Report No. EVE-15-69-3

LOW PRESSURE ULTRAFILTRATION SYSTEMS FOR WASTEWATER CONTAMINANT REMOVAL

Rolf T. Skrinde
Tsuan Hua Feng
Philip A. Lutin
W. Leigh Short

Progress Report for Federal Water Pollution Control Administration

research grant WP-01408-01, 1 June 1968 — 1 March 1969

ENVIRONMENTAL ENGINEERING
DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF MASSACHUSETTS
AMHERST, MASSACHUSETTS

LOW PRESSURE ULTRAFILTRATION SYSTEM FOR WASTEWATER CONTAMINANT REMOVAL

FWPCA Research Grant No. WP-01408-01

Progress Report for Period 1 June 1968 - 1 March 1969

1 March 1969

Rolf T. Skrinde, T. H. Feng, P. A. Lutin, and W. L. Short

University of Massachusetts, Amherst, Massachusetts

Reported herein is a summary of research progress on Grant No. WP-01408-01, entitled REVERSE OSMOSIS TREATMENT OF WASTEWATERS, from its inception in June 1968 to date. The laboratory apparatus, initially a single cell system, has been redesigned at this point to include three cells in series in a single reservoir recycling arrangement. Although reverse osmosis processes for wastewater treatment contain membranes which selectively pass water, the slight permeability of these membranes to solutes as well has resulted in increasing use of the term ultrafiltration to describe the process. The terms reverse osmosis and ultrafiltration are therefore used interchangeably in this report.

I. OBJECTIVE, SCOPE, AND THEORY

RESEARCH OBJECTIVE

The purpose of this research is to obtain data needed to evaluate and apply reverse osmosis as a process for the treatment of wastewaters. In particular, an improved understanding of the mechanism of separating organic materials from water is essential to development of more suitable membranes and better geometric design of ultrafiltration cells.

The objectives of this study are to:

a. Obtain data essential to development of design parameters, including data on liquid diffusion rates, efficiency of separating organic pollutants, and cell operating characteristics for presently-available membranes utilizing waters containing selected organic and inorganic chemicals.

b. Apply the above data in developing membrane separation techniques for advanced treatment of organic industrial wastes and municipal sewage. In addition to the development of membranes and cells specific to wastewater treatment, this phase of the investigation will consider systems in which reverse osmosis may be utilized in conjunction with chemical additives such as activated carbon and polyelectrolyte coagulant aids. The systems developed will be tested on municipal sewages and industrial wastes.

The reverse osmosis process has been developed to a sophisticated state of technology for desalination of sea water, as shown by the large

number of papers published on membranes for separating relatively small sized inorganic ions from water. Since the osmotic pressure of sea water is approximately 350 pounds per square inch (psi), reverse osmosis desalination must be carried out at pressures in excess of this. The first desalination membranes produced only about one gal/ft^2-day of pure water at pressures of 1500 psi, and were therefore far from economically feasible.

Through intensive efforts in membrane research, films of extremely thin cross section and relatively high flux rate have been developed. The salt rejection efficiency has been found to vary with film thickness and porosity, as well as other variables such as temperature, and as a rule those membranes which exhibit the highest flux at lowest operating pressures allow some permeation of salts. Pilot plants now in operation for desalination purposes are designed on the basis of 10 to 20 gal/ft^2-day flux at operating pressures of 600 to as high as 1500 psi.

Although advances in membrane technology for demineralization of water have encouraged a few field studies on reverse osmosis treatment of contaminated waters, the development of membranes and systems for separation of organic fractions from water must now necessarily be based primarily upon work on inorganic salts, since relatively few studies have been made thus far on pure organic compounds. Organic molecules of larger size than inorganic ions should conceivably be amenable to separation from water by more porous membranes than are used for desalination by reverse osmosis. The use of more porous membranes would allow operation of ultrafiltration systems at more economically feasible pressures than the 600 to 1500 psi now used in the vast majority of

reverse osmosis units. With these considerations in mind, a major objective of the studies reported herein is to investigate the removal of organic materials from water at operating pressures of 30 to 50 psi. Of the many major companies producing ultrafiltration equipment, only one has approached membrane treatment in this pressure range, even though new membrane technology gives every indication that low pressure operation is feasible now and surely to be more highly developed in the very near future.

SCOPE

The initial phase of the research has been concerned with the determination of flux rates, removal efficiencies, and other operating characteristics of currently available membranes in order to determine those conditions conducive to most efficient removal of pure organic contaminants in solution. Special attention has been devoted to ultrafiltration membranes which exhibit relatively high flux rates at operating pressures in the range of 50 psi.

The initial studies have consisted of investigating removals of pure organic compounds ranging in size from those with molecular weights in the range of a few hundred (phenolic derivatives and pesticides) to those with molecular weights of several thousand (polysaccharides). Both alkyl and aryl geometric configurations of molecules have been included. The compounds investigated to date have been alkyl benzene sulfonate, lindane, pentachlorophenol, glucose, sucrose, raffinose, and dextrans of varving molecular weights. The range of dextran molecular weights is 10,000 to 110,000.

The data obtained in pure compound studies is being utilized in evaluating presently-known membranes and reverse osmosis processes for their potential in wastewater treatment, and in developing conceptual designs of better membrane processes for reverse osmosis treatment of wastewaters. A basic consideration is the collection and evaluation of data on the basis of the following conditions:

1. Relationship of molecule size and configuration to permeation of organic compounds through reverse osmosis membranes. Some of the organic compounds are in a homologous series. These studies will aid in determining the mechanisms of transport of both water and organics through the membranes.
2. Effect on flux and rejection efficiency of temperature, pressure, and geometry of the membrane cell.
3. Mechanism of flux decrease with time.

THEORY

In the past several years there has been a wealth of articles published on the theoretical aspects of reverse osmosis or ultrafiltration. The initial impetus behind these studies came from desalination studies rather than the use of reverse osmosis systems in water pollution control.

The theoretical work published generally falls into one of three classes:

1) A study of the flow mechanism through the membrane itself.

2) A study of the velocity and concentration profiles for both

laminar and turbulent flow across the membrane, for various system geometries.

3) Attempts to characterize the membrane and molecular parameters of the rejected solute(s) to enable prediction of the operating characteristics and solute rejection of any system.

The above three areas will be discussed below in some detail.

I. Mechanism of Flow Across the Membrane

Because of the wide variety of membrane materials, it is likely that no single theory will describe the behavior of all of them. Since the Loeb-Sourirajan type cellulose acetate membrane is most widely used, much of the theoretical studies conducted to date concern this type of membrane. Michaels, et al[1] have presented a thorough discussion of the flow of water across cellulose acetate membranes and conclude that the flow equation developed by Merten[2] is valid.

$$N_A = K_1(\Delta P - \Delta\Pi)^* \qquad \text{Eq. 1}$$

However, salt (solute) transport is much more complex and three possible transport mechanisms have been postulated:

1) Diffusion of ions within the membrane due to concentration difference.

2) Diffusion of ions in small pores (of approximately the same size as the solute molecule) due to both pressure and

* See end of section for nomenclature.

concentration gradients.

3) Hydrodynamic flow of salt solution through large pores (large relative to the size of the solute molecules).

Recent work by Sherwood[3] and Kimura and Sourirajan [4] suggest that a simpler model may be used.

Sherwood[3] suggests the following equations:

$$N_s = K_2 \Delta P C_{sw} + K_3 (C_{sw} - C_{sp}) \qquad \text{Eq. 2}$$

$$N_A = K_1 (\Delta P - \Delta \pi) + K_2 \Delta P \Delta C_{Aw} \qquad \text{Eq. 3}$$

Kimura and Sourirajan simplified the above expressions by neglecting pore flow ($K_2 = 0$). Ultimately, if sufficient information is available the brine (solute) side diffusion region and the membrane barrier could be treated as a coupled composite body problem. This has been attempted by Sherwood[3] and Kimura and Sourirajan[5]. Another approach is to treat the membrane selectivity in terms of a constant rejection parameter, first defined by Brian[6].

$$R = 1 - \frac{C_{sp}}{C_{sw}} \qquad \text{Eq. 4}$$

This reduces the composite body problem to a single body convective diffusion problem in which R appears as a boundary condition. Using this approach and the simplifications suggested above, a membrane may then be characterized by two parameters: the rejection efficiency, R, and the solvent permeability coefficient of the membrane, K_1.

