CHAPTER III

LITERATURE SURVEY

3.1 Reverse Osmosis

In recent years, extensive work has been done, and considerable progress has been made, with respect to the application of the reverse osmosis process for the specific practical problems of water treatment and solution concentration. Several reverse osmosis pilot plants have been designed, built, and operated, and considerable engineering experience is now available on the design, construction, operation, and performance of such plants. In this chapter some of the available experiences on the subject are reviewed from the points of view of practical applications and engineering developements.

3.1.1 Reverse Osmosis for treatment of hard water

Hardness is of special concern in municipal and industrial water supply. Hard water requires much soap before a lather is formed, and hard water deposites sludges or on surfaces with which it comes into contact and in vessels and boilers in which it is heated. The substances responsible are calcium and magnesium ions, and to a lesser extent (becaues of their normally smaller concentrations) those of iron, manganese, strontium, and aluminium. In the operation of boilers, foaming, priming, scale formation, caustic embrittlement and corrosion increase with operating pressure. Foaming and priming entrain moisture and solids in steam. The solids carried over may then be deposited in steam lines, turbines,

and other equipment. The tolerances for hardness (expressed as ppm $CaCO_3$) of water are 80, 40, 10 and 2 for boilers operating in the pressure ranges below 150, 150 to 250, 250 to 400, and over 400 psig respectively.

Therefore the treatment of hard waters to produce boiler feed waters of acceptable quality is an important industrial problem. The application of reverse osmosis for the treatment of hard waters was investigated by Hauck and Sourirajan, and some of their results are presented in Table 3.1 to 3.3 and Figure 3.1.

Table 3.1 gives the results obtained with three films (membranes) $CaCl_2$, $MgCl_2$, and a 1 : 1 mixture of $CaCl_2$ and $MgCl_2$ were used as solutes. Three different initial feed concentrations (300, 500 and 800 ppm expressed as $CaCO_2$) were tested. The hardness and flux of product water were determined corresponing to 90 per cent volume fraction product recoveries. The results showed that product water hardness of 2 ppm or less were botained with film H-1 with an average product rate of 38 gal/day/ft^{2*} at 1,000 psig. Under the same conditions, the hardness of product water obtained ranged from 17 to 45 ppm for film H-2 and 22 to 64 ppm for film H-3 with corresponding average product rates of 43.6 and 49.2 gal/day/ft^2.

Table 3.2 illustrates the performance of film H-4 for the separation of iron, manganses, strontium and aluminium irons present in low concentrations. The data show that the technique can be successfully applied for such separations.

*Units use in this chapter are those use in the original published data.

Data of Hauck and Sourirajan (1969)

Film no.	System	Feed water hardness (ppm $CaCO_3$)	Product water	
			Hardness (ppm $CaCO_3$)	Product rate (gal/day/ft²)
H-1	$CaCl_2$-H_2O	302	2	38.6
	$CaCl_2$-H_2O	498	2	42.3
	$CaCl_2$-H_2O	782	2	41.4
	$MgCl_2$-H_2O	315	<1	41.1
	$MgCl_2$-H_2O	516	<1	37.4
	$MgCl_2$-H_2O	800	2	36.1
	($CaCl_2$ + $MgCl_2$)-H_2O	300	<1	34.2
	($CaCl_2$ + $MgCl_2$)-H_2O	495	<1	36.7
	($CaCl_2$ + $MgCl_2$)-H_2O	807	<1	35.1
H-2	$CaCl_2$-H_2O	302	17	42.8
	$CaCl_2$-H_2O	504	21	42.8
	$CaCl_2$-H_2O	806	26	42.6
	$MgCl_2$-H_2O	315	24	49.2
	$MgCl_2$-H_2O	509	36	43.7
	$MgCl_2$-H_2O	829	45	41.5
	($CaCl_2$ + $MgCl_2$)-H_2O	304	19	43.5
	($CaCl_2$ + $MgCl_2$)-H_2O	504	28	43.8
	($CaCl_2$ + $MgCl_2$)-H_2O	805	41	42.6
H-3	$CaCl_2$-H_2O	301	28	45.2
	$CaCl_2$-H_2O	508	42	50.4
	$CaCl_2$-H_2O	802	64	51.2
	$MgCl_2$-H_2O	302	29	51.6
	$MgCl_2$-H_2O	505	43	51.7
	$MgCl_2$-H_2O	806	60	47.3
	($CaCl_2$ + $MgCl_2$)-H_2O	289	22	51.9
	($CaCl_2$ + $MgCl_2$)-H_2O	498	36	50.0
	($CaCl_2$ + $MgCl_2$)-H_2O	812	52	43.5

Operating pressure: 1000 psig
Product recovery: 90%

Table 3.2 Separation of iron, manganese, strontium and aluminium ions in aqueous solution

Data of Hauck and Sourirajan (1969)

System	Solute concentration in feed (ppm)	Product water	
		Solute concentration (ppm)	Product rate (gal/day/ft²)
$FeCl_3$-H_2O	795	40	19.0
$MnSO_4$-H_2O	500	<1	25.7
$SrCl_2$-H_2O	485	17	23.7
$AlCl_3$-H_2O	503	11	26.9

Film No.: H-4
Operating pressure: 1000 psig
Product recovery: 90%

Table 3.3 illustrates the performance of films H-1 and H-2 for softening some natural hard waters obtained from different sources.

Figure 3.1 Shows the effect of pressure on the quality and flux of product water with a feed whose hardness was 500 ppm. Since solute separation generally decreases with decrease in operating pressure, data of this type determine the minimum operating pressure necessary for specific applications. The results showed that film H-1 could give product water hardness of 2 ppm or less in the entire pressure range 200 to 1,000 psig tested.

Data of Hauck and Sourirajan (1969)

Film no.	Source of feed water	Feed water hardness (ppm $CaCO_3$)	Product Water	
			Hardness (ppm $CaCO_3$)	Product rate (gal/day/ft^2)
H-1	Coalinga, Calif.	843	<1	26.5
H-1	Webster, S. D.	610	<1	28.6
H-1	Roswell, N. M.	641	4	29.6
H-1	San Diego, Calif.	340	2	30.4
H-1	Indianapolis, Ind.	247	4	30.0
H-2	Coalinga, Calif.	843	12	40.1
H-2	Webster, S. D.	610	5	43.2
H-2	Roswell, N. M.	641	14	42.9
H-2	San Diego, Calif.	340	7	45.1
H-2	Indianapolis, Ind.	247	11	45.0

Operating pressure: 1000 psig
Product recovery: 90%

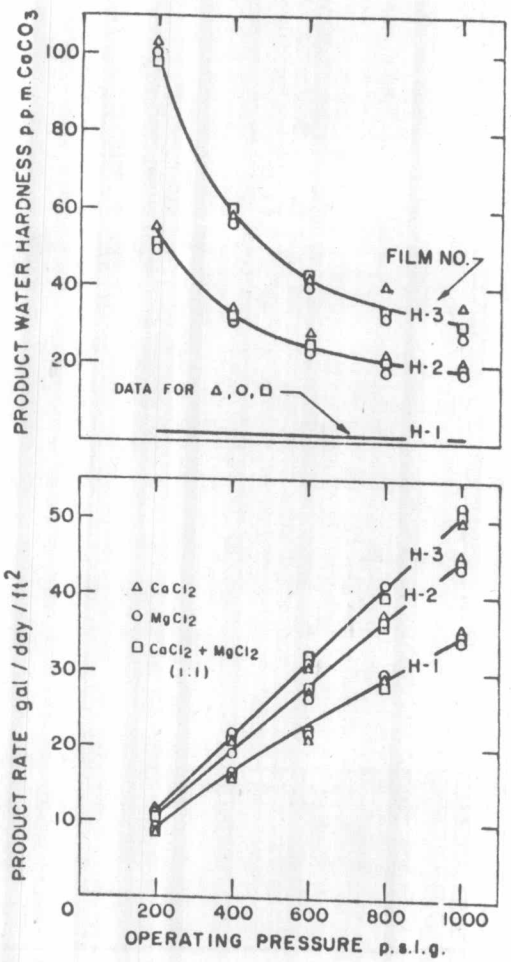


Figure 3.1 Effect of pressure on membrane performance for reverse osmosis water softening. Data of Hauck and Sourirajan (1969).

