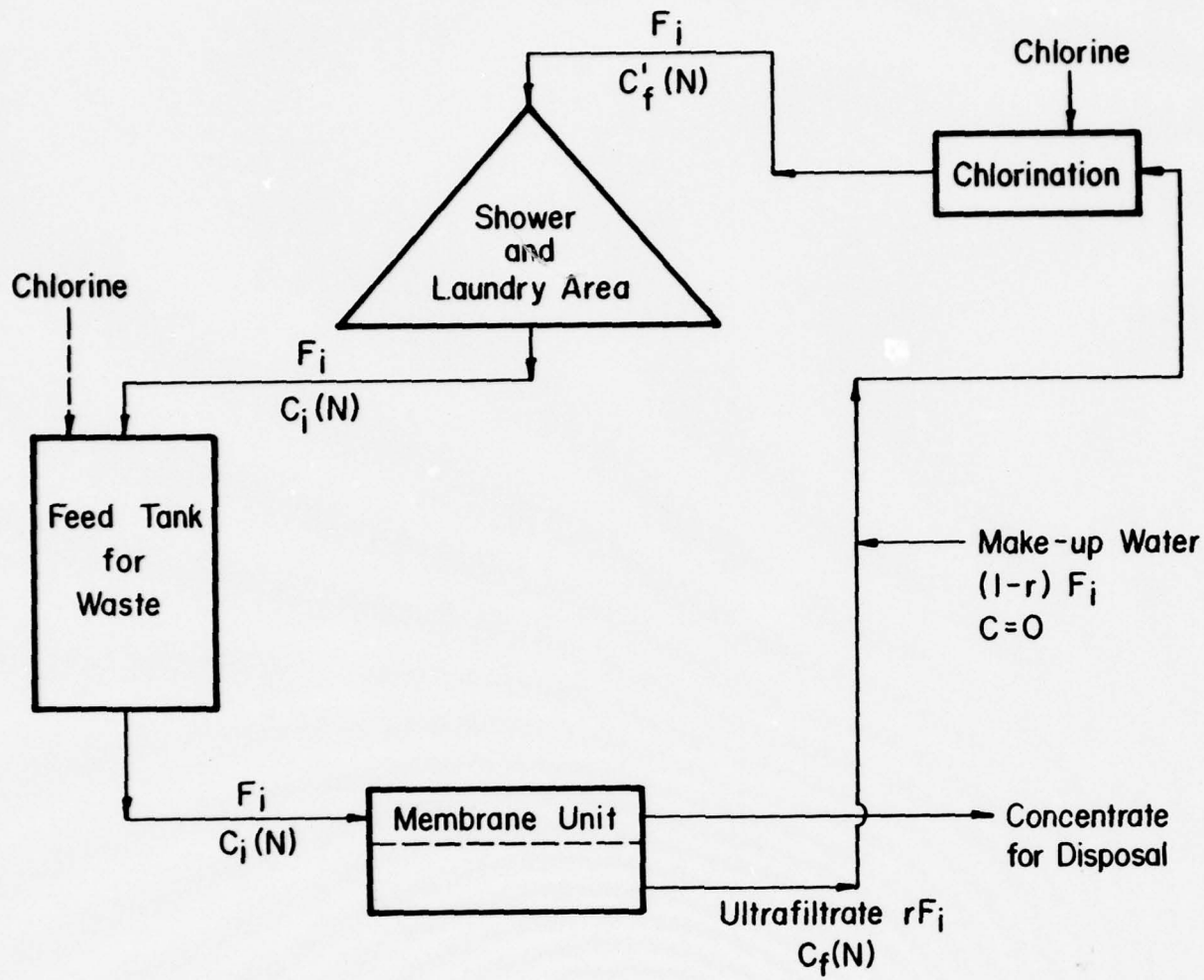

Figure 23. Process schematic for shower and/or laundry waste treatment and ultrafiltrate recycle and reuse.

requirements involving multiple-module arrangements.

The predicted behavior of the full-scale ultrafiltration process was calculated initially to treat the waste from the zero recycle pass, $C_i = C_i(0)$ (Figure 23), by assuming feed conditions of flow rate = 1000 cm^3/sec, the waste compositions as tabulated in the Experimental Section, and that each module contained 4600 cm^2 of membrane area with 90 inner stages. The inner stages were assumed to be connected in series, and because the water recovery in each of these stages was small, the desired precision by an iterative method was obtained. For the computations of water flux and ultrafiltrate concentrations in each inner stage, Equations 5-9 were used.

For both laundry and shower wastes, the membrane area requirements were higher with the parallel (one bank of parallel modules) arrangement compared to the tapered arrangement, and the area per unit ultrafiltrate flow was substantially increased at higher recoveries because recirculation of a fraction of the concentrate stream would have to be employed with the parallel arrangement to maintain the proper channel velocity in each module. For example with laundry wastes at a fractional water recovery of 0.9, operation at U = 500 cm/sec (Re = 14,000) would require 149 modules with the parallel arrangement, compared to 134 modules with the tapered arrangement (banks of parallel modules in series with each successive bank containing a smaller

number of modules). With the tapered arrangement, membrane module (total area) requirements at different operating channel velocities were computed for both laundry and shower wastes, and at 0.9 water recovery are shown in Table 6. With laundry wastes, the membrane unit should not be operated at $U \leq 200$ cm/sec, because of the extreme gel polarization problem.

The solute removal with multiple-module arrangements (for example in terms of total organic carbon) is defined as,

$$\text{Solute removal, } R^* = 1 - \frac{C_{favg}}{C_i} \qquad (10)$$

where C_{favg} is the average ultrafiltrate concentration from all modules: the values can be determined by computer simulation for various arrangements. For any system, when the power on C in Equation 6 (or 9) is greater than zero, it can be shown that the tapered arrangement is optimum. The effects of water recovery on solute(s) removal from laundry and shower wastes are shown in Figures 24 and 25, respectively. For both wastes, removal with the tapered arrangement was consistently greater than with the parallel arrangement. With the parallel arrangement, the sharp drop in removals above a water recovery of about 0.7 was primarily due to the increase in bulk solute concentrations produced by concentrate stream recirculation. It should be noted that the laboratory-scale data on rejection (using Equation 4) presented

TABLE 6. CALCULATED NUMBER OF MODULES FOR TAPERED ARRANGEMENT AT r = 0.9

Waste	U, cm/sec	Re	Number of Modules*
Laundry	200	5,600	326
Laundry	300	8,400	182
Laundry	500	14,000	134
Shower	200	5,600	148
Shower	300	8,400	135
Shower	500	14,000	127

*Membrane area of each module is 4600 cm^2.