Johnson and Bennion [7] have taken a slightly different approach to the problem of describing transport through the membrane. They derived[8] a set of equations to describe the flux of binary electrolytes in membranes. Utilizing their equations applied to the transport of sodium chloride and magnesium chloride, they were able to show that the coupling terms were negligible for water flux, but that they are significant for salt flux. This is somewhat in contradiction to the simplifications suggested above.

Johnson and Bennion also presented data on the effect of temperature and composition on the flux rates and coupling terms. Temperatures of 40 to 95°F were studied at concentrations up to 0.1 N.

As a conclusion to this section, the development is given for an equation for the combined solute and water fluxes through a membrane. Neglecting water flux by pore flow:

$$N_A = K_1 (\Delta P - \Delta \Pi) \qquad \text{Eq. 5}$$

Assuming that the osmotic pressure is directly proportional to solute concentration:

$$N_A = K_1 \Delta P \left[1 - \left(\frac{C_{sw} - C_{sp}}{C_{so}} \right) \frac{\Pi_o}{\Delta P} \right] \qquad \text{Eq. 6}$$

The salt flux across the membrane is

$$N_s = (N_A + N_s) C_{sp} \qquad \text{Eq. 7}$$

Combining (6) and (7):

$$(N_A + N_s) = \rho V_w = \frac{K_1 \Delta P}{1 - C_{sp}} \left[1 - \left(\frac{C_{sw}}{C_{so}} \right) \left(1 - \frac{C_{sp}}{C_{sw}} \right) \frac{\pi_o}{\Delta P} \right] \quad \text{Eq. 8}$$

i.e. the combined fluxes may be characterized by K_1 and R. $(1 - \frac{C_{sp}}{C_{sw}})$

II. Solute Side Diffusion Problem

The analytical methods, described below used to attack this problem generally involve the following assumptions:

a) Laminar, isothermal flow (turbulent flow is described briefly later)

b) Incompressible flow

c) Constant viscosity, density, and diffusivity.

d) Constant ΔP

e) Constant permeation velocity. (Vw)

Subject to these assumptions the equations to be solved are:

Continuity equation

$$\nabla \vec{v} = 0 \quad \text{Eq. 9}$$

Equation of Motion

$$\rho \left(\frac{D\vec{V}}{Dt} \right) = -(\nabla \vec{p}) + \mu(\nabla^2 \vec{v}) + (\rho \vec{g}) \quad \text{Eq. 10}$$

Continuity equation for solute

$$\frac{DC_s}{Dt} = D\nabla^2 C_s \quad \text{Eq. 11}$$

plus the general boundary condition at membrane solution interface:

$$V_w C_{sw} - D \left.\frac{\partial C_s}{\partial y}\right|_w = V_w C_{sp} = (1-R)\, V_w C_{sw} \qquad \text{Eq. 12}$$

The problem then becomes the solution of the above equations for a given geometry and flow conditions. In addition, the cases of the so-called entrance region and fully developed flow must be considered. Another possible configuration is transient (batch reverse osmosis) and continuous steady state operation.

Solution of the above equations is difficult; however, the results obtained from approximations are exceedingly useful in the study and prediction of concentration polarization. One of the important features of separation by reverse osmosis is that for nearly all systems the Schmidt number ($\mu/\rho D$) is very large (about 560 for salt-water systems). This means that the kinematic viscosity is 560 times greater than the diffusion coefficient and that momentum is transferred much more rapidly than mass by molecular transport. Thus, solute concentration will be quite high at the membrane surface in order for the concentration gradient to be sufficiently large for the solute to diffuse back to the bulk stream.

Solutions to the differential equations given above for transient operation have been published by Raridon, Dresner, and Kraus[9], Nakano, Tien and Gill[10], and Williams[11]. The reader is referred to these articles for specific details and assumptions made by the authors.

The number of published papers analyzing operation of a continuous laminar flow reverse osmosis system is extensive. Dresner[12]

analyzed the case of laminar flow between parallel plates. Using an expression developed by Berman[13] for the axial and transverse velocity profiles, Dresner obtained approximate solutions valid for the inlet and downstream sections of the channel. Sherwood et al[14] also studied the same problem but employed a more accurate form of the velocity equation developed by Berman. Fisher, Sherwood and Brian[15] extended their work to laminar flow in tubes. Results of all of these theoretical studies are summarized and compared by Sherwood[16].

All of the above studies have shown that there is a high degree of polarization in laminar flows. This would suggest that buoyancy effects may be important. To this end Ramandahan and Gill[17] considered the mechanism of free convection in a hyperfiltration system. The momentum and diffusion equations, coupled with the inclusion of a buoyancy term were solved using a perturbation technique.

Theoretical studies have also been published for a non-constant permeation rate. Results of these studies have been presented by Gill, Tien, and Zeh[18], Brian[6], Gill[19], [20], and Srinivasan et al[21], [22].

The theoretical studies of the solute side problem of concentration polarization in laminar flow have shown that concentration polarization is a very significant problem and that methods must be devised to limit it.

All of the preceeding studies have been concerned with laminar flow in reverse osmosis (ultrafiltration) systems. Turbulent flow systems have also received considerable attention in the past few years.

In laminar flow the important transport mechanisms are axial convection, radial (or transverse) convection and radial molecular diffusion. In turbulent flow transport of mass by radial eddy diffusion is important in determining concentration profiles.

Sherwood[14, 16], and Brian[23] have employed the Nernst film theory and Deissler[24] eddy diffusion models for turbulent transport to describe concentration polarization in reverse osmosis systems. These models assume that all the resistance to mass transfer is concentrated in a very thin region next to the interface. The film theory also assumes this thin layer to be laminar. From these assumptions and employing the Chilton Colburn j_D factor analogy the required mass transfer coefficient may be calculated. Also the solute concentration at the membrane surface may be estimated.

Theoretical calculation of the velocity and concentration profiles for turbulent flow is not as well advanced as for laminar flow. In particular the analyses break-down for relatively large distances from the inlet where the fraction of feed removed is sufficient to alter the eddy diffusivity. However, the theory does show that for systems having the same inlet and wall Reynolds numbers concentration polarization increases with increasing values of the Schmidt number. In general use of the either the film theory or eddy diffusivity models will give comparable answers.

III. Prediction of Solute Rejection from Molecular Parameters

To date relatively little research has been published on attempts to predict solute rejection from a knowledge of such parameters as membrane pore size, molecular diameter, molecular configuration, etc. One of the more extensive series of experimental studies in this regard was conducted by Blunk[24]. He investigated solute rejection for a fairly wide range of types and sizes of organic molecules. From an analysis of the data Blunk concluded that the relative ratio of pore diameter and molecular diameter cannot solely be used to correlate solute rejection.

Merten et al[25] very recently published results of their and other studies on organic removal by reverse osmosis, including tertiary treatment of sewage effluent, fruit juices, pulping wastes and sugars.

Most of the studies which they discuss are for cellulose acetate systems. These membranes serve as an excellent barrier to colloids, other suspended matter and dissolved organics. Significant permeation rates were observed for some (not all) small organics. Those with high permeation rates were usually oxygenated organics. There would appear to be a large amount of theoretical and experimental work still to be done in the area of predicting solute rejection from readily measurable membrane and molecular parameters.