Film type: CA-NRC-18; feed concentration: 500 ppm; product recovery: 75%.

3.1.2 Reverse osmosis for production of ultrapure water[1]

The developement of new industries in the electronics, semiconductor, and nuclear areas, and the expansion of many old industries such as the pharmaceutical, utility and electrochemical fields have created a demand for large quantities of ultrapure water. A leading contributor to the field of production of ultrapure water is the electrical power industry. The use of boilers operating at or close to critical pressure is on the increase. Typical specifications for feed water quality for subcritical boilers (operating at 1,800 to 2,400 psig) and supercritical boilers (operating at pressure above 3,200 psig) are respectively 0.5 and 0.05 ppm total dissolved solids (Calman and Kingsbury, 1966). Production of such ultrapure water can be accomplished by repeated application of the reverse osmosis process to the available feed water. This is illustrated by the data of Table 3.4 where the feed was a composite of the product waters obtained from the processed hard water (hardness = 300 to 800 ppm $CaCO_3$). The product water obtained by twice operated reverse osmosis process is suitable as feed for subcritical boilers. An additional reverse osmosis processing of the above water can give water suitable as feed for supercritical boilers. Since the data given in Table 3.1 and 3.4 refer to 90 per cent product recovery and the product rates obtained are sufficiently high (36 gal/day/ft^3 at 1,000 psig), the technique of repeated operation of the reverse osmosis process might prove economical for the production of large quantities of ultrapure water.

Table 3.4 **Results of repeated reverse osmosis operation**
Data of Hauck and Sourirajan (1969)

System	Feed water* hardness (ppm $CaCO_3$)	Product water		
		Recovery (%)	Hardness (ppm $CaCO_3$)	Product rate (gal/day/ft^2)
$CaCl_2$-H_2O	2.25	25	0.125	35.2
$CaCl_2$-H_2O	2.25	50	0.125	35.8
$CaCl_2$-H_2O	2.25	75	0.175	35.2
$CaCl_2$-H_2O	2.54	90	0.225	36.6
$MgCl_2$-H_2O	2.14	25	0.120	35.2
$MgCl_2$-H_2O	2.14	50	0.140	35.7
$MgCl_2$-H_2O	2.14	75	0.140	35.9
$MgCl_2$-H_2O	2.18	90	0.260	36.6

* **Product obtained from a once processed hard water.**

Film no.: H-1
Operating pressure: 1000 psig

3.1.3 Reverse Osmosis for treatment of plating wastes (1)

The waste effluent from metal finishing plants contain numerous toxic constituents (Promisel, 1960). The toxicity limits to fish life with respect to, for example, copper, lead, zinc, and chromium are 0.02, 0.01, 0.2 and 1.0 ppm respectively (Hawksley, 1967). Hence the treatment of plating wastes, especially the dilute wastes, is a serious problem in the metal finishing industry. Since profuse rinsing is a prerequisite of a sound finish, very large quantities of water are involved; and further, some of the waste constituents may be some economic value (Lancy 1955). Consequently, the problem of treatment of plating wastes is important from the points of view of water pollution control, water re-use, and waste recovery. The

data given are for 90 per cent recovery in a single stage reverse osmosis process using 500 ppm of solutes. The actual concentration of solutes in plating wastes is usually much less. Since essentially the same degree of separation can be expected at lower concentrations , more than one reverse osmosis processing may not be necessary in many situations.

In any case, by repeated operation of the process with 90 to 95 per cent recovery in each operation, product water of any desired quality can be obtained along with concentrated solutions suitable for waste recovery.

Table 3.5 **Separation of some salts present in plating wastes**
Data of Hauck and Sourirajan (1969)

System	Solute concentration in feed (ppm)	Product	
		Solute concentration (ppm)	Product rate (gal/day/ft^2)
$ZnSO_4$-H_2O	535	48	20.7
$Pb(CH_3COO)_2$-H_2O	504	32	20.4
$CuSO_4$-H_2O	500	8	19.2
$NiCl_2$-H_2O	500	14	19.2
CrO_3-H_2O	512	22	21.5
$SnCl_2$-H_2O	500	49	20.8
$AgNO_3$-H_2O	500	135	22.6
$Fe(SO_4)_2(NH_4)_2$-H_2O	525	19	20.1
$Ni(SO_4)_2(NH_4)_2$-H_2O	515	22	20.9
$Cr(SO_4)_3$-H_2O	500	9	22.1
$HAuCl_4$-H_2O	500	109	19.1

Film no.: H-4
Operating pressure: 1000 psig
Product recovery: 90%

3.1.4 Reverse Osmosis for treatment of sewage water (1)

The present primary and secondary sewage treatment facilities have as their main objectives the removal of biochemical exygen demand and suspended solids. These treatments are not designed to remove nitrates, phosphates, or the nonbiodegradable surfactants. The removal of the latter would be the objective of tertiary sewage treatment facilities which are not extensive in use today Reverse osmosis can effectively take the place of tertiary treatment, and offer an effective means of upgrading sewage water to a quality practically suitable for all water uses. Some pilot plant results of sewage water treatment by reverse osmosis have been reported, (Bray et al., 1965 ; Sudak and Nusbaum, 1968) and they will be summarised later in this chapter.

Table 3.6 give the results obtained with a typical film and a number of samples of raw sewage water obtained from the Ottawa City primary sewage treatment plant. Experiments were made at two operating pressures, 1,000 and 500 psig, with particular reference to the removal of biochemical oxygen demand, nitrate, phosphate, alkyl benzene sulphonate, and total dissolved solids. The performance of the membrane was found to be very good with respect to the removal of all the above contaminants. The average biochemical oxygen demand removals were 85.8 and 80.8 per cent respectively at 1,000 and 500 psig. Under the conditions of the experiments made, the average separations of nitrates, alkyl benzene sulphonates, and phosphates were 50.3, 93, and > 99 per cent respectively. The average product rates were 32.7 and 18.3 gal/day/ft^2 at 1,000 and

500 psig respectively. The above results indicate that the reverse osmosis process using the Batch 18 type porous cellulose acetate membranes has the potentiality of becoming an economics means of renovation of waste waters.

Table 3.6 **Reverse osmosis for sewage water treatment**
Data of Hauck and Sourirajan (1969).

Solute or Equivalent	Solute concentration in feed (ppm)	Operating pressure (psig)	Product	
			Solute concentration (ppm)	Product rate (gal/day/ft^2)
Biochemical oxygen demand	24	1000	3	29.6
	46	1000	8	35.8
	37	1000	2	38.4
	25	1000	5	31.0
	36	1000	5	28.7
	44	500	15	14.6
	46	500	8	16.2
	24	500	5	19.6
	37	500	7	18.8
	21	500	4	18.4
NO_3^-	0.24	1000	0.1	34.2
	0.50	1000	0.25	34.0
	0.07	1000	0.03	28.7
PO_4^-	2.5	1000	0.01	34.2
	1.8	1000	0.01	34.0
	3.5	1000	0.02	29.7
Alkyl benzene sulphonate	0.7	1000	0.05	29.6
	0.8	1000	0.05	35.8
	0.4	1000	0.02	38.4
	1.2	1000	0.08	31.0
	1.5	1000	0.10	28.7
	1.8	500	0.20	14.6
	0.8	500	0.08	16.2
	1.2	500	0.01	19.6
	1.1	500	0.01	18.8
	1.3	500	0.01	18.4
Total dissolved solids	284	1000	32	29.6
	454	1000	9	35.8
	76	1000	0.1	38.4
	324	1000	9	31.0
	278	1000	7	28.7
	434	500	49	14.6
	385	500	19	16.2
	350	500	30	19.6
	265	500	23	18.8
	294	500	62	18.4

Film no.: H-5
Feed: Raw sewage water
Product recovery: 90%

The separation and product rate data in Table 3.1 to 3.6 do not represent the limits obtainable in the reverse osmosis process. By increasing the mass transfer coefficient on the high-pressure side of the membranes, significantly better performance can be obtained with a given membrane in most cases.