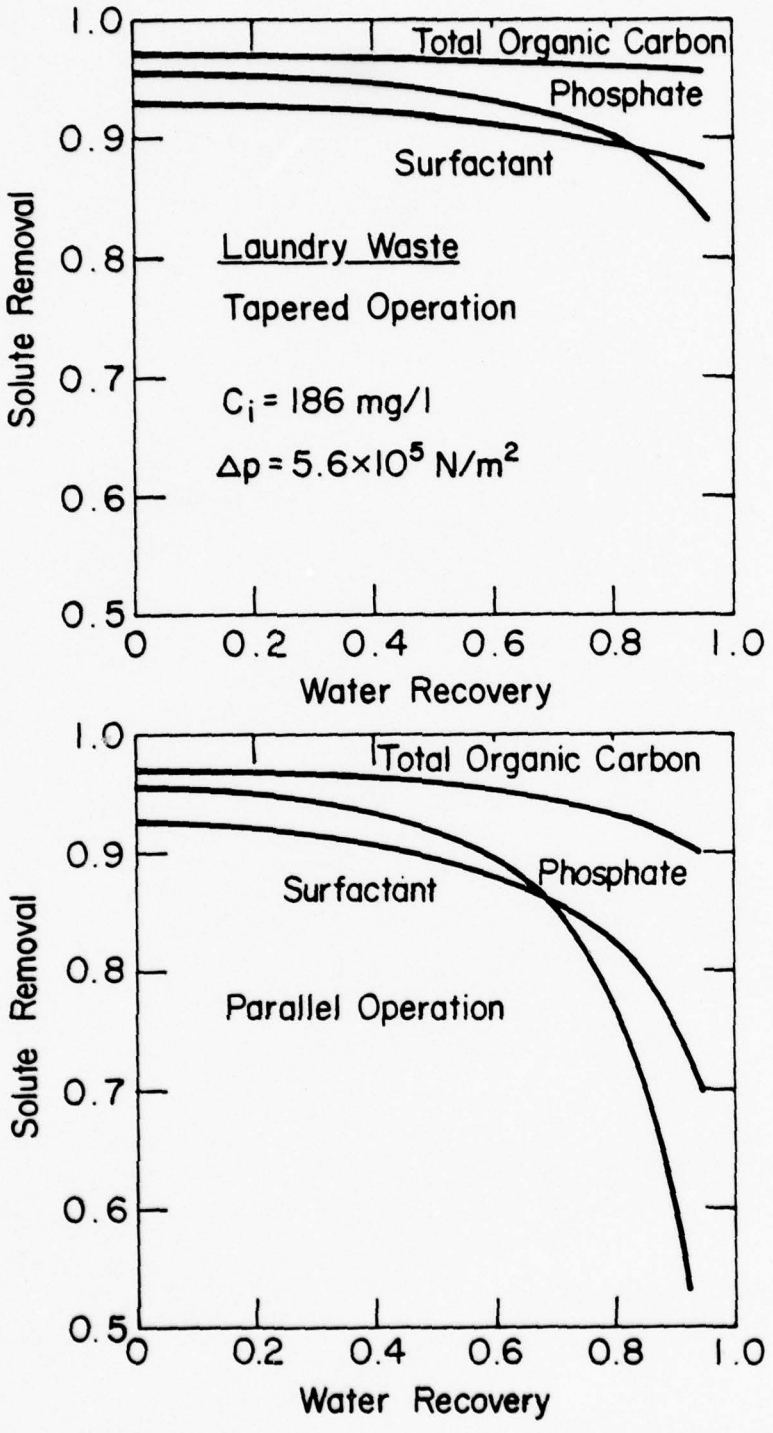

Figure 24. Predicted removals of organic carbon, phosphate, and surfactant from laundry wastes for specified water recoveries with parallel or tapered operation.

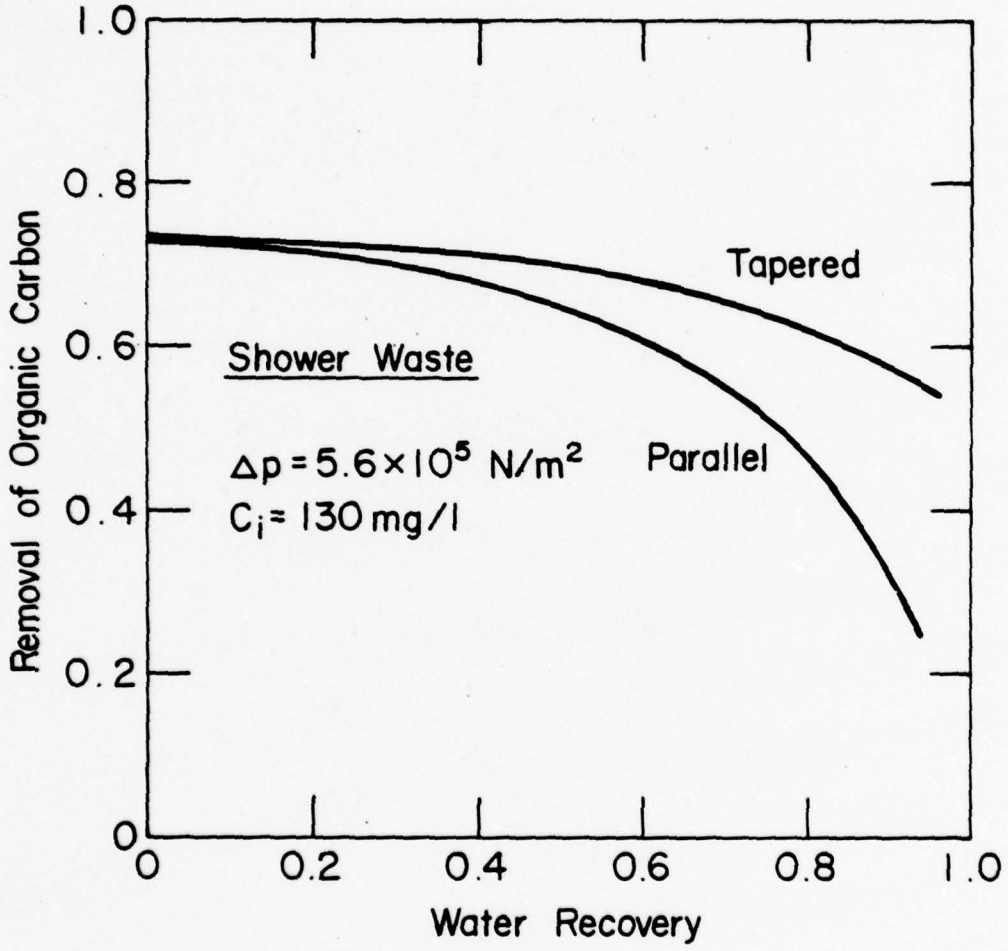

Figure 25. Predicted removal of organic carbon from shower wastes for specified water recoveries with parallel or tapered operation.

in previous sections corresponds to solute removal at zero water recovery in Figures 24 and 25.

Experimental organic carbon removal data for synthetic and actual shower wastes are shown in Figure 26 (data points) as a function of water recovery. The experimental points were obtained in the laboratory in a batch (semi) concentration mode, in which only the concentrate stream was continuously returned to the ultrafiltration feed tank and the ultrafiltrate was continuously recovered at a slow rate. The equivalence of operation in the tapered multi-module arrangement and in the batch (semi) mode, can be readily proven analytically. The slow water recovery rate allowed the validation of the steady-state relationship between C_f and C (Equation 9) at any instant of the batch (semi) mode and made it equivalent to tapered operation. The solid line in Figure 26 is the same curve as that for the tapered arrangement in Figure 25.