Nomenclature

C_{Aw} = mass fraction of solvent on solute side of membrane

C_s = mass fraction of solute

C_{sw} = mass fraction of solute on solute side of membrane

C_{sp} = mass fraction of solute in product stream

D = molecular diffusion coefficient

$\vec{g}$ = gravitational acceleration vector

K_1 = solvent permeability coefficient of membrane defined by Eq. 1

K_2 = pore flow coefficient of membrane defined by Eq. 2 and Eq. 3

K_3 = solute permeability coefficient of membrane defined by Eq. 2

N_A = solvent flux

N_s = solute flux

ΔP = applied pressure drop across membrane

R = membrane rejection factor defined by Eq. 1

t = time

$\vec{V}$ = velocity vector

V_w = permeation velocity of solute through the membrane

y = transverse or radial coordinate

Greek Letters:

μ = absolute viscosity of solution

Π_o = osmotic pressure corresponding to concentration C_s

$\Delta\Pi$ = difference in osmotic pressure on either side of the membrane

ρ = density of solution

Operators:

∇ = generalized "del" operator

∇^2 = generalized Laplacian

D = substantial derivative

∂ = partial derivative

II. EXPERIMENTAL APPARATUS, METHODS, AND MATERIALS

MULTI-CELL SYSTEM

Preliminary studies using a single ultrafiltration cell as the filtration mechanism in a laboratory constructed recycling system, demonstrated that the cell was well-suited for research type investigations. This cell, developed by the Dorr-Oliver Company of Stamford, Connecticut, was constructed of acrylic plastic and possessed sufficient structural strength for withstanding operating pressures up to 100 psi (maximum range utilized in low pressure ultrafiltration research). Based upon the success of these studies, a similar but multi-cell laboratory unit was utilized for the research described in this section of the report.

The schematic diagram shown in Fig. 1 represents a flow sheet of that multi-cell ultrafiltration system. The basic unit, purchased from the Dorr-Oliver Company, was modified for operational convenience and is described in detail below.

COMPONENTS OF THE ULTRAFILTRATION SYSTEM

The three gallon capacity reservoir, as depicted in the schematic diagram and shown in the photograph of Fig. 2, was constructed of stainless steel to accommodate a maximum working pressure of 100 psi. The reservoir may be pressurized from an external tank of nitrogen gas visible on the left. Modifications to the factory supplied reservoir included a sampling tap (simple gate valve), temperature probe (thermistor), and cooling coil. The cooling coil circulates water from an external constant temperature source and maintains a 20 ± 0.5°C reservoir temperature.

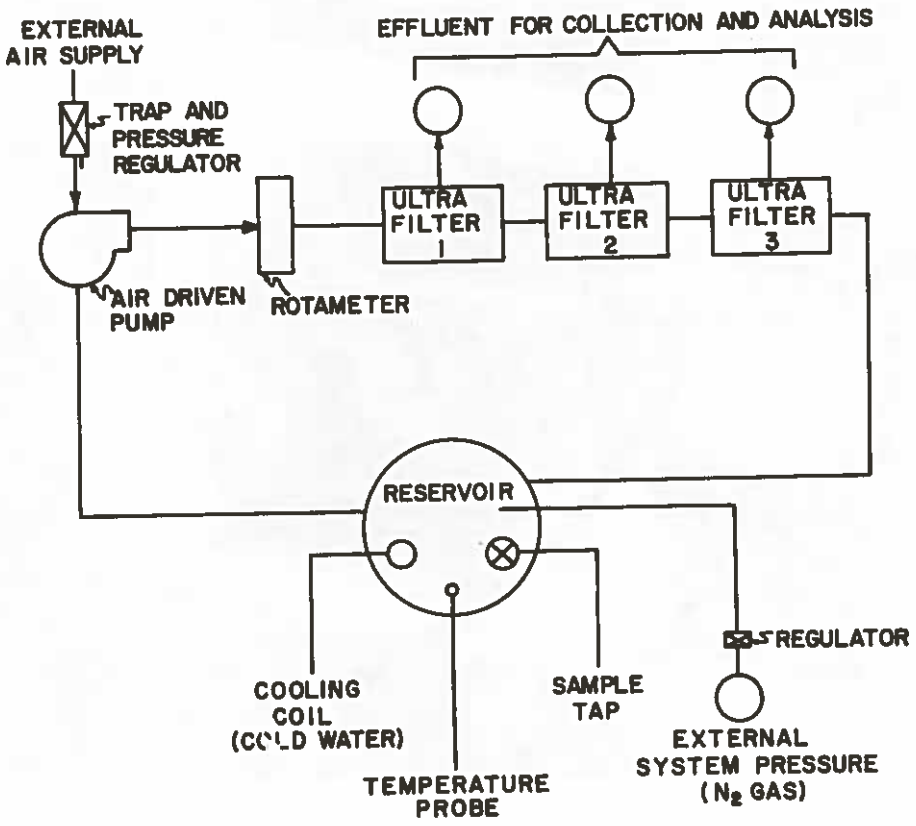

Figure 1. FLOW DIAGRAM OF THE MULTI-CELL LABORATORY ULTRAFILTRATION UNIT.
System filtration pressure is provided by external pressurized nitrogen gas. The pump is powered by a standard laboratory air supply which is trapped and regulated prior to use as the driving force.

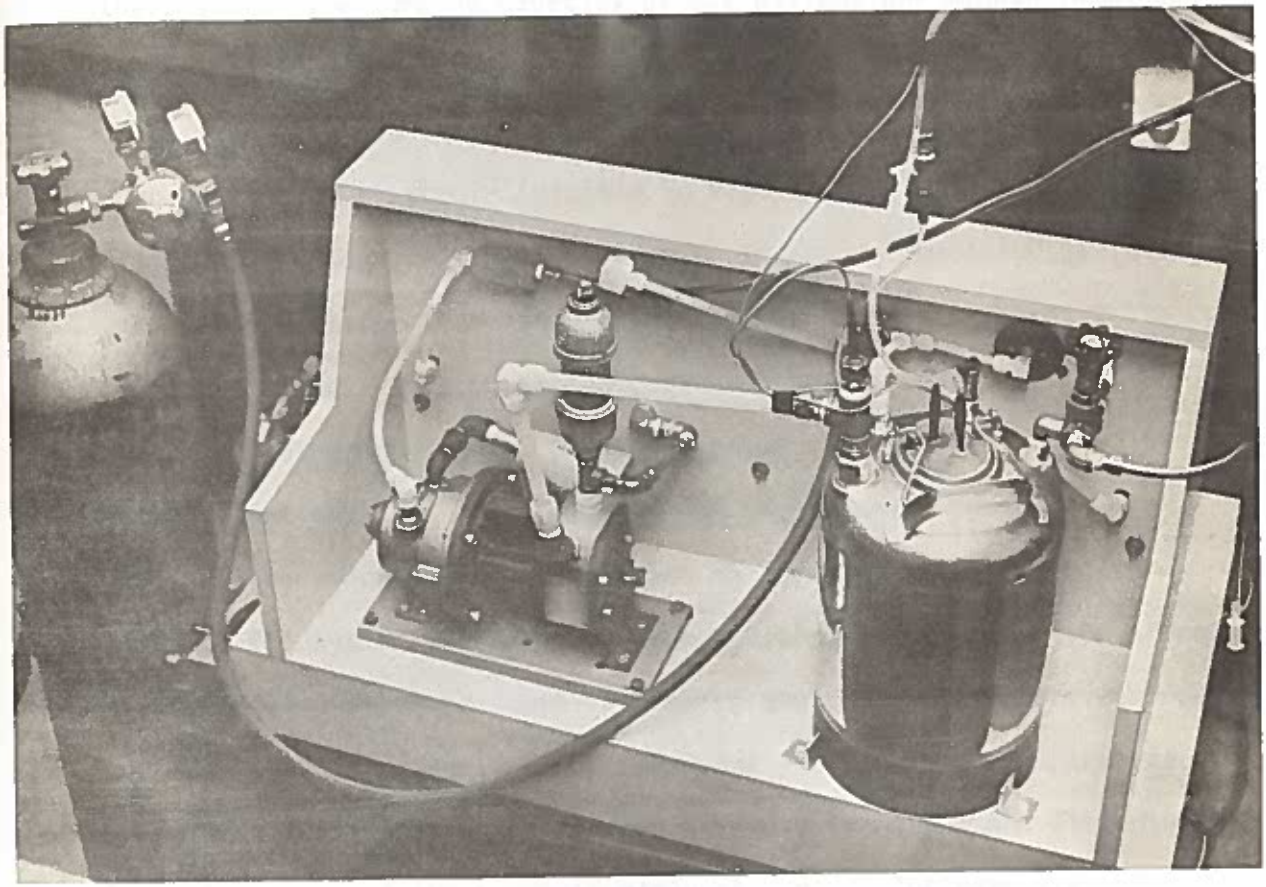

Figure 2. REAR VIEW OF THE LABORATORY ULTRAFILTRATION UNIT. The reservoir has been modified to include a sample tap (right), cooling coil (internal, center), and temperature probe (left). A blowoff valve is visible to the left of and behind the sample tap. The air driven pump is fitted with an air cushion damper to equalize flow variations.