3.1.5 Reverse Osmosis for treatment of waste waters from the pulp and paper industry (1)

The pulp and paper industry is a large user of water. An average size pulp mill producing 150 to 500 tons or cellulose pulp for making paper and allied products may commonly use from 5 to 50 million gallons of water dialy. A large part of this water can be processed by reverse osmosis and reused again the concentrated wastes may be disposed of more economically by conventional methods of evaporation and burning. Therefore the application of reverse osmosis for the treatment of waste waters from the pulp and paper industry in an area of great practical importance from the points of view of waste water treatment, water renovation, and water pollution control. Some limited amount of work has been reported on the subject, a summary of which is given below.

A variety of effluent paper mill waste waters has been tested with reference to this application by Wiley et al (1967). An Ammerlaan et al (1968), using the commercially available reverse osmosis units supplied by Gulf General Atomic and Havens Industry. Some of their results are summarised in Table 3.7

Table 3.7 **Reverse osmosis for treatment of paper mill waste waters**

Data of Wiley et al. (1967)

Sample	Flux (gal/day/ft²)	mg/litre Solids	C.O.D.[2]	Chloride	pH	OD[3]
Process feed[1]		1960	945	430	2.2	8.75
Product Water						
Membrane grade A*	6.1	14	100	36	2.6	0.194
Membrane grade C	7.0	72	132	251	2.2	0.261
Membrane grade B	10.9	822	516	400	2.3	3.63
Concentrated stream						
Membrane grade A*		12,120	6655	3260	2.2	80.4
Membrane grade C		6940	4366	1964	1.9	44.8
Membrane grade B		5160	3405	852	2.2	31.7

* A = Dense; C = Intermediate; B = Coarse

1 First stage sulphite bleach plant effluent
2 Chemical oxygen demand
3 Optical density at 281 millimicrons (a measure of the lignin content)

Reverse osmosis test unit: Gulf General Atomic A, B, and C Modules (Size 4)
Operating pressure: 450 psig
Feed rate: 1.8 gal/min
Product recovery: 80%

Table 3.7 gives the results obtained with the processing of first stage sulphite bleach plant effluent with the three Gulf General Atomic modules. The reductions obtained with the use of the "dense" type A membranes in term of chemical oxygen demand (94 per cent), chlorides (92 per cent) and excellent colour removal between the process feed and product water, as well as the recovery of these components in the concentrate stream, are of significant interest to the pulp and paper industry.

3.1.6 Reverse Osmosis for treatment of whey (1)

After some years of plant operation the first large industrial plant came into operation in May 1972, at the diary Val d'Or at St. Aignan des Guess in France. The plant concentrates 80 to 90 ton whey per day at a concentration ratio of 1 : 4. The average capacity

is 220 l permeate/m^2/20 hr. and experience so far has shown a membrane lifetime of at least 8 months at this capacity. The whey has to be centrifuged in self-cleaning contrifuges and low pressurized. The plant is a batch plant and is cleaned after each 20 hour operation. The BOD of the permeate is 2-400 mg O_2 per litre. Membranes type 985 (DDS) are used. The operating pressure is 25-45 kg/cm^2 using the lower pressure at the start of a batch.

3.1.7 Reverse Osmosis for treatment of skim milk[1]

Several small industrial plants are now in operation for reverse osmosis of skim milk. Although one might expect the main application to be preconcentration before drying, the main application so far has in fact been preconcentration before production of ice cream.

Normally skim milk powder is used for an increase of the fat-free dry substance in ice cream. Instead of this reverse osmosis of skim milk is possible. The advantages are :

1. Better flavour of the ice cream; all "powder" taste is removed.
2. Better texture, allowing reduced fat content to obtain the same quality.
3. Great finance saving.

Each 28 m^2 module can treat 9,000 l skim milk producing 3,900 litre permeate per day.

3.1.8 Reverse Osmosis for treatment of egg white[1]

Several industrial plants for the concentration of egg white are installed. The capacity is approximately 7 tons egg white concentrated to half volume per 20 hour.

A special membrane configuration and special care with the pumping has been found necessary to destruction of the whipping properties.

Egg white powder produced from concentrate has a higher bulk density and better whipping properties than direct spray dried egg white.

3.1.9 Juice concentration by Reverse Osmosis[3]

Concentration of juices using a single RO membrane material cellulose acetate were studied. Apple juice and orange juice were chosen because they illustrate a spectrum of chemical and physical characteristics of fruit juices. The performance of the membrane is correlated with those characteristics. Process measurements were made under ideal conditions in small laboratory channel. Concentrates were prepared in a prototype unit suitable for food use and in commercial unit designed for water purification.

For purpose of the Reverse Osmosis process, a fruit juice can be considered to be a rather complex aqueous solution or suspension of sugar, acids, flavoring, and pectic substances. The sugars, both hexoses and disaccharides, and the organic acids are

the major contributors to the osmotic pressure of the juice. Concentrating solutions of sugars and most organic solids by Reverse Osmosis can be done easily with high permeation rates and excellent solute retention with existing membrane.

Apple juice was pressed from crushed Washington Red Delicious apples using a rack and cloth cider press. As pressed; it had the composition shown in Table 3.8 . Orange juice was reamed from California Valencia oranges. Seed and large pulp were removed by passing the juice through an 80 - Mesh screen. This is the only physical pretreatment for experimental concentration.

Table 3.8 Measured properties of the feed juices

Juice	Soluble solids °Brix	Osmotic prressure psi	Sugars,% Total	Sugars,% Reducing	Titratable acid meq/100ml	pH	Pectin %	Viscosity 25°C cp
Red Delicious Apple As pressed	14.4	300	14.0	11.4	1.6	4.5	0.11	1.95
Red Delicious Apple Clarifled	13.9	300	13.0	10.6	1.4	4.4	0.06	1.41
California Valencia Orange	10.5	215	8.1	4.2	12.1	8.3	-	-

The most successful membrane is a cellulose acetate membrane developed by Munjikian and Loeb (Munjikian, 1967). With the doctor blade, a film 0.010 thick is cast on the glass from a solution of cellulose acetate (25 weight percent, Eastman 398-10), acetone (45%) and formanide (30%). After drying for 30 sec.in air at room temperature,

the membrane and glass are immersed in ice water for 1 hour. The membrane is treated for 10 additional min. in water at a prescribed temperature between 25 and 100°C to obtain the desired selectivity.

The finished membrane is about 0.004 in. thick and is mostly a very porous water plasticized gel of cellulose acetate.

For most of the work repeated here, the membrane was supported on a sintered stainless steel surface in a channel depicted schematically in Figure 3.2. The channel was 1 in. wide, 0.1 in. deep and 17 in. long. Feed juice was circulated under pressure pass the membrane. Flow conditions were carefully controlled to minimize the effects of solute build up at the surface of the membrane.

In Figure 3.3 the permeation rate of orange juice was measured at various pressure and concentration. The pressure at which the permeation rate is zero, that is, the intercept on the pressure axis, indicates the osmosis pressure of each feed juice.

Table 3.9 indicates a decrease in the rate coefficient with an increase in the concentration of juice. The decrease is more accurately associated with the higher pressure required at the higher concentrations. Under high pressure the porous sub-structure of the membrane compacts and offers additional resistance to water permeation.