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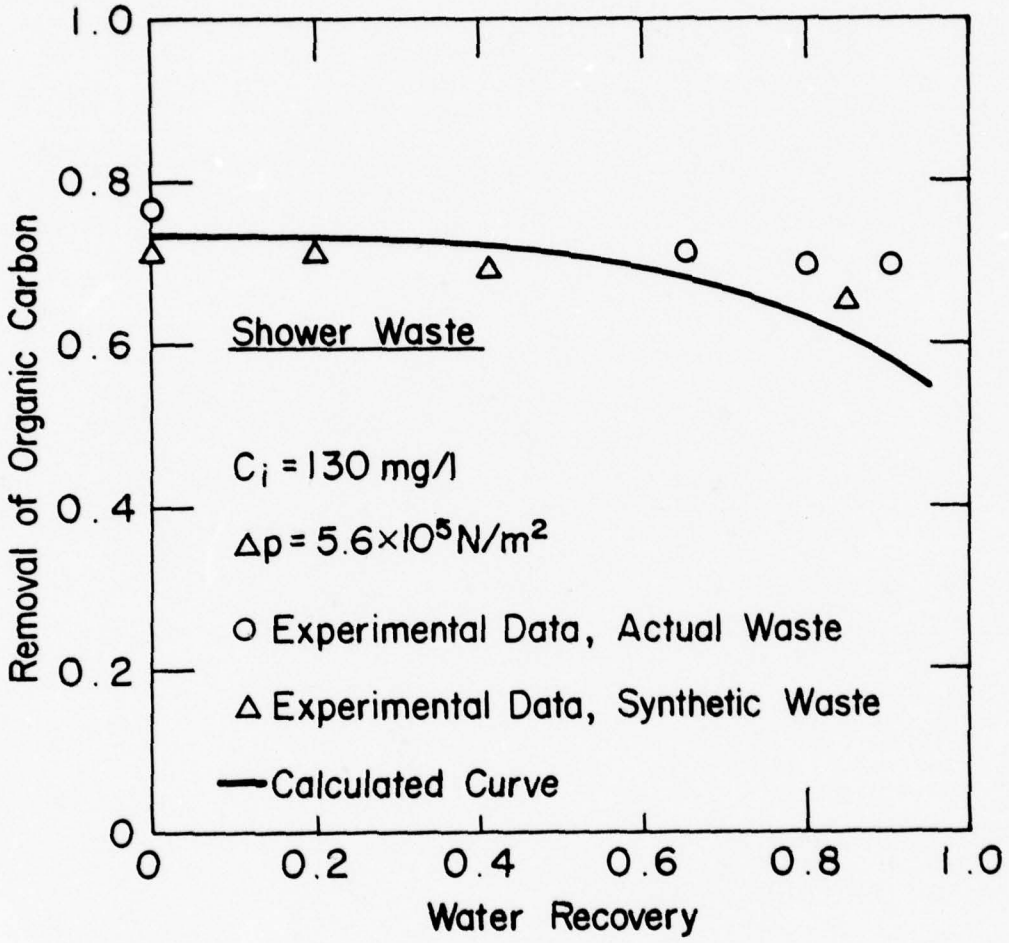

Figure 26. Calculated and experimental relations between organic carbon removal and water recovery for shower wastes.

Miltiple-pass Recycle: Ultrafiltrate Reuse. In an integrated water recycle system (as shown in Figure 23), the knowledge of the concentration of solute(s) in the shower and/or laundry water at the water re-use point (C'_f (N)) at various numbers of recycle passes, N, is important from the point of view of toxicity and of water quality required to meet bathing or laundering needs. C'_f (N) can easily be predicted from the value of C_f (N); C_f (N) for various numbers of recycle passes involving high water recovery can be computed by solving the recursive mass balance equations after each pass along with the computer simulation model for the tapered module arrangement described in the previous section for the zero recycle pass. For the simpler case involving the assumption of a constant mass [F_i C_i (N)] of solute generated by the shower or laundry in each cycle and the assumption that the overall removal, R* (Equation 10), is independent of N, the following equation can be derived from recursive mass balances,

$$\frac{C'_f\ (N)}{C_i(0)} = [r(1 - R^*)]^{N+1} + r(1 - R^*)\ \frac{1 - [r(1 - R^*)]^N}{1 - r(1 - R^*)} \qquad (11)$$

The values of R* as a function of r (such as Figures 24 and 25 for zero pass) must be obtained from the computer simulation model. Table 7 shows some typical values of C'_f (N) as fractions of C_i (0),

TABLE 7. CALCULATED VALUES OF SOLUTE CONCENTRATION AT THE WATER REUSE POINT (C'_f (N))

Removal R*		Water Recovery, r = 0.9		Water recovery, r = 0.95	
		N = 10	N = 100	N = 10	N = 100
1.0		C'_f (N) = 0 for all r and N			
0.75	C'_f (N) =	0.29 $C_i(0)$	0.29 $C_i(0)$	0.31 $C_i(0)$	0.31 $C_i(0)$
0.50		0.82 $C_i(0)$	0.82 $C_i(0)$	0.90 $C_i(0)$	0.90 $C_i(0)$
0.25		2.0 $C_i(0)$	2.1 $C_i(0)$	2.4 $C_i(0)$	2.5 $C_i(0)$
0		6.2 $C_i(0)$	9.0 $C_i(0)$	8.2 $C_i(0)$	19.0 $C_i(0)$

the waste generated in the zero recycle pass, for several assumed values of R*. For N > 10 and R* $\geq$ 0.3, C'_f (N) is virtually independent of N as shown in the Table.

The results of an extensive series of actual ultrafiltration experiments involving multiple-pass operation (water recovery of 0.9 in each pass) are shown in Figure 27. The first ultrafiltration run was made in the laboratory with an actual shower waste (C_i (0) = 220 mg/l); experiments corresponding to successive numbers of recycle passes were made by chlorinating (to maintain 0.8 - 1.0 mg/l Cl_2 at 30 min contact) the ultrafiltrate and adding the proper amounts of 1 X shower waste constituents along with 10% make-up water. Figure 27 shows excellent agreement between the calculated curves (based on R* shown) and the experimental points. The maximum value of organic carbon build-up would only be 0.3 C_i (0), while the maximum value of total dissolved solids build-up would be 1.0 C_i (0). Although no multiple-pass ultrafiltration experiments with laundry wastes were conducted, the maximum steady state value of the ratio of C'_f (N) to C_i (0) (for r = 0.9 and 10% make-up water) would be only 0.03 for organic carbon, and 0.10 for phosphate, because of high membrane removals (Figure 24), and 0.95 for dissolved solids. Finally, it should be noted that typical post-chlorination dosages of 10 mg/l for shower water and 2.0 mg/l for laundry water would be required to maintain 0.8 - 1.0 mg/l Cl_2.