The sample to be filtered is circulated from the reservoir by means of the pump shown on the left in Fig. 2. The pump itself is unique in that it is air driven, thereby lowering inherent additions of heat to the system. The pumping capacity of 2.5 gallons per minute (gpm) was controlled $\pm$0.1 gpm by means of a rotameter on the front side of the unit. The only modification to the pump was the addition of an air cushion damping reservoir (visible in Fig. 2) to eliminate the amplitude of flow pulsation. Air was supplied to the pump from a 100 psi laboratory air line. A filter trap and pressure reducing valve preceeding the pump insured a clean, dry, constant pressure drive for operation.

The photograph in Fig. 3 shows a clear view of the front of the ultrafiltration unit. The rotameter at right center indicates the pumping rate which is varied by means of the pump speed controller. Although the system pressure was controllable directly from the nitrogen cylinder's two-stage pressure regulator, the unit was factory equipped with an auxilliary gage and control valve visible in the upper left.

The ultrafiltration cells were arranged in series and fitted with brass stopcocks at the permeate effluent ports. The permeate was forced through the ports (fitted with flexible tubing) and collected in the graduate cylinders visible in the lower right corner of Fig. 3.

An exploded view of an ultrafiltration cell is depicted in Fig. 4. In actual use, as shown in Fig. 3, the units were inverted. After insertion of the membrane between the porous spacer and "O" rings, the upper and lower portions of each cell were clamped together by means of the bolts and wing-nuts visible in Fig. 3.

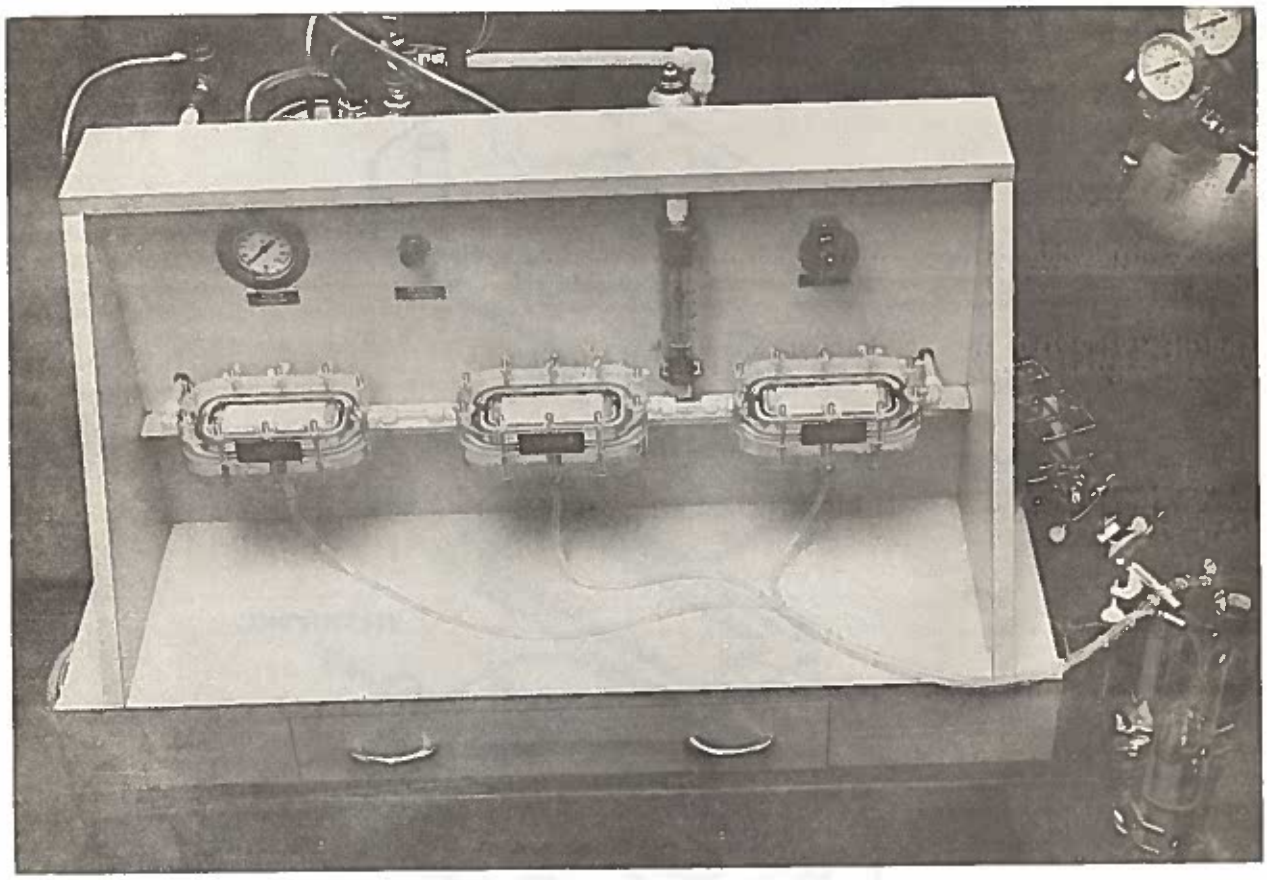

Figure 3. FRONT VIEW OF THE LABORATORY ULTRAFILTRATION UNIT. The system pressure gage and controller are visible at the upper left. Flow rates are regulated by the pump speed controller (upper right) and reflected by the rotameter. The compressed gas cylinder maintains a constant filtration pressure. Permeate from each cell is collected in the graduated cylinders (lower right). Stopcocks at the permeate drainage ports are barely visible beneath each cell.