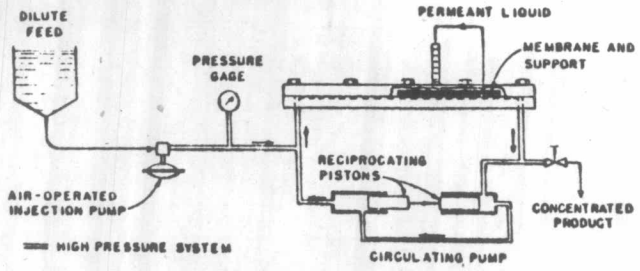


Fig 3.2 Channel and circulation system.

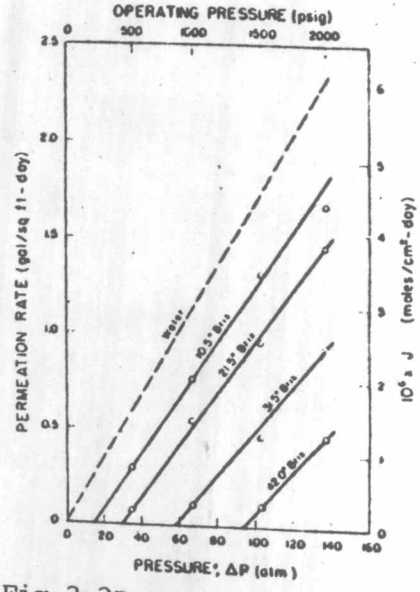


Fig.3.3 Permeation rate through cellulose acetate membrane from orange juice.

Table 3.9 Experimental osmotic pressure and permeation rate coefficients for orange juice and a cellulose acetate membrane.

Orange juice concentration °Brix	Osmotic pressure psia	Permeation rate coefficient, K gal./ft²-day/atm
0 (water)	0	1.66 X 10⁻²
10.5	210 (15 atm.)	1.51
21.5	430 (30 atm.)	1.36
31.5	850 (58 atm.)	1.20
42.0	1370 (93 atm.)	1.08

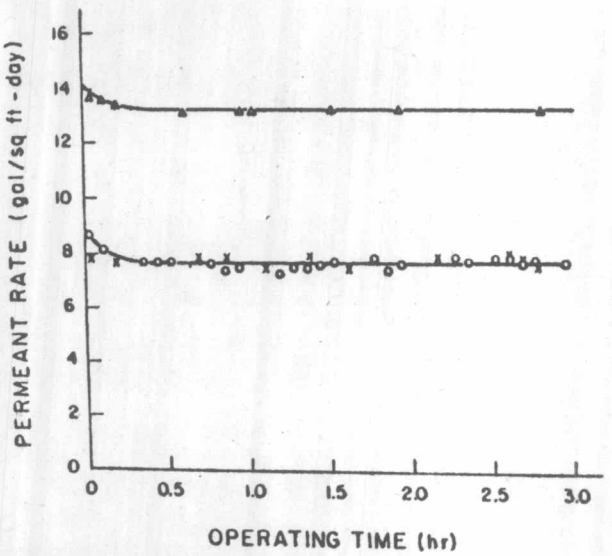


Fig 3.4 Typical permeation rates for a new cellulose acetate membrane, showing the effects of operating time and pectin content of apple juice. Operating pressure was 1,500 psig. The feed was water, Δ; and 14° Brix apple juice as pressed, O, and clarified, X.

In Figure 3.4, typical permeation rates of apple juice are plotted vs time. The feed juice was not allowed to concentrate but was maintained at 14° Brix by rapid circulation. The operating pressure was 1,500 psig. After an initial decrease, the permeation rate appears to remain constant for at least several hours with a rate of about 0.1 gfd/atm.

3.2 Ultrafiltration

Ultrafiltration in particular appeared from the early 70 is a very promising process in a large number of different industrial separation steps in the pharmaceutical and food industry, in the treatment of industrial water containing macromolecules and colloids etc. Large scale industrial applications of ultrafiltration are, however, still in the early stages of development and acceptance, largely because of the slow evolution of high performance, dependable, low cost and long-lived membrane modules suitable for high capacity service.

3.2.1 Ultrafiltration in sewage treatment systems[19]

In 1966 Dorr-Oliver embarked on a development program directed toward the utilization of membranes in complete sewage treatment. Shown sehematically in Figure 3.5 it is comprised of a reactor which is tied into a membrane loop. The reactor is fed with comminuted raw sewage, and contains an activated sludge culture. Mixed liquor is continuously withdrawn from the reactor, and passed over an ultrafiltration membrane, through which the carrying liquid (water) and inorganic salts permeate. The concentrate from the loop is returned to the reactor.

One system of this type, with a capacity of approximately 3,000 gal/day, has been in continuous operation in a small Connecticut industrial plant for more than two years treating sanitary waste.

The process is essentially as indicated in Figure 3.5.

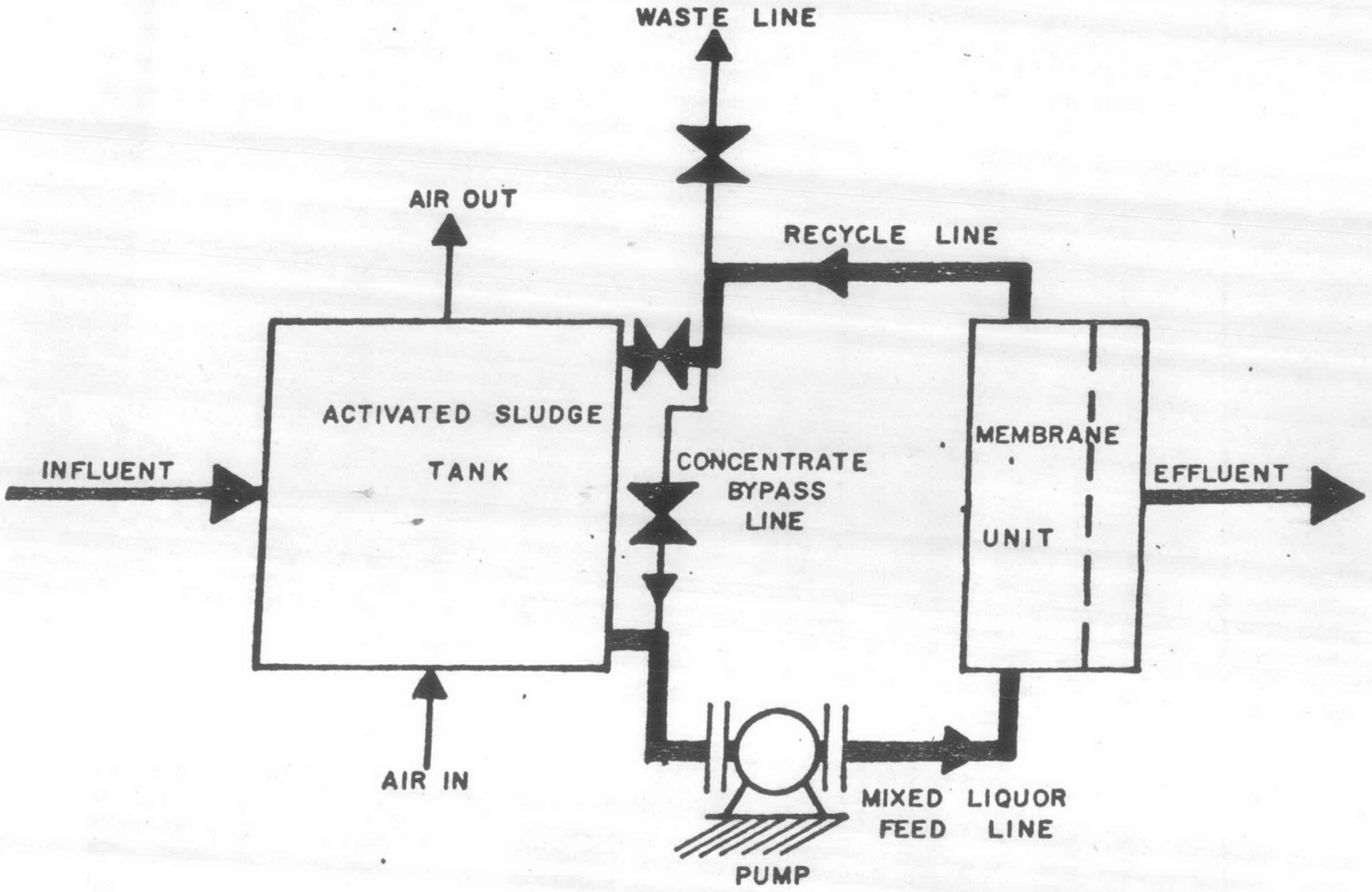
A heat exchanger is also provided for exchanging heat between the incoming raw sewage feed and the effluent. This unit required because of the low temperature (average of 37°F) at which the raw sewage influent is received. A 3,000 gallon reactingvessel operating at atmospheric pressure is provided. Located in the tank are aeration means. At the surface of the tank, spray nozzles are provided for foam control.