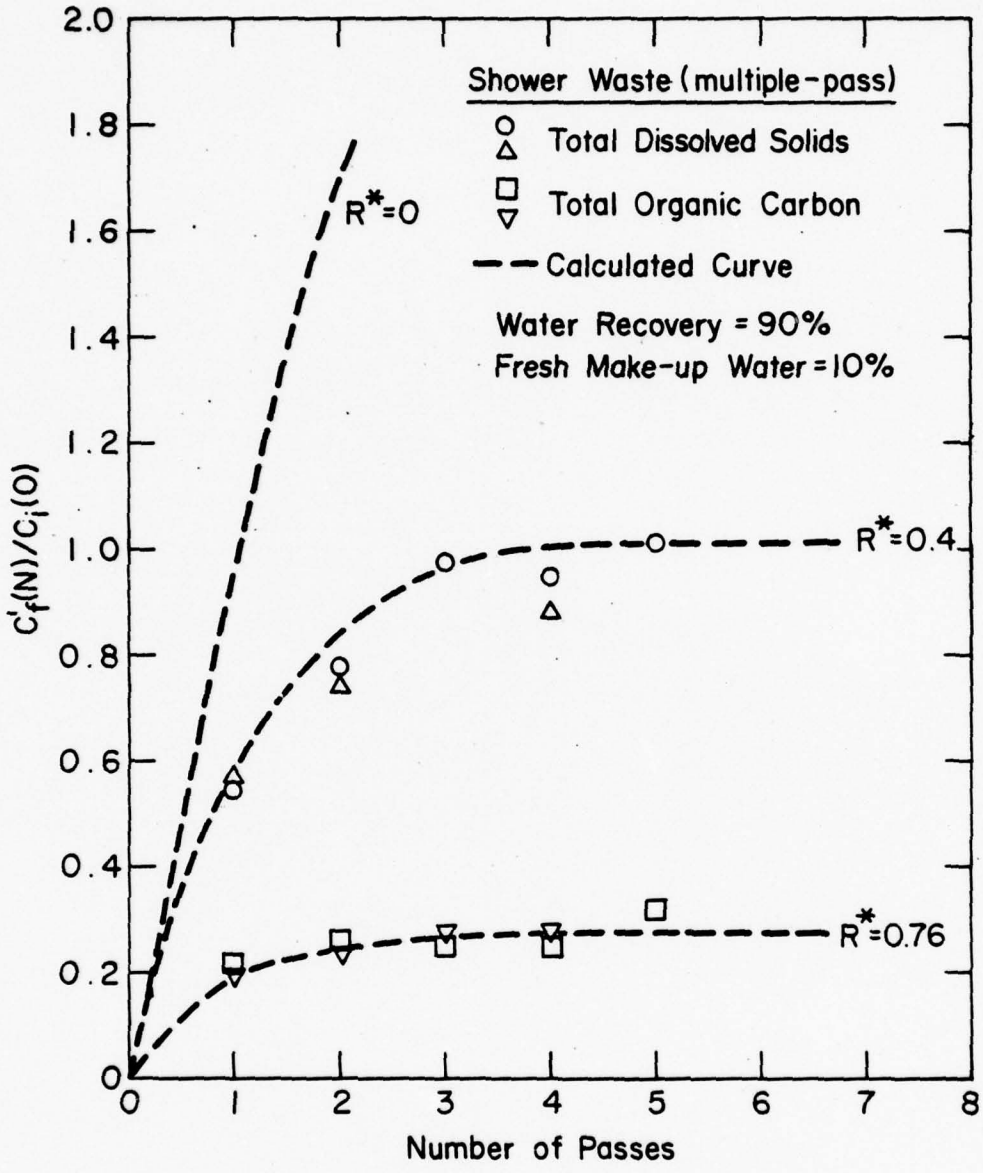

Figure 27. Effect of multiple recycle passes on water quality at the reuse point.

Irritancy and Toxicity Studies. To determine the safety of recycled ultrafiltrate as shower and/or laundry water, a thorough toxicity and irritancy (dermal, ocular, and oral) study on mice and rabbits was conducted with various shower and laundry waste solutions. All toxicity and irritancy tests were carried out by Witherup and Emmett[24] at the University of Cincinnati Medical Center. All samples were evaluated with respect to their immediate toxicity when given orally to mice, as a primary skin irritant when kept in contact with the intact and abraded skin of rabbits, and as an irritant to the ocular tissue of the rabbits. The quantitative data obtained were correlated with the total organic carbon concentration and total solids concentration of the samples.

A total of 95 samples of laundry and shower wastes was evaluated. The samples included ultrafiltrates produced by ultrafiltration of actual and synthetic wastes, concentrated ultrafiltrates and actual wastes (by freeze concentration), concentrate streams from high recovery ultrafiltration runs, and synthetic 1 X to 1000 X filtered (through 0.45 μ filter) and unfiltered (raw) wastes. In order to produce positive toxicity and irritation responses, solutions had to be concentrated: with the freeze concentrator, a maximum concentration factor of twenty was achieved, and mass balances on the ice

phase and water phase showed less than a 10% loss in organic carbon(Figure 28). Most raw wastes and high concentration synthetic wastes were filtered through 0.45 μ filters to simulate the worst conditions of ultrafiltration unit operation (removal = 0 for all soluble constituents). All samples were chlorinated to 1.0 mg/l free available chlorine (at 30 min contact mixing time) prior to the toxicity and irritancy tests.

Witherup and Emmett[24] have detailed the irritancy and toxicity evaluation procedures and scoring criteria. All ultrafiltrates, including those concentrated by the freezing process, caused no irritation to the skin or eyes of rabbits and evidenced no oral (to mice) toxicity. The primary skin irritation scores of various shower and laundry waste samples are shown in Figures 29 and 30. as a function of the total organic carbon concentration. When the skin irritation score was greater than or equal to a value of five, the sample was rated as a primary skin irritant (positive reaction). With both shower and laundry wastes, samples containing even up to 8000 mg/l organic carbon (such as 100 X raw shower waste) elicited only mild reaction, indicating at least a 200:1 safety factor for ultrafiltrate reuse. All ultrafiltrates, including those corresponding to a high number of multiple passes, exhibited irritation scores less than 2.0.

For eye irritation scores, the test was considered positive[24] if three or more animals in the test group (six rabbits) exhibited a