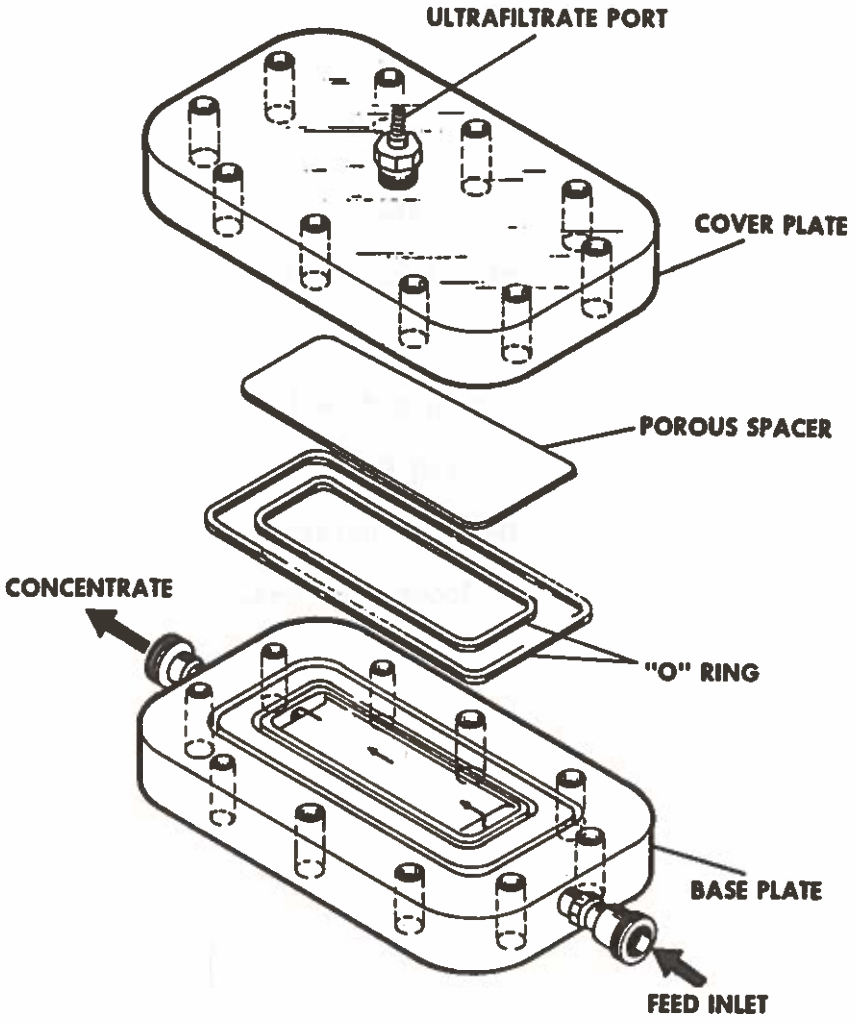

Figure 4. ASSEMBLY VIEW OF ULTRAFILTRATION CELL. Membranes are sandwiched between the "O" rings and porous spacer prior to bolting the cell halves together. In operation (as in Fig. 3) the cells are inverted.

Since each cell was of standard area (i.e.--the area surrounded by the inner "O" ring), flux rates were easily computed by measuring the rate of permeate flow through each cell. The addition of stopcocks to each drainage port permitted the use of any, all, or none of the cells as needs dictated.

EXPERIMENTAL METHODOLOGY

The following methodology was developed for determining the overall efficiency of the ultrafiltration system in removing contaminants from an incompressible fluid media. It is of maximum import to note that the unit employed was operated with a pump drive pressure of 50 psi and a system filtration pressure of 40 psi. At these relatively low operating pressures, standard compression fittings could be employed on all tubing, and all system joints were leak-proof when sealed with ordinary "Teflon" pipe tape.

Sample preparations: For the initial series of laboratory tests, pure chemicals were mixed with distilled water and filtered through the unit. Initial substrate concentrations were set at 500 mg/l, with quantities based on reservoir volume of 11 liters. Substrate detection in both the reservoir and permeate was based on the Chemical Oxygen Demand (COD) test as outlined in Standard Methods[26]. In order to relate substrate concentration to COD, a series of dilutions was prepared for every chemical and analyzed for COD. A calibration curve relating COD to unremoved substrate concentration was then prepared for each chemical.

Operational procedure: Initially, the stopcocks at all three permeate drainage ports were closed and the reservoir filled with prepared test sample. The pump was then started and the flowrate adjusted to a predetermined level. Air initially present was bled from the system by means of a blowoff valve visible on the reservoir in Fig. 2. Nitrogen gas was then introduced into the reservoir and the pressure adjusted by means of the regulators visible in Fig. 3. Before opening the permeate drainage ports, a reservoir sample was drawn from the tap shown in Fig. 2. This sample served as a check on the initial substrate concentration. The ultrafiltration system was in equilibrium (i.e., equal pressure on both sides of the membrane) at this point.

To initiate the ultrafiltration process, the stopcocks on the permeate drainage ports were then opened. This resulted in a pressure drop across the membranes, from full system pressure on the upper face to atmospheric pressure on the permeate drainage side. Cumulative permeate measurements were taken hourly for each cell.

After four hours of operation, a 50 ml sample was taken from each drainage tube, as well as the reservoir tap. Each sample was analyzed for COD and the results converted to mg/l substrate present. The reservoir sample served as a convenient check, in that any reducation in substrate concentration of the permeate should be reflected by an increased substrate concentration in the reservoir.

Each laboratory "run" extended over an 8 hour period with the above sampling technique repeated at the close of each test.

MEMBRANE MATERIALS AND SUBSTRATES

The membranes employed for testing with the multi-cell ultrafiltration unit were supplied by the Dorr-Oliver Company. In view of the fact that membrane technology is currently in its embryonic stages, the following proprietary description of the membranes was authorized by a representative of the supplier:

> "The ultrafiltration membranes used in these systems are non-cellulosic organic polymers. The membranes are a asymmetric; that is, they are comprised of an extremely thin surface layer (or skin) and a porous substructure of the same material. The porous substructure is required solely for mechanical strength. The skin is approximately five microns in thickness; whereas, the total membrane thickness is six to 8 mils. Since pressures of 20 to 50 pounds per square inch are usually used in these systems, the membranes are reinforced with a non-woven material to give added support."

In addition, each membrane was supported by a phenoxy spacer (Fig. 4) to insure a tight seal within the cell.

All three ultrafiltration cells were fitted with identical membranes for each substrate series filtered. Upon completion of investigations on a series of substrates through one type of membrane, a new type membrane was installed and tested with the same compounds. Two types of membranes investigated to date were factory designated as AP-006 and BP-009 respectively.

The following series of substrates were filtered through the system fitted with membrane AP-006 and then with membrane BP-009.

Substrate	Formula weight (approx)
Glucose	180
Sucrose	342
Raffinose	595
*Dextran T-10	10,000
*Dextran T-20	20,000
*Dextran T-40	40,000
*Dextran T-70	70,000
*Dextran T-110	110,000

*Products of the Pharmacia Company, Uppsala, Sweden

This series was chosen to determine the effect of increased molecular weights on substrate removal via the mechanism of ultrafiltration.

III. EXPERIMENTAL RESULTS AND DISCUSSION

MULTI-CELL UNIT

Studies utilizing sugars and higher molecular weight carbohydrate organic compounds for the initial multi-cell ultrafiltration investigations are in progress at the present time. Results reported here are, therefore, of a preliminary nature. A considerable quantity of raw data has been collected, which is included below. Analyses in depth must depend upon completion of the pure compound organic studies, and at this point the research program is proceeding according to the schedule set forth originally.

AP-006 MEMBRANE

Each of the three cells in the multi-cell unit was fitted with identical AP-006 membranes. Permeate from each cell was collected and analyzed separately, constituting three replicate sets of data for each investigation.

As described in Chapter II, the three cells were connected in series, with the bulk fluid being recycled back to a single reservoir. In filtering the Dextran series of organics at high solute rejection efficiencies, concentrations of solute in the system increased with time owing to the buildup of rejected solute remaining within the recycling system. This resulted in an opportunity to correlate solute rejection with concentration for each of these compounds.

The experimental data collected utilizing the AP-006 membrane is presented in Table 1. The data has been programmed for computer analysis, with the initial UMASS FAST FORTRAN program shown in the

TABLE 1

REMOVAL OF SOLUTES USING AP-006 MEMBRANE AT 40 PSI, 1.0 GPM, AND 20.0°C

Substrate	Time (Hr)	Substrate Concentration (mg/l)				Per Cent Removal			
		Reservoir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Glucose	4	457.1	453.1	449.2	457.1	1.0	2.0	0	1.0
	8	524.0	512.2	535.9	531.9	2.0	-2.0	-2.0	-0.7
Sucrose	4	393.9	488.7	503.3	496.0	-24.0	-28.0	-26.0	-26.0
	8	488.7	466.8	488.7	503.3	-4.0	0	-3.0	-2.3
Raffinose	2	498.8	505.1	515.6	498.8	-1.0	-3.0	0	-1.3
	4	528.1	482.0	492.5	498.8	9.0	7.0	6.0	7.3
	6	532.3	513.5	513.5	500.9	4.0	4.0	6.0	4.7
	8	540.7	500.9	505.1	484.1	7.0	7.0	10.0	8.0
Dextran 10	2	536.8	333.7	332.0	330.2	38.0	38.0	38.0	38.0
	4	550.9	328.5	370.8	374.0	40.0	33.0	32.0	35.0
	6	543.9	326.7	324.9	346.1	40.0	40.0	36.0	38.7
	8	603.9	367.3	362.0	353.2	39.0	40.0	42.0	40.3

TABLE 1 (continued)

Substrate	Time (Hr)	Substrate Concentration (mg/l)				Per Cent Removal			
		Reservoir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Dextran 20	2	494.8	309.7	300.5	306.0	37.0	39.0	38.0	38.0
	4	568.1	295.0	320.7	287.7	48.0	44.0	49.0	47.0
	6	601.1	309.7	317.0	315.2	48.0	47.0	48.0	47.7
	8	689.1	350.0	344.5	353.7	49.0	50.0	49.0	49.3
Dextran T40	4	492.3	238.9	246.1	221.0	51.0	50.0	55.0	52.0
	8	697.1	233.6	240.7	230.0	66.0	65.0	67.0	66.0
Dextran T70	4	561.9	232.6	236.2	218.3	59.0	58.0	61.0	59.3
	8	701.5	75.2	64.4	57.3	89.0	91.0	92.0	90.7
Dextran T110	4	523.7	340.7	362.3	351.5	35.0	31.0	33.0	33.0
	8	566.7	358.7	376.6	412.5	37.0	34.0	27.0	32.7

Appendix. Modifications of this program and the development of additional sub-routines will allow analysis of the laboratory data and correlation with theoretical concepts of reverse osmosis and ultrafiltration. Selected portions of the remote console "Teletype" printout are shown in Table 1.