Ultrafiltration membranes are arranged in four parallel loops around the reactor. Each loop is comprised of eight modules providing 480 sq. ft of membrane surface per loop. Type APA membranes (Table 3.11) are used.

The unit was operated on the normal plant influent; that is, sanitary sewage and industrial waste. The unit was operated continuously twenty-four hours per day. The feed contained an average of 713 mg/l COD, and an average of 354 mg.l BOD over this period. The ultrafiltrate average 27 mg.l of COD, and less than 1 mg/l BOD. The flux sustained at a value of 12 gal/sq. ft/day, with an average pressure drop across the membranes of 20 psi. The superficial velocity of mixed liquor through the membrane units was 5 ft/sec.

The concentrattion of the activated sludge solids in the reactor gradually increased during the period of the run from 2,200 mg/l to over 5,200 mg/l, when one membrane loop (480 sq. ft.) was used.

In the case where two membrane loops (960 sq.ft) were operated during the period May 4 through May 15, the solids concentration near the end of the run approached 7,600 mg/l.



WASTE TREATMENT FLOW SHEET

FIG. 3.5 SEWAGE TREATMENT

TABLE 3.10

Membrane	Manufacturer	Chemical Type	Water Permeability GFD @ 30psi	Retentivity Solute	MW	%Ret.	Max. T °C
Diaflo UM-05	Amicon	polyelectrolyte	7	sucrose	342	80	50
Diaflo UM-2	Amicon	polyelectrolyte	17	sucrose	342	60	50
Diaflo UM-10	Amicon	polyelectrolyte	50	dextran	10,000	100	50
HFA 200	Abcor	cellulosic	100	dextran	20,000	95	50
Iopor APA	Dorr-Oliver	substituted aromatic polymer	150	polyethylene glycol	16,000	95	80
Iopor XPA	Dorr-Oliver	substituted aromatic polymer	250	pepsin	35,000	95	80
Diaflo PM-30	Amicon	substituted aromatic polymer	290	ovalbumin	45,000	95	120

3.2.2 Ultrafiltration in electropainting [2]

Another recently developed example of the use of ultrafiltration membranes in continuous reaction systems is their application in the electrophoretic painting process.

In the process, metal parts are passed through and completely immersed in a water-base primer. During passage through the tank, d-c voltage is imposed between the metal parts and an anode in the tank causing paint solids to deposit at high density in the metal. The dipping tank can be considered as a chemical reactor in which a complex set of electrochemical and chemical reactions are occuming continuousty. Paint solids, solvent and water are added to the tank, and because solid are being removed from the tank with the metal parts, water and impurities accumulate in the tank. Low pressure ultrafiltration membranes have been applied extensively in this process for the removal of water and impurities from the dip tank on a continuous basis.

More recently this use has been expanded to permit recovery of paint solids and reuse of water in the systems for rinsing adhering paint from the metal part as it leaves the tank. In effect, a countercurrent washing system has been devised which minimizes the use of fresh deionized water to the system, and for all practical purposes eliminates a substantial pollution problem by recovering paint solids normally lost to the sewer. The result is substantial savings in paint solids, and elimination of a serious pollution problem. The flowsheets for the systems are shown in Figure 3.6

The ultrafiltration membranes used in these systems must,

of course, be especially adapted to the resistant of the organic solvents used in electropainting. The molecular weight cut-off of the membranes currently in use is approximately 45,000 (protein). The units are operated at low pressure drops across the membranes in the range of 10-30 psi. Flux level of 6 to 12 gal/sq ft/day can be sustained. Membrane life in the system is approaching one year.