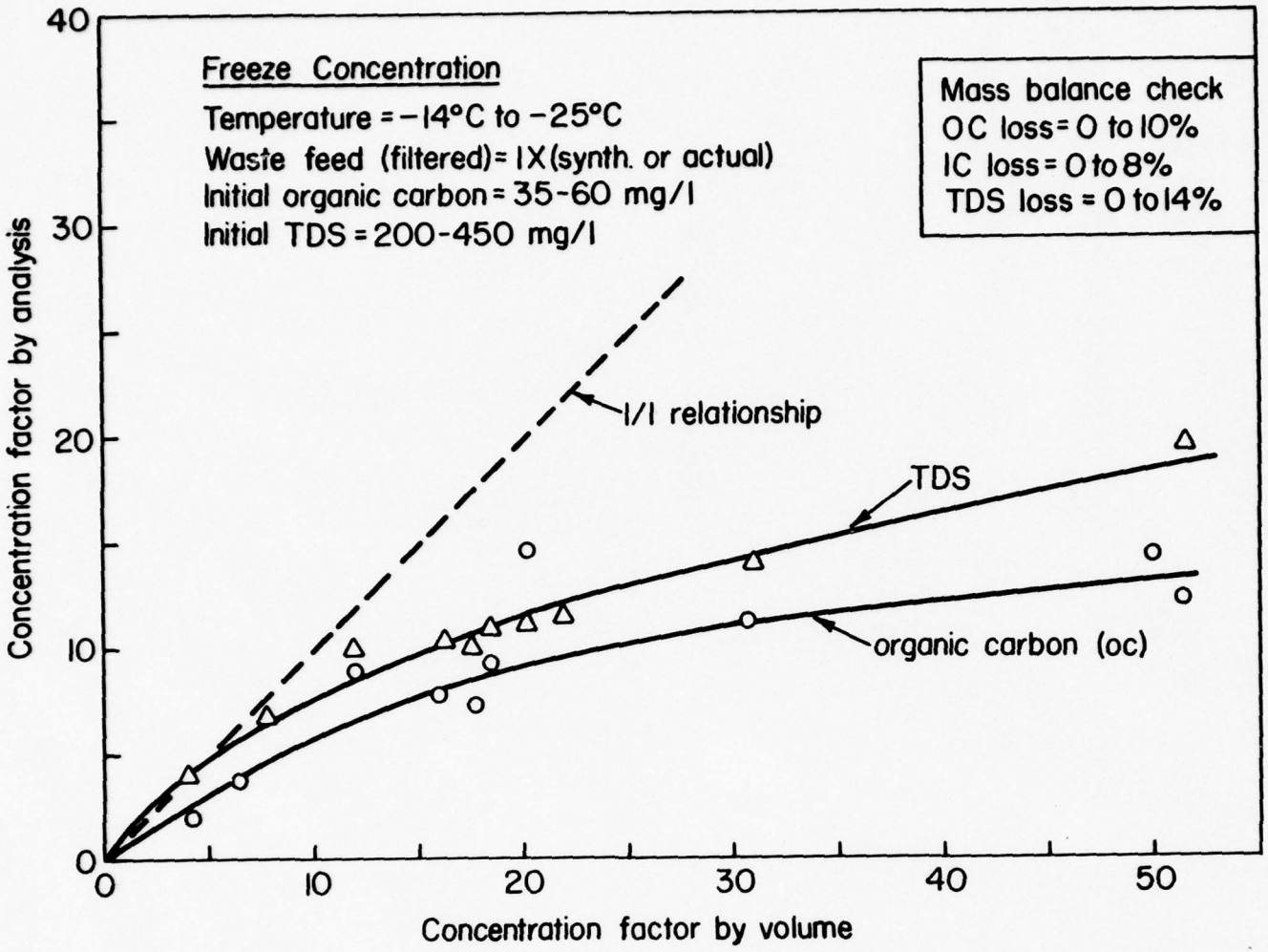

Figure 28. Actual concentrations achievable with a freeze concentrator.

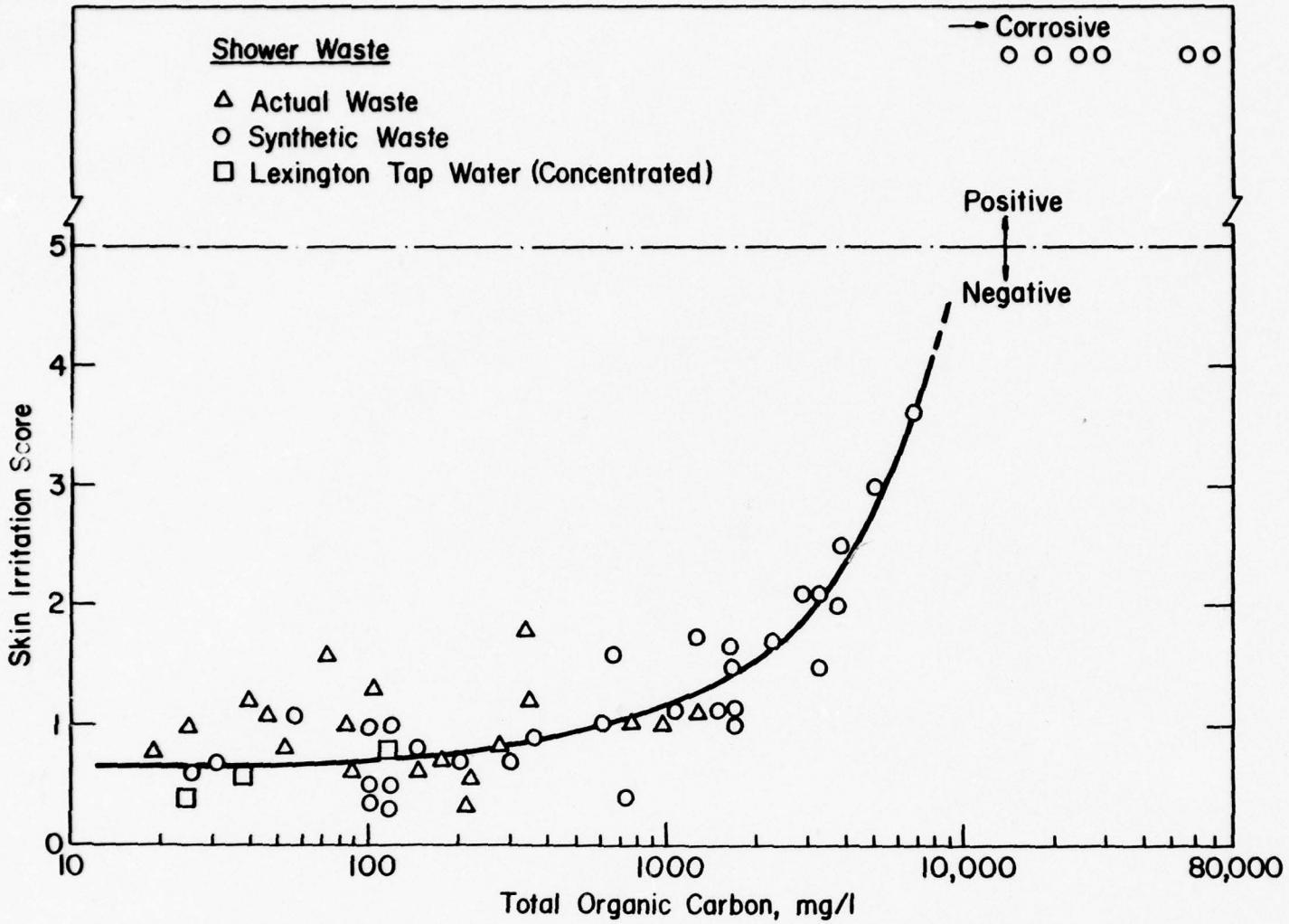

Figure 29. Dependence of skin irritancy behavior on organic carbon concentration for shower wastes.