It can be seen that the AP-006 membrane was ineffective in rejecting small sugar molecules, such as glucose and sucrose, with separation efficiency on the order of 6 to 10 per cent beginning with the filtration of raffinose. It is to be noted that the molecular weights of these compounds increase from 180 to 342 to 595 respectively, indicating that in this series poor rejection occurs at molecular weights below the range of 500 to 1000.

The lowest molecular weight Dextran was rejected with considerably greater efficiency than was raffinose. The difference in molecule size between compounds of molecular weight 595 and those of molecular weight 10,000 is however, extremely great. Compounds with molecular weights between these values remain to be investigated in order to explore further the relationships between solute rejection and molecular size and configuration.

The Dextran series of compounds with molecular weights from 10,000 to 70,000 were removed by the AP-006 membrane with increasing efficiency in direct proportion to their molecular weight. There was, in addition, increasing rejection efficiency with duration of filtration. This would suggest that a film of solute was building up on the surface of the membrane during the ultrafiltration experiment, or that molecules of solute became entrapped in the intertices of the membrane as filtration proceeded,

thereby increasing the "tightness" of the membrane with time. It was interesting to note that permeate flux rates did not significantly change throughout eight hour ultrafiltration periods of each particular study. On the other hand, the average flux rate over the eight hour test period tended to decrease with increasing size of solute molecules. On the AP-006 membrane this flux rate varied from 35 gals/ft^2/day with Glucose to 20 gals/ft^2/day with Dextran 110.

Dextran 110, with a molecular weight of 110,000 was rejected with less over-all efficiency than the Dextran 70. The initial removal efficiency for the two compounds was similar, but in the Dextran 110 experiments the removal efficiencies did not increase with time.

BP-009 MEMBRANE

The series of studies utilizing the BP-009 membrane was carried out in a manner identical with those on the AP-006 membrane. The results of these studies are shown in Table 2. It can be seen that solute rejection utilizing this membrane was somewhat similar to that of the AP-006 membrane but some differences, based upon initial investigation, can be noted. Although the sugar compounds, glucose, sucrose, and raffinose, were poorly rejected with approximately the same efficiency as with the AP-006 membrane, the major difference between the two membranes can be noted in the Dextran series. The lower molecular weight Dextrans were rejected in the 60 to 70 per cent efficiency range, while on the AP-006 membrane the lower weight Dextrans were rejected only in the 35 to 50 per cent range. Rejection of the large Dextran molecules was generally more pronounced throughout the BP-009 studies. It is interesting to note that the per cent

TABLE 2

REMOVAL OF SOLUTES USING BP-009 MEMBRANE AT 40 PSI, 1.0 GPM, AND 20.0°C

Substrate	Time (Hr)	Substrate Concentration (mg/l)				Per Cent Removal			
		Reservoir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Glucose	3	496.1	456.7	464.6	456.7	8.0	6.0	8.0	7.3
	8	472.4	480.3	480.3	464.6	-2.0	-2.0	2.0	-0.7
Sucrose	3	495.4	491.6	480.5	521.4	1.0	3.0	-5.0	-0.3
	8	499.1	514.0	461.8	484.2	-3.0	7.0	3.0	2.3
Raffinose	3	567.1	545.8	537.3	597.0	4.0	5.0	-5.0	1.3
	8	520.2	503.2	511.7	494.7	3.0	2.0	5.0	3.3
Dextran 10	3	514.4	253.7	185.8	250.1	51.0	64.0	51.0	55.3
	8	893.1	289.4	242.9	300.1	68.0	73.0	66.0	69.0

TABLE 2 (continued)

Substrate	Time (hr)	Substrate Concentration (mg/l)				Per Cent Removal			
		Reser-voir	Left Cell	Middle Cell	Right Cell	Left Cell	Middle Cell	Right Cell	Average
Dextran 20	3	515.1	155.6	100.1	148.2	70.0	81.0	71.0	74.0
	8	756.0	177.9	122.3	185.3	76.0	84.0	75.0	78.3
Dextran T40	3	561.1	84.3	73.3	91.7	85.0	87.0	84.0	85.3
	8	718.7	84.3	73.3	104.5	88.0	90.0	85.0	87.7
Dextran T70	3	547.0	16.4	12.8	27.3	97.0	98.0	95.0	96.7
	8	743.9	87.5	69.3	--	88.0	91.0	--	89.5
Dextran T110	3	618.3	201.9	118.2	50.9	67.0	81.0	92.0	80.0
	8	723.8	200.0	170.9	76.7	72.0	76.0	89.0	79.0

rejection did not increase substantially throughout the course of the 8 hour experiment with the BP-009 membrane as was the case with the AP-006 membrane. In fact, in two of the experiments, there was a slight decrease in rejection efficiency near the end of the run as compared with that obtained at the end of three hours. The BP-009 membrane was in general a more "tight" membrane, with flux rate varying from 25 gals/ft^2/day on glucose to 10 gals/ft^2/day on Dextran 110. It was observed in the case of the BP-009 membrane that although efficiency of rejection was low with glucose and other small molecules, increased molecule size resulted in greater solute removal than was observed utilizing AP-006 membranes.

DISCUSSION AND RESULTS

The multi-cell ultrafiltration studies indicate, on the basis of the preliminary data, that the separation of organic matter from water by membranes at low operating pressures is feasible when utilizing "loose" membranes. The particular membranes under investigation at the present time allow a water flux rate of as high as 35 gals/ft^2/day at 40 psi which is within an economic range of production of potable water from a contaminated source. Although these studies show that the two porous membranes investigated are not suitable for separating small organic ions and molecules from aqueous solution, such separation was not anticipated because of the characteristics of the membrane.

It must be emphasized that the studies on porous membranes are only now well-initiated and research productivity will be increasing in magnitude as the studies progress. Basic questions such as determination of concentration polarization characteristics and the nature of membrane fouling

will be solved through the development of much more data than is presently available from the few months in which the multi-cell laboratory unit has been operating.

Progress to date on multi-cell studies can be summarized by stating that the laboratory unit has been installed and has been operating successfully for several series of runs on pure organic compounds. Redesign of the unit in order to make minor improvements has been carried out since initiation of the studies, and the results have indicated to date that other modifications will be made in the near future. These will consist primarily of returning the permeate to the makeup reservoir so that the bulk fluid will contain a consistent concentration of solute throughout each study. Data collection has been organized, and a computer program for analysis of data has been developed and implemented.

IV. SINGLE CELL EXPERIMENTAL RESULTS

The initial ultrafiltration studies, upon which investigations described in the preceeding chapters were based, were initiated on a single ultrafiltration system construction in the laboratory. The cell utilized in this system, shown in Fig. 5, was found to be satisfactory for continued studies without modification. Three such cells were then utilized in the milti-cell system.