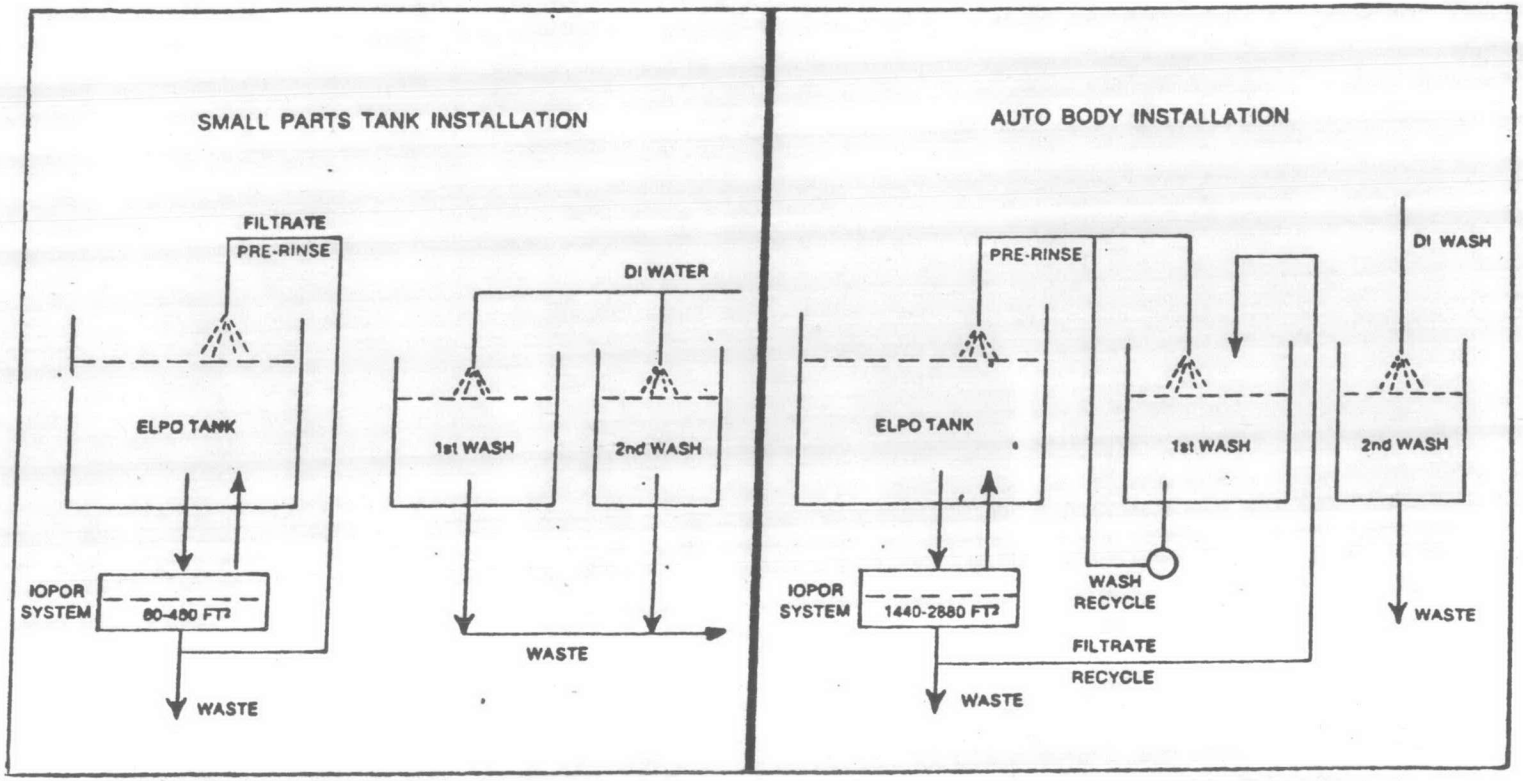


FIG.3.6 ELECTROCOAT FLOWSHEET

3.2.3 Ultrafiltration applications in recovery of protein from cheese whey [8]

Cheese whey is the fluid portion of milk obtained after coagulation of casein during the manufacture of cheese or casein. It contains half of the milk solids most of the lactose, 20% of the protein, and most of the vitamins and minerals. Two gallons of milk (17 pounds) yield one pound of cheese and one pound of whey solids. Table 3.12 compares the composition of the supernatant whey resulting from the cheddar and cottage cheese making processes. Even though 70% of the nutritive value of milk residue in the whey, it is often disposed of as waste.

Recovered whey protein can be used in a number of ways. The large cheese factories sell it as animal feed supplement and as fertilizer. It may also be used in human food products such as bread, processed cheese, sherbet, or candy. It has been found that whey mixed with skimmed milk has a composition remarkably similar to human milk, and is currently being sold as a formula for in fants. The lactose may be recovered as a pharmaceutical; the lactic acid as a food grade acidulant. Whey may also be fermented to produce yeast.

Table 3.12 **Composition of cheese whey showing its food values (*20*)**

Components	From cheddar cheese, %	From cottage cheese, %
Total solids	7.31	6.53
Lactose and lactic acid	5.20	4.39
Protein (amino acid nitrogen)	0.87	0.86
Ash	0.53	0.61
Fat	0.71	0.67

Ultrafiltration has the capability of fractionating the proteins from the unwanted salts, leactic acid, and lactose. For example, analysis in Laboratories has indicated that a PM-10 membrane mill pass all of the solids except for the protein (as expected, some amino acids do pass through the membrane). If disired, a UM-05 membrane may then be used to recover 80% of the lactose.

The "two state" whey processing data are summarized in Table 3.13. It will be noticed that while lactice acid (molecular weight of 90) was partially transmitted throught the second stage membrane, the COD level was still substantially reduced.

Table 3.12 Ultrafiltration of cottage cheese whey (37)

	Feed stream	First-stage permeate	Second-stage permeate
Total solids, %	7.8	6.8	1.8
COD, ppm	65,600	54,100	800
Protein and amino acid N_2, %	0.6	0.15	0.002
Lactose, %	3.9	3.5	0.05
Lactic acid, %	0.52	0.52	0.11

Chain and Selldorff have compared UF processing costs with two-stage vacuum evaporation (see Figure 3.7 and 3.8.). The relative advantage of UF is shown to increase at low capacities, presumably because the modular construction of UF units keeps the equipment costs roughly proportional to size, whereas small evaporators have higher unit costs than larger ones.

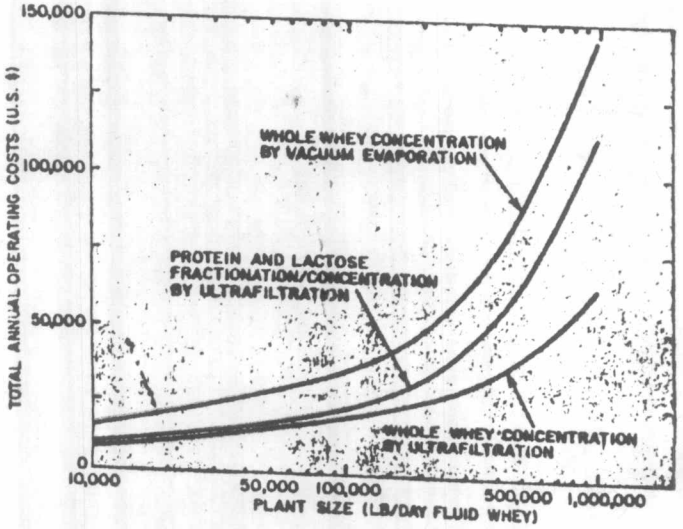


Figure 3.7 Operating costs for concentrating whey by-products

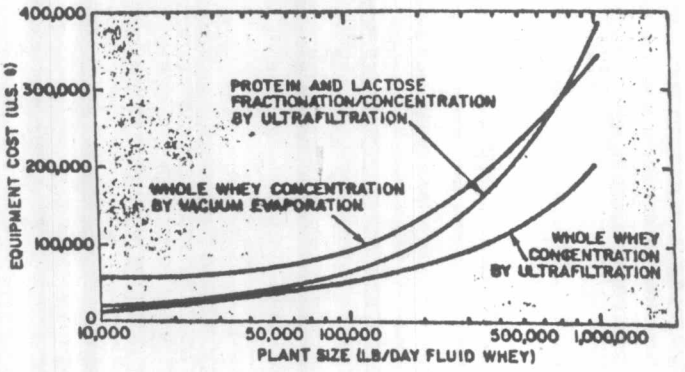


Figure 3.8 Equipment costs for concentrating whey by-products

Typical flux rates for concentration of 6.5% whey in thin channel ultrafiltration equipment with PM-10 membranes are displayed in Figrue 3.9

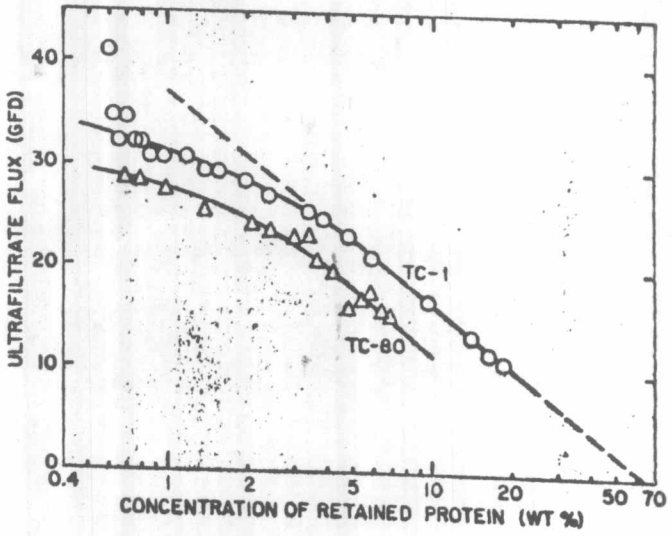


Figure 3.9 Concentration of whey with PM-10 membrane
TC-1: 0.15 sq ft of PM-10 membrane, 30-mil channels, 0.63 GPM recirculation rate at 75°F and 40 psig; TC-80: 9 sq ft of PM-10 membrane, 30-mil channels, 16.75 GPM recirculation rate at 71°F and 40 psig

A PM-10 membrane retained mearly constant flux for 120 hours with both 13% and 26% solids, and without any flushing. Thus, thin channel ultrafiltration appears to be capable of selective fractionation of whey proteins from lactose, lactic acid, and salts at high stable flux rates. The economics for such a process should be more favaorable than anything reported.

3.2.4 Ultrafiltration in concentration of milk[8]

Another important diary process that stands to benefit from the application of UF is the concentration of milk. Three products have found wide consumer acceptance - evaporated milk (some of the water removed), condensed milk (some water removed, some sugar added), and dried milk (all water removed). Evaporation or drum drying tends to caramelize the milk sugars, resulting in a significant change in taste. In addition, heating may denature the milk proteins and destabilize the casein rendering it less dispersible and less soluble.