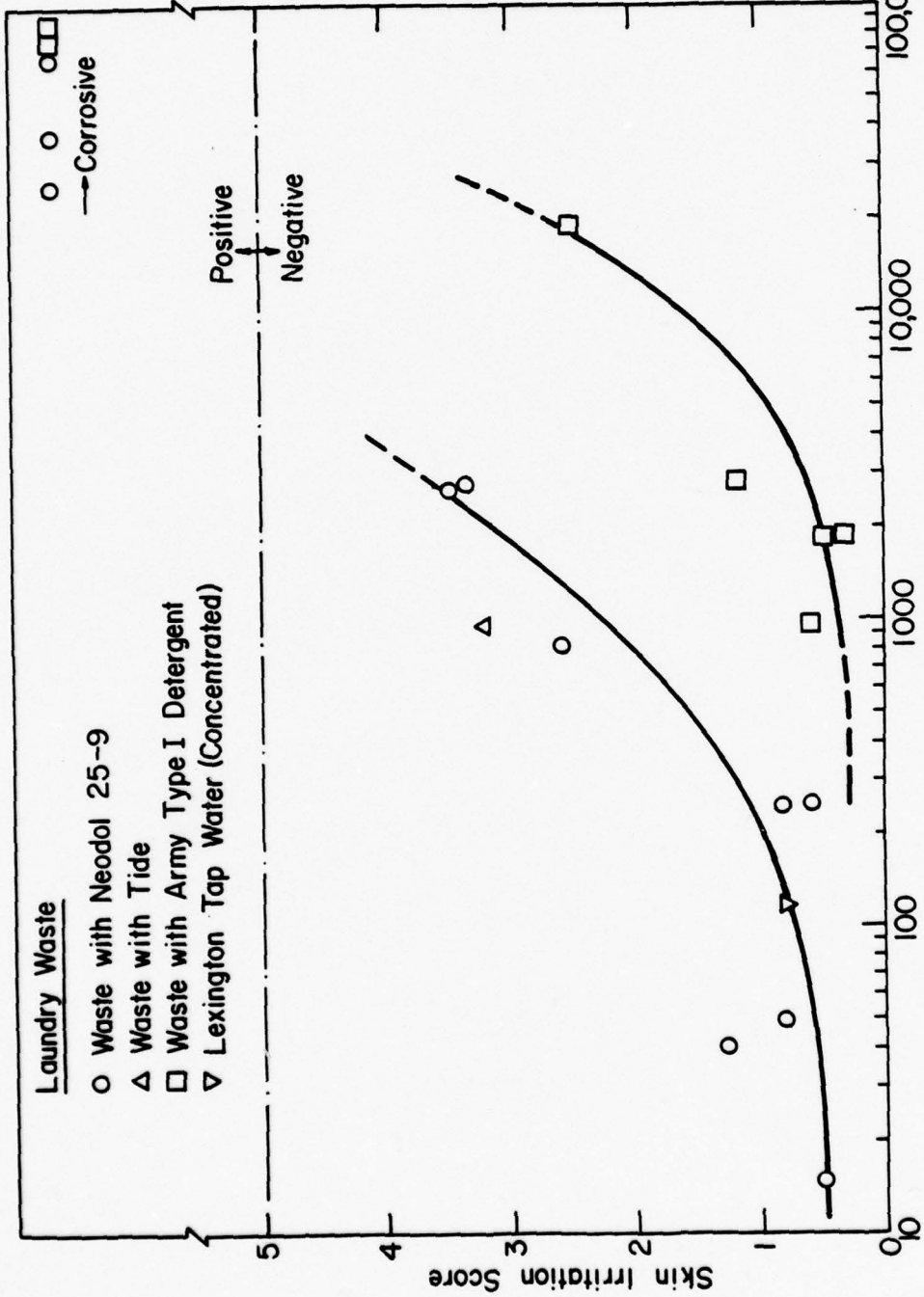

Figure 30. Dependence of skin irritancy behavior on organic carbon concentration for laundry wastes.

positive reaction. Eye irritation scores of various shower waste samples are shown in Figure 31 For most samples (organic carbon up to 7000 mg/l), the test scores were less than 1.0. The maximum score number of 6.0 was observed with a 500 X filtered (through 0.45 μ) solution containing 70,000 mg/l organic carbon. Laundry waste samples containing more than 2500 mg/l organic carbon (100 X filtered) showed positive reactions, as presented in Figure 32.

Ten of the water samples were also evaluated for mutagenicity in microbial assays. The samples included shower wastes containing up to 8000 mg/l organic carbon (100 X raw waste) and laundry wastes containing up to 2600 mg/l organic carbon (100 X filtered). All ten samples were found to be non-mutagenic, as tested by Litton Bionetics, Inc., Kensington, Maryland. Finally, six samples (which were already evaluated for mutagenicity and animal irritancy and toxicity) were carefully selected for human volunteer studies,[24] involving skin irritation. Twenty-one day continuous, closed patch tests were carried out with 21 volunteers.

The results of the human volunteer studies are compared with the animal studies in Tables 8 and 9. Similar irritancy trends are shown for both humans and animals. Mild irritation (Score 1) is defined as "erythema with definite margin;" strong irritation (Score 3) is defined as "vesiculation pustule formation or fissures." The seventh pass ultrafiltrate shown in Table 8