The results of the single cell studies are included as an appendix to the report. A relatively "tight" cellulose acetate membrane was utilized for these studies. This membrane rejected small molecule organic solutes, with molecular weights in the order of several hundred. Three compounds, lindane, alkylbenzene sulfonate, pentachlorophenol were investigated. The cellulose acetate membrane was particularly effective in rejecting ABS molecules and less effective in removing lindane and pentachlorophenol.

The single cell studies, like the multi-cell studies to date, have been preliminary in nature and have resulted in development of equipment, laboratory procedures, and initial data sufficient to provide the basis for the concerted research effort now in progress.

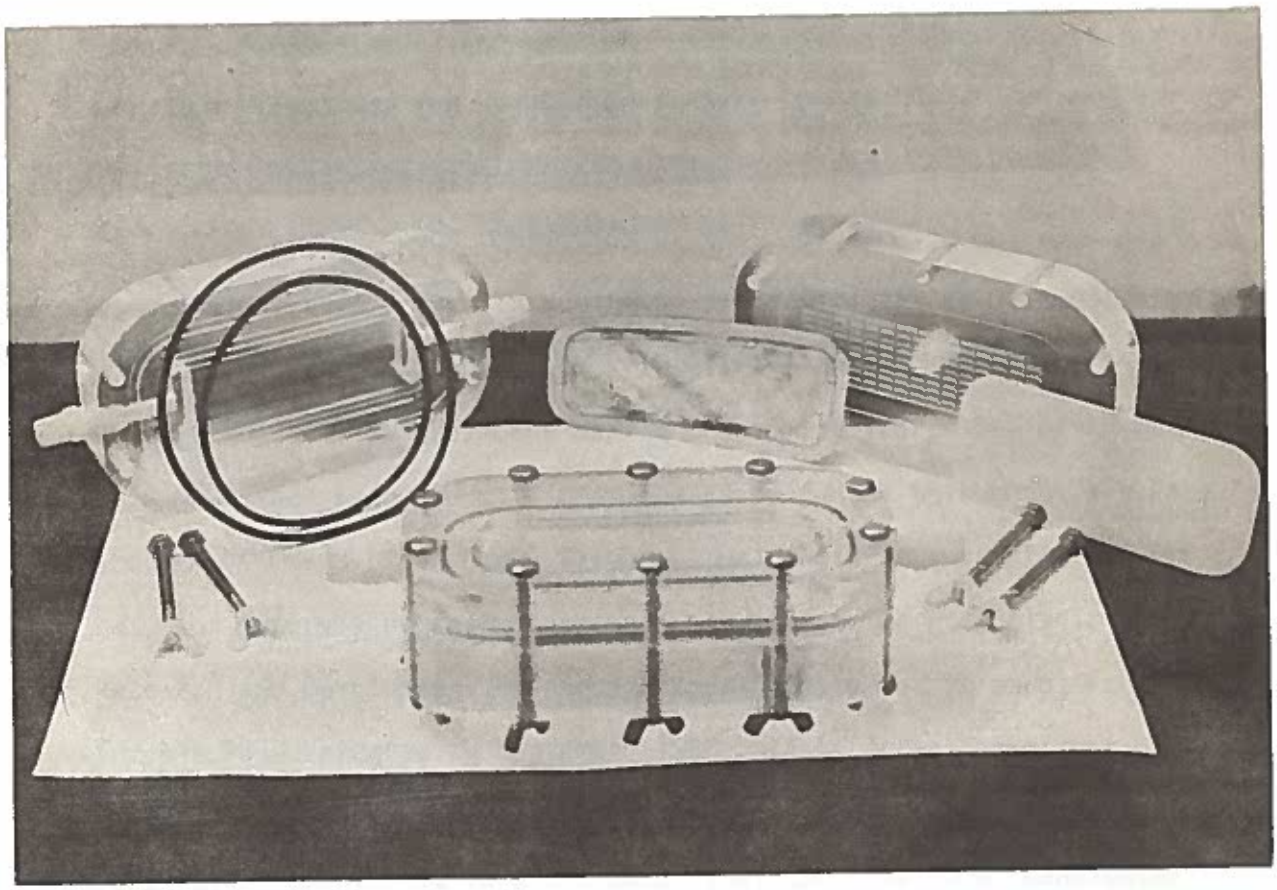

Figure 5. RESEARCH ULTRAFILTRATION CELL.
Shown are a complete cell in the foreground and its component parts in the background. The component parts consist primarily of the membrane, its porous backing, and the lucite cell body. In this photograph the membrane has been used for a series of studies, and therefore it is coated with a deposit of contaminants which have been removed from the water.

V. FUTURE WORK

The ultrafiltration research studies are expected to increase substantially in volume over the next year. Over the past year three Ph.D. candidates and two M.S. candidates have been associated with the study, and the production to date has been one M.S. thesis. The Ph.D. candidates will begin devoting full time to the ultrafiltration studies upon completion of their doctoral coursework and examinations this year. In addition, two additional Ph.D. candidates will begin their research studies in ultrafiltration of organic contaminants at low pressures during the coming year. One of these, a chemist, has been and will continue to be funded throughout her Ph.D. program by means of an FWPCA Research Training Grant, and the other has been supervising reverse osmosis studies at the Ft. Belvoir Army Research and Development Research Laboratories prior to enrolling for his Ph.D. program in September 1968. It is anticipated that his ultrafiltration studies will be supported by sources other than the FWPCA 01408 Grant. It is anticipated that the five Ph.D. candidates plus several Master candidates continuing research over the next two years will provide an extensive amount of research information on ultrafiltration, concentration polarization problems, development of better membranes and systems, and other facets pertaining to ultrafiltration of organic contaminants at low pressures.

REFERENCES

1) Michaels, A. S., Bixler, H. J., and Hodges, R. J., J. Colloid Sci. 20, 1034 (1965).

2) Merten, U., Ind. Eng. Chem. Fund. 2, 229 (1963).

3) Sherwood, T. K., Brian, P. L. T., and Fisher, R. E., IEC Fund. 6, 2 (1967).

4) Kimura, S., and Sourirajan, S., A. I. Ch. E. J. 13, 497 (1967).

5) Kimura, S., and Sourirajan, S., I. E. C. Proc. Design Development. 7, 41 (1968).

6) Brian, P. L. T., I. E. C. Fund. 4, 439 (1965).

7) Johnson, J. S., and Bennion, D. N., C. E. P. Symposium Series No. 90, 270 (1968).

8) Bennion, D. N., U. C. L. A. Dept. Eng. Rept. No. 66-17 (Mar. 1966).

9) Raridon, R. J., Dresner, L., Kraus, K. A., Desalination. 1, 210 (1966).

10) Nakano, Y. C., Tien, C., Gill, W. N., A. I. Ch. E. J. 13, 1092 (1967).

11) Williams, F. A., Univ. of Calif., San Diego, AMES-QR-220-3 (Sept. 1967).

12) Dresner, L., Oak Ridge Natl. Lab. Report 3621 (May 1964).

13) Berman, A. S., J. Appl. Phys. 24, 1232 (1953).

14) Sherwood, T. K., Brian, P. L. T., Fisher, R. E., M. I. T. Desalination Lab. Report 295-1 (1963).

15) Fisher, R. E., Sherwood, T. K., Brian, P. L. T., M. I. T. Desalination Lab. Report 295-5 (1964).

16) Sherwood, T. K., Brian, P. L. T., Fisher, R. E., and Dresner, L., I. E. C. Fund. 4, 113 (1965).

17) Ramanadhan, K., Gill, W. N., paper presented A. I. Ch. E. meeting Tampa (May 1968).

18) Gill, W. N., Zeh, D. W., Tien, C., I. E. C. Fund. 4, 433 (1965).

19) Gill, W. N., Zeh, D. W., Tien, C., Int. J. Heat Mass. Transf., 9, 907 (1966).

20) Gill, W. N., Tien, C., Zeh, D. W., I. E. C. Fund. 5, 367 (1966).

21) Srinivassan, S., Tien, C., Gill, W. N., Chem. Eng. Sci. 22, 417 (1967).

22) Srinivassan, S., Tien, C., Desalination, 3, 5 (1967).