Ultrafiltration may be used to concentrate the milk proteins alhermally with attendant lower expense. In addition, because of the permeability of UF membranes to salts and lactose, special dictary milks that are salt free and desugared are possible at no extra cost. Other salts may be substituted after concentration, if appropriate. Naturally, UF cannot take the product to dryness, but it can concentrate the solid to 25-50 wt.%, reducing the load on a spray dryer substantially and resulting in a less costly product.

Data representative of thin channel ultrafiltration of skimmed milk proteins are presented in Figure 3.10 Casein represents 80% of the total protein, with the other 20% comprised of lactalbumin and lactoglobulin.

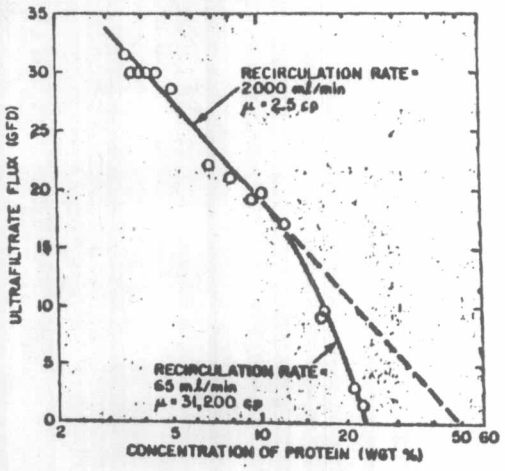


Figure 3.10 Concentration of skim milk proteins with PM-30 membrane (0.15 sq ft) in TC-1 (30-mil channels) at 30 psig

3.2.5 Ultrafiltration in the concentration of egg white (9)

There are two major problems associated with the processing of egg white "browning" and the denaturation of proteins. The use of egg white in the candy and baking industry is predicated on its ability to form foams stable enough to support relatively large quantities of flour and or sugar.

Ultrafiltration is an economical process for concentrating egg albumen while removing glucose, but without denaturation of proteins, browning, or loss of functional propertics of the final

product UF appears to have several advantages over RO for this application.

(1) UF provides a ready means for removing glucose while concentrating protein;

(2) with RO, high concentrations are difficult to achieve because of the exponential increase in osmosis pressure with concentration (70 psi at 12%, several thousand psi at higher concentrations), the permeabiltiy of UF membranes of sugar and salts eliminates any significant osmotic pressure,

(3) there is less danger of damaging the product during depressurization with UF than with RO; the higher pressures attendant in RO mean higher shear forces when releasing the fluid from the high pressure zone to atmospheric pressure.

The data of Figure 3.11 compare flux rates obtained during the concentration of egg albumen with thin channel ultrafiltration and with RO. An initial protein concentration of 10% was selected to correspond to the gross chemical composition of liquid egg white shown in Table 3.14. The PM-30 UF membrane passed everything but the protein, whereas the cellulose acetate membrane (RO) retained some of the glucose and salts as well (final concentrate had 0.5% glucose, 0.23% sodium, 0.20% potassium, 0.30% mg/ml phosphorous, and 0.097 mg/ml of calcium.

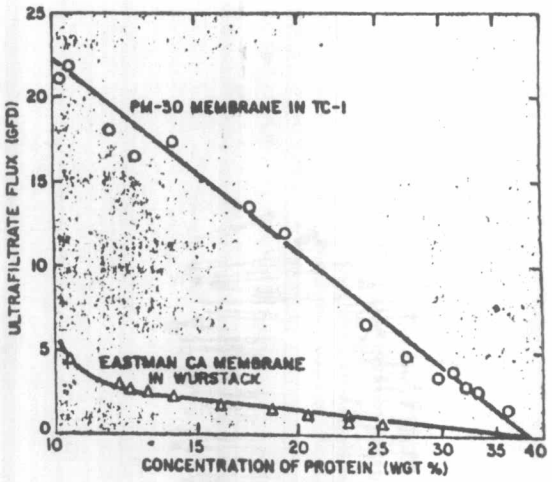


Figure 3.11 Concentration of egg albumen
TC-1, 0.13 sq ft of membrane at 40 psi, recirculating 1,800 ml/min through 30-mil channels; Wurstack data (42) at 900 psi

Table 3.13 Gross chemical composition of liquid egg white

Total solids	12.3%
Protein	10.7%
Free glucose	0.38%
NaCl	0.3%

3.2.6 Ultrafiltration in concentration of gelatin and glue (10)

Gelation is a colloidal protein substance whose principle value depends on its coagulative, protective, and adhesive powers. It swells up and absorbs 5-10 times its weight of water; water containing only 1% of gelation by weight will form a jelly when cold. The industry reconizes three different types of gelatin :

(1) edible;

(2) photographic; and

(3) inedible.

Glue falls into the latter category and may be looked upon as an impure gelatin. All types are derived by hydrolysis of collagen (mol.wt. of 100,000) the white fibres of the connective tissues of the animal body found particularly in the skin (corium), bone (ossein), and tendons. Gelatin is of course a widely consumed food - a popular dessar, easily assimilated, which aids the digestion of other foods by ferming an emulsion with fats and proteins.

Gelatin is manufactured by queous extraction at elevated temperature (60^{o}- 75^{o}C) from calf skin, pigskin, or animal bones. Since the extract contains only 3-15% gelatin, it must be concentrated. A satisfactory edible gelatin contains only 10% moisture and 89.7% protein. Normally, the concentration is carried out in steam evaporators followed by drum dryers; unfortunately, elevated temperatures tend to degrade the product.

In addition, the salts present in crude gelatin tend to degrade the polymer structure; for this reason, ion exchange resins are commonly employed to remove ash. Edible gelatin should contain no more than 0.3% ash.

Ultrafiltration can perform the required concentration at lower temperatures with simultaneous removal of ash. It is of course true that even with UF, elevated temperature (50^{o}C and above) must be used to keep the gelatin solution liquid. Figure 3.12 is

illustrative of the elevated temperature ultrafiltration of gelatin. Normally, for protein solutions, elevated temperatures result in higher flux rates. Although the molecular weight distribution of gelatin extends all the way from 500 to 100,000, its colloidal nature ensures virtually complete retention by a PM-30 membrane (ultrafiltrate from a 10% gelatin solution contained only 0.273% gelatin). Therefore , ultrafiltration has the capability of producing a higher quality product at lower cost, replacing evaporation and ion exchange.

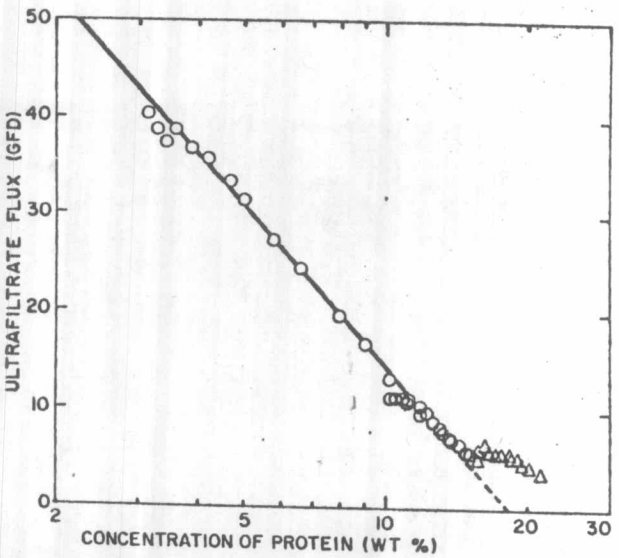


Figure 3.12 Concentration of gelatin with PM-30 membrane in TC-1 at 70°C
0.13 sq ft of membrane, 30-mil channels, recirculation rate of 1,600 ml/min

3.2.7 Ultrafiltration in treatment of animal blood (10)

Animal blood is a valuable protein source that can be used in food for human consumption and for pharmaceutical products, but it must be collected and processed hygienically.