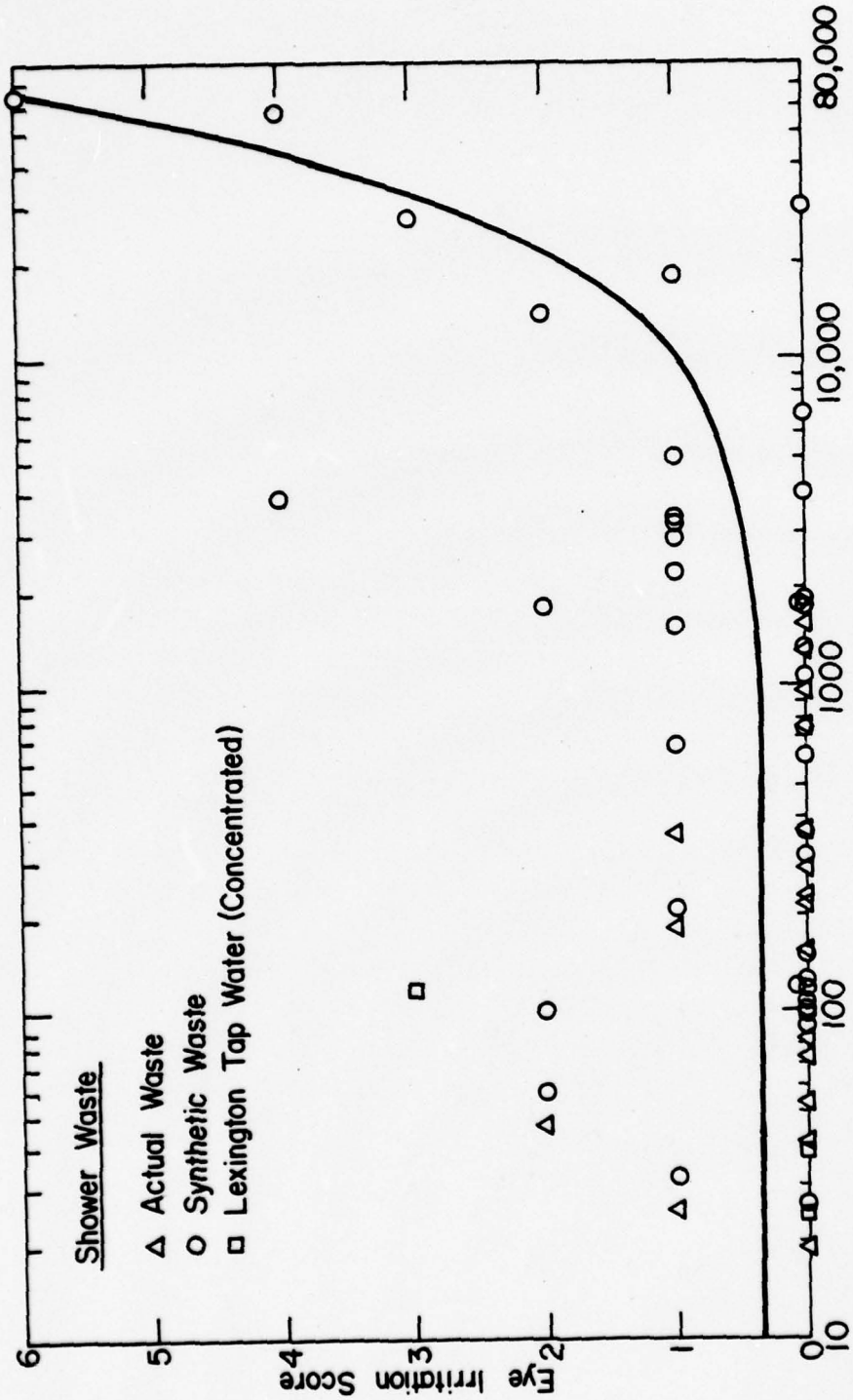

Figure 31. Dependence of eye irritancy behavior on organic carbon concentration for shower wastes.

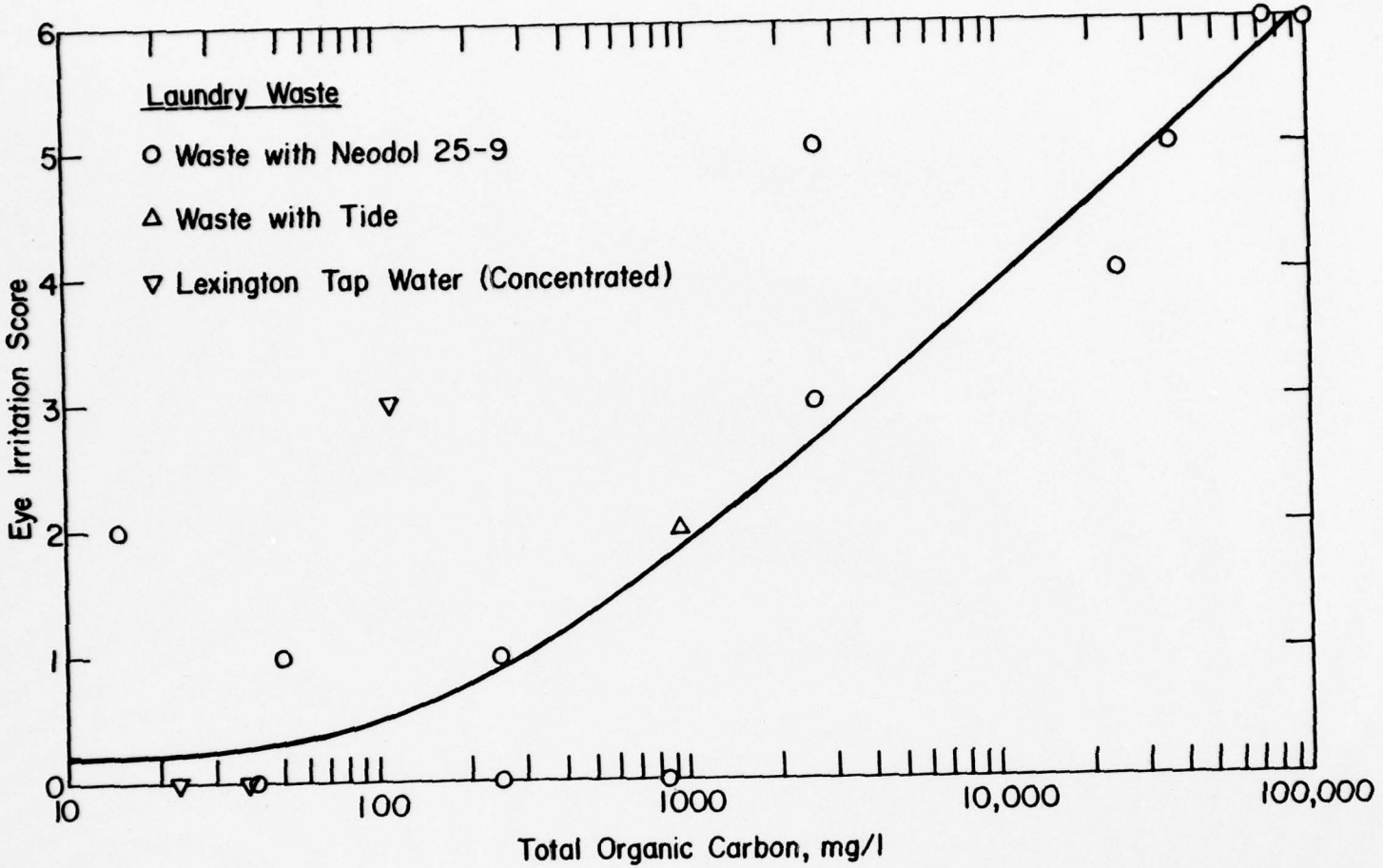

Figure 32. Dependence of eye irritancy behavior on organic carbon concentration for laundry wastes.

TABLE 8. TYPICAL IRRITATION RESPONSES OF VARIOUS SHOWER WASTES

Sample	Concentration		Irritation (Rabbits)		Skin Irritation Behavior (Human)
	TOC, mg/l	TS, mg/l	Skin	Eye	
Synth. 500 X (filtered, 0.45μ)	28,000	47,000	Corrosive*	3*	-
Synth. 200 X (filtered, 0.45μ)	4,942	9,500	3.0	1	-
Synth. 100 X (raw)	8,167	20,800	3.6	[illegible]	irritating**
Synth. 50 X (filtered, 0.45μ)	1,556	2,174	1.1	1	-
Actual (concentrate stream from UF unit)	1,427	4,020	0.6	0	no irritation
Actual (7th pass ultrafiltrate)	200	727	1.6	0	no irritation
Actual + Urine (ultrafiltrate)	51	280	0.8	0	no irritation
Tap water	3	180	0.4	0	no irritation

*primary irritant
**mild irritation at 6 days, strong irritation at 14.5 days

TABLE 9. TYPICAL IRRITATION RESPONSES OF VARIOUS LAUNDRY WASTES

Sample	Concentration		Irritation (Rabbits)		Skin Irritation Behavior (Human)
	TOC, mg/l	TS, mg/l	Skin	Eye	
Synth. 500 X (filtered, 0.45μ)	72,000	248,000	5.4*	6*	-
Synth. 100 X (filtered, 0.45μ)	2,643	72,340	3.5	4*	-
Synth. 50 X (filtered, 0.45μ)	800	28,000	2.6	0	irritating**
Synth. 10 X (ultrafiltrate)	50	4,800	0.8	1	-
Synth. 75 X with Army Type I detergent (filtered, 0.45μ)	2,370	55,000	1.2	0	no irriation

*primary irritant
**mild irritation at 10 days, strong irritation at 11.5 days

was obtained by using a microporous filter (Amicon DP06) as the membrane to simulate a worst condition. The oral toxicity tests (with mice) showed that 100 X or higher dosages of shower and laundry wastes produced toxic responses. The LD_{50} value (TOC) for shower wastes was 2.4 gm/kg and the LD_{50} value for laundry wastes was 2.7 gm/kg. The above detailed toxicity and irritancy studies clearly evidence that ultrafiltrates can be reused with a large safety factor, even at a very high number of reuse passes.