23) Brian, P. L. T., Ch. 5 in "Desalination by Reverse Osmosis" (Merten editor) M. I. T. Press (1966).

24) Blunk, R., M.S. thesis U. C. L. A. 1964.

25) Merten, U., Nusbaum, I., Miel, R., Gulf General Atomics Report GA 8744.

26) AWWA, WPCF, and APHA, Standard Methods for the Examination of Water and Wastewater, 12th Ed., American Public Health Assoc. Inc., New York (1965).

ACKNOWLEDGMENTS

The authors wish to express their greatful appreciation to Mr. Donald Newton, Donald Tang and Daniel Smola, graduate students in Environmental Engineering at the University of Massachusetts, for their assistance in the preparation of this report and their efforts and interest in making these studies possible.

A special word of thanks is extended to Mrs. R. Irene Clarke for her skill and patience in preparing the manuscript.

APPENDIX

UMASS FAST FORTRAN PROGRAM FOR ULTRAFILTRATION DATA ANALYSIS

```
010 PROGRAM REVOS
015 PRINT 20
021 INPUT,INS
022 NYES-3HYES
023 NO=2HNO
024 IF( INS.EQ.NYES )26,25
025 IF( INS.EQ.NO ) 51,20
026 PRINT 27
027 FORMAT(*ENTER DATA AS FOLLOWS*)
028 PRINT 29
029 FORMAT(*N,F,ST,DLRES,DLCEL,MW,IT*)
030 PRINT 31
031 FORMAT(*WHERE*)
032 PRINT33
033 FORMAT(*N=THE NUMBER OF SAMPLING PERIODS PER RUN*)
034 PRINT 35
035 FORMAT(*F=THE FACTOR FOR CONVERTING COD TO MG/LITER*)
036 PRINT 37
037 FORMAT(*ST=THE NUMBER OF ML. NEEDED TO STANDARDIZE TITRANT*)
038 PRINT 39
039 FORMAT(*DLRES AND DLCEL=THE DILUTION RATIOS FOR THE RESERVOIR
040A AND THE CELLS*)
041 PRINT 42
042 FORMAT(*MW=THE MOLECULAR WEIGHT OF THE SOLUTE*)
043 PRINT 44
044 FORMAT(*IT=THE TIME INTERVAL BETWEEN SAMPLES*)
045 PRINT 46
046 FORMAT(*THEN ENTER THE FOLLOWING FOR EACH TIME INTERVAL*)
047 PRINT 48
048 FORMAT(*RES,LC,MC,RC:.WHERE THESE ARE THE DIFFERENCES IN ML.TITRANT
049A BETWEEN*)
050 PRINT 51
051 FORMAT(*THE BLANK AND THE SAMPLES FROM EACH CELL AND THE RESERVOIR*)
```

```
052 DIMENSION COD(30,4),CONC(30,4), SEPAR(30,3), PCNT(30,3)
053 II=1
054 READ,NUMB
055 READ, TEMP,PRES,FLOW
060 READ,N,F,ST,DLRES,DLCEL,MW,IT
062 ITM=0
065 CODF=2.5*400.0/ST
070 DO 507 I=1,N
075 READ,RES,XLC,XMC,RC
080 COD(I,1)=CODF*DLRES*RES
085 COD(1,2)=CODF*DLCEL*XLC
090 COD*I,3)=CODF*DLCEL*XMC
095 COD(I,4)=CODF*DLCEL*RC
100 CONC(I,1)=F*COD(I,1)
105 CONC(I,2)=F*COD(I,2)
110 CONC(I,3)=F*COD(I,3)
115 CONC(I,4)=F*COD(I,4)
135 SEPAR(I,1)=CONC(I,1)/CONC(I,2)
140 SEPAR(I,2)=CONC(I,1)/CONC(I,3)
145 SEPAR(I,3)=CONC(I,1)/CONC(I,4)
150 PCNT(I,1)=(CONC(I,1)-CONC(I,2))/CONC(I,1)
155 PCNT(I,2)=(CONC(I,1)-CONC(I,3))/CONC(I,1)
160 PCNT(I,3)=(CONC(I,1)-CONC(I,4))/CONC(I,1)
165 IF(I.GT.1)500,170
170 IF(MW.EQ.198)215,175
175 IF(MW.EQ.342)230,180
180 IF(MW.EQ.595)245,185
185 IF(MW.EQ.10000)260,190
190 IF(MW.EQ.20000)275,200
200 IF(MW.EQ.40000)290,205
205 IF(MW.EQ.70000)305,210
210 IF(MW.EQ.110000)320,215
215 PRINT220
220 FORMAT(*RESULTS OF GLUCOSE RUN*//)
```

```
225 GO TO 400
230 PRINT 235
235 FORMAT(*RESULTS OF SUCROSE RUN*//)
240 GO TO 400
245 PRINT 250
250 FORMAT(*RESULTS OF RAFFINOSE RUN*//)
255 GO TO 400
260 PRINT 265
265 FORMAT(*RESULTS OF DEXTRAN 10 RUN*//)
270 GO TO 400
275 PRINT 280
280 FORMAT(*RESULTS OF DEXTRAN 20 RUN*//)
285 GO TO 400
290 PRINT 295
295 FORMAT(*RESULTS OF DEXTRAN 40 RUN*//)
300 GO TO 400
305 PRINT 310
310 FORMAT(*RESULTS OF DEXTRAN 70 RUN*//)
315 GO TO 400
320 PRINT325
325 FORMAT(*RESULTS OF DEXTRAN 110 RUN*//)
400 PRINT 405
405 FORMAT(*NO OF     COD TO     ML. TO          DILUTION*)
410 PRINT 415
415 FORMAT(*SAMPLES   CONC       STANDARDIZE     FACTORS*)
420 PRINT 425
425 FORMAT(*PER RUN   FACTOR     TITRANT         RES     CELL*)
430 PRINT 435,N,F,ST,DLRES,DLCEL
435 FORMAT(15,F11.3,F15.3,F10.1,F9.1//)
440 PRINT 445
445 FORMAT(*MOLECULAR                REVERSE OSMOSIS SYSTEM*)
450 PRINT 455
455 FORMAT(*WEIGHT          TEMP.       FLOW(GPM)      PRES(PSI)*)
460 PRINT 465,MW,TEMP,FLOW,PRES
```

```
465 FORMAT(19,F12.1,F10.1,F15.1//)
470 PRINT 475
475 FORMAT(5X,*CHEMICAL  OXYGEN  DEMAND     SOLUTE    CONCENTRATION*)
480 PRINT 485
485 FORMAT(5X,*RESER  LEFT  MIDDLE   RIGHT  RESER  LEFT   MIDDLE   RIGHT*)
490 PRINT 495
495 FORMAT(*TM  VOIR   CELL   CELL    CELL  VOIR    CELL   CELL     CELL*)
500 PRINT 505,ITM,(COD(I,J),J=1,4),(CONC(I,J),J=1,4)
505 FORMAT(13,F8.1,F6.1,F6.1,F8.1,F8.1,F6.1,F6.1,F8.1)
506 ITM=ITM+IT
507 CONTINUE
508 PRINT 509
509 FORMAT(5X,*-------------------------------------------------*/)
510 PRINT 515
515 FORMAT(5X,*RESERVOIR CONC/CEL CONC                    PCNT REMOVAL*)
520 PRINT525
525 FORMAT(5X,*LEFT     MIDDLE    RIGHT         LEFT       MIDDLE     RIGHT*)
530 PRINT 535
535 FORMAT(*TM  CELL     CELL      CELL         CELL       CELL       CELL*)
536 ITM=0
537 DO 555I=1,N
540 PRINT545,ITM,(SEPAR(I,J),J=1,3),(PCNT(I,J),J=L,3)
545 FORMAT(13,F6.2,F10.2,F10.2,F9.2,F10.2,F9.2)
550 ITM-ITM+IT
555 CONTINUE
556 PRINT 557
557 FORMAT(5X,*-------------------------------------------------*/)
560 IF(NUMB.EQ.II)575,565
565 II=II+1
570 GO TO 60
575 END
580 ENDPROG
```