Operating Costs of Membrane Unit. Because the membrane unit must be able to treat laundry and/or shower wastes, an operating channel velocity (Table 6) of 500 cm/sec (Re = 14,000) should be used to minimize concentration polarization. For a typical laundry or shower waste at a feed stream flow rate of 1000 cm^3/sec (23,000 gal/day), 90% water recovery could be achieved with 6.2×10^5 cm^2 of membrane area (in tapered arrangement), for operation at $\Delta p = 5.6 \times 10^5$ N/m^2. Assuming a two year membrane life, the membrane replacement cost ($20.00/$ft^2$ membrane area) per 1000 gal of ultrafiltrate would be $0.89. Because the pressure loss is proportional to $U^{2.0}$, optimum operation must be a compromise between pumping costs, membrane replacement costs, and the adverse effects of membrane fouling at low velocities. At a 500 cm/sec operating velocity, the overall pumping cost per 1000 gal of water would be about $1.30. At 90% water recovery, 95% removal of organic carbon and 52% removal of dissolved solids could be achieved with laundry wastes, and 75% removal of organic carbon and 45% removal of dissolved solids could be obtained with shower wastes.

CONCLUSIONS

The feasibility of ultrafiltration with non-cellulosic membranes is established to achieve adequate solute(s) removal at high water recovery from laundry and shower wastes and to enable the reuse of the recycled ultrafiltrate for non-potable, human contact purposes. All membrane evaluations were conducted in continuous-flow units (with and without high water recovery), treating laundry wastewaters containing a nonionic surfactant, polyphosphates, silicates, hypochlorites, clay particulates, and oil, and treating shower wastewaters containing aliphatic acid soaps, toothpaste, hair oil, shampoo, insect repellent, scouring powder/disinfectant containing phenylphenol, and soil.

In addition to the extensive studies conducted with a laboratory-scale, thin-channel system (using Millipore PSAL membranes), various commercially-available membrane modules in tubular, plate and frame, and hollow fiber configurations were evaluated. Both tubular UOP-225 (1.27 cm diameter) and hollow fiber Romicon HF 20 - PM 5 (0.05 cm fibers) showed drastic flux losses (50 - 75%) and flux recovery problems (after each successive use) with actual shower wastes. The flux recovery after cleaning and flushing sequences was considerably better with tubular UOP-X117 (1.27 cm diameter) and hollow fiber Romicon HF 43 - AM 2 (0.11 cm fibers), and an average water flux of 5×10^{-4} - 6×10^{-4} $cm^3/cm^2 sec$ was obtained.

Of all the membranes tested, Millipore PSAL provided minimum flux drop and maximum solute(s) rejection, including 40 - 60% rejection of dissolved solids (conductivity) because of the ionic nature (negatively-charged) of the membrane. An operating channel velocity of 500 cm/sec (Reynolds Number = 14,000) and transmembrane pressure of 5.6×10^5 N/m^2 were selected as the optimum operating parameters. A gel-polarization-limited condition was observed at a channel velocity < 100 cm/sec for shower wastes.

A computer simulation scale-up procedure showed tapered, multiple-module arrangements to be the optimum, both in terms of solute(s) removal and membrane area requirements, because of the limited need for concentrate recycle. For laundry or shower wastes at a feed flow rate of 1000 cm^3/sec (23,000 gal/day), 90% water recovery could be achieved with 6.2×10^5 cm^2 of total membrane area (average ultrafiltrate flux of 14×10^{-4} cm^3/cm^2 sec), resulting in operating costs (membrane replacement + pumping) of $2.19 per 1000 gallons of product water. At 90% water recovery, greater than 90% removal of organic carbon and phosphate and 52% removal of dissolved solids could be achieved from laundry wastes, and with shower wastes, 75% removal of organic carbon and 45% removal of dissolved solids could be obtained. In addition to ultrafiltration unit design, the possible build-up of organic carbon and dissolved solids in the recycled water was calculated (and verified by experiments)

through a unique model. With 90% water recovery and 10% make-up water in each pass, the maximum value (at a high number of recycle passes) of the ratio of the solute concentration in the water at the reuse point to the solute concentration in the waste from the zero recycle pass would be only 0.03 for organic carbon, 0.10 for phosphate, and 0.95 for total dissolved solids in the case of laundry water and 0.30 for organic carbon and 1.0 for dissolved solids with shower water.

A thorough toxicity and irritancy (dermal, ocular, and oral) study on mice and rabbits was conducted with various concentrated ultrafiltrates and concentrated feed solutions (1000-fold concentration), and the results showed that the ultrafiltrate water could be reused with a large safety factor (200:1), even at a very high number of recycle passes, without any danger of skin and eye irritation. For example, with shower and laundry wastes, samples containing even up to 800 mg/l organic carbon (such as 100 X raw shower waste) showed no positive skin irritation. The results of animal studies were further verified by human volunteer studies (skin irritancy), which showed a similar irritation behavior trend with organic carbon concentration (or total solids).

NOMENCLATURE

C	average organic carbon concentration in channel on high pressure side, mg/l
C_f	concentration of organic carbon in ultrafiltrate stream, mg/l
C_{favg}	average concentration of organic carbon in ultrafiltrate stream from multiple modules (Equation 10), mg/l
C_f (N)	average concentration of solute in ultrafiltrate stream for "N" th recycle pass, mg/l
C_f' (N)	concentration of solute at water reuse point, mg/l
C_i	concentration of organic carbon in feed stream to ultrafiltration unit, mg/l
C_i (0)	concentration of solute in feed stream to ultrafiltration unit for zero recycle pass, mg/l
d	hydraulic diameter of channel, cm
F_i	flow rate of feed stream to ultrafiltration unit, cm^3/sec
J_w	water (ultrafiltrate) flux, cm^3/(sec cm^2 membrane area)
K_s	mass transfer coefficient, cm/sec
N	number of water recycle passes
P	average phosphate concentration in channel on high pressure side, mg/l
P_f	concentration of phosphate in ultrafiltrate stream, mg/l
P_i	concentration of phosphate in feed stream to ultrafiltration unit, mg/l

Δp	average transmembrane pressure difference, N/m^2
r	fractional water recovery (total ultrafiltrate flow rate per unit feed flow rate)
R	solute rejection (Equation 4)
R*	solute removal (Equation 10)
R_m	resistance of ultrafiltration membrane to water flux, $N/m^2/cm/sec$
U	average channel velocity, cm/sec

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