Blood is a complex solution which consists of two main fractions :

(1) Plasma liquid, which is honey coloured and contains proteins (70%) and salts (15%)

(2) Corpuscles, which contain the red and white cells of the blood (94% protein)

If the albumin/globulin fraction of blood can be isolated from hemoglobin, other cellular protein, sugars, and salts, it can be used for human and animal consumption. Although standard procedures for isolating protein from blood by chemical selective precipitative processes are available, they are complicated and costly.

In the present process, thin channel ultrafiltration is used to concentrate and desalt the blood plasma protein and the globin protein fractions. After significant dewatering by UF, spray drying or vacuum drying removes the remaining moisture to produce a white, nonhydroscopic, free flowing powder containing 50% protein and resembling powdered milk.

Concentration of plasma proteins is a straight forward application of UF. Figure 3.13-3.15 are typical data for ultrafiltration of human blood, human plasma, and bovine serum. It has been established that the UM-10 and PM-30 membranes are completely retentive for blood proteins, while completely permeable to known blood toxins like inulin of urea.

Of greater interest to the application is the effect of protein concentration on UF flux rates in human and bovine plasma

shown in Figure 3.14-3.15. It is of course true that a considerable amount of salt is removed in the process of concentration. The fact that UF purifies as it concentrates avoids the problem of concentrating salts along with the proteins, thus avoiding possible protein denaturating. Based on these data, it appears that UF can do the job cheaply and effectively, and that the process is amenable to economic large-scale production.

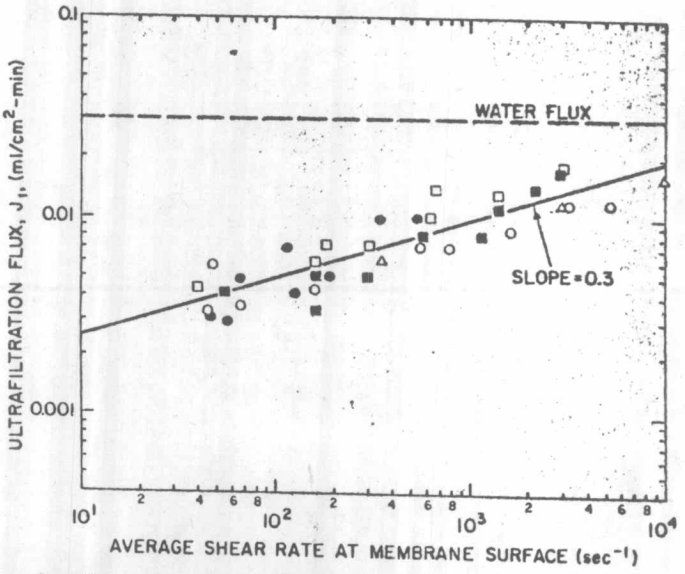


Fig.3.13 Effect of fluid shear rate on ultrafiltration rate
Whole blood and plasma, UM-10 membrane, ΔP = 10 psi; Esmond cell, L = 13 cm. O, whole plasma, 35 mils; ●, whole blood, 35 mils; □, whole plasma, 17 mils; ■, whole blood, 17 mils; △, whole plasma, 5 mils

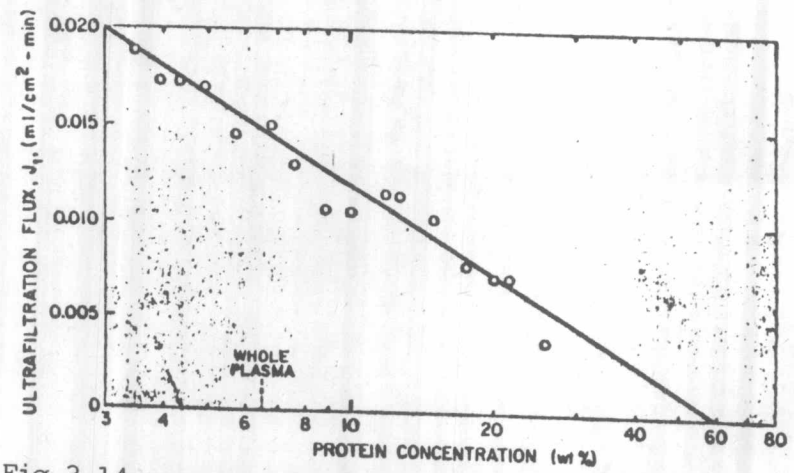


Fig.3.14 Effect of concentration on the ultrafiltration rates of human blood plasma in a thin channel, laminar flow, recirculating system UM-10 membrane, ΔP = 10 psi; ca. 8-mil channels; Esmond cell

In addition to concentration of the protein fractions, UF may also be used to separate the red cells from the blood plasma. Although centrifugation is commonly employed, the convenience and low cost of UF in the separation of red cells from blood plasma may well make this process more attractive than centrifugation. The data of Figure 3.16 show UF flux data for a 0.6 micron Diapor microporous filter as a function of channel velocity in a single pass thin-channel operation.

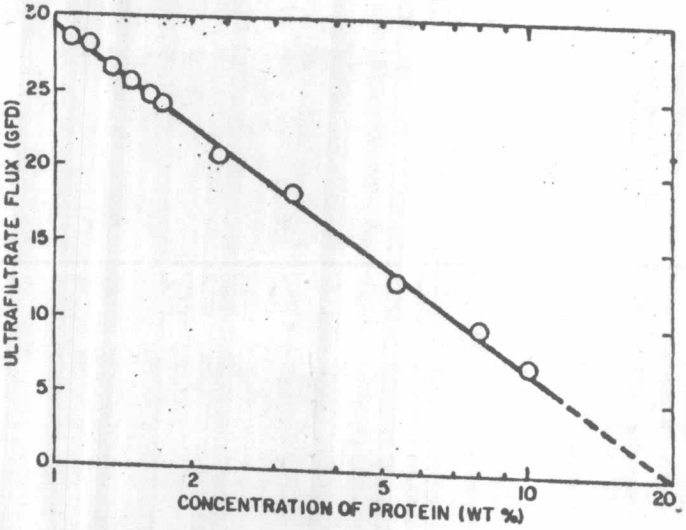


Fig.3.15 Concentration of bovine serum in TC-20 with PM-30 membrane
Two sq ft, 10-mil channels, recirculation rate of 3,000 ml/min

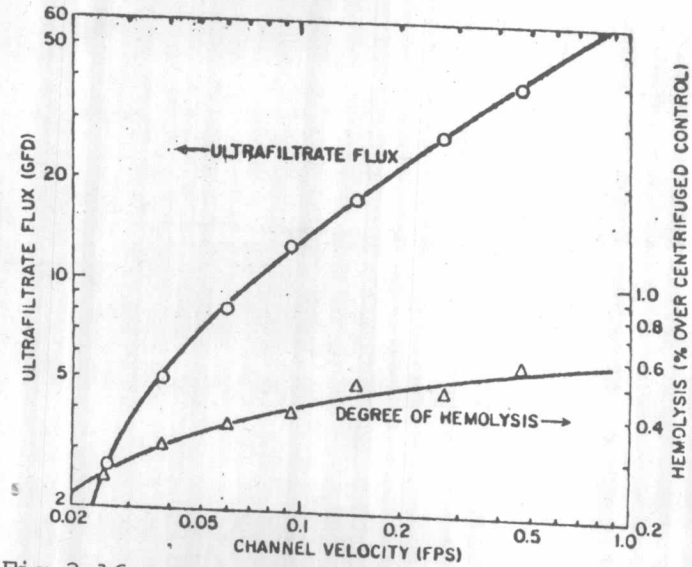


Fig.3.16 Separation of whole blood into red cells and plasma with diapor 0.6 μ filter
Hematocrit of 41%, ACD anticoagulated; 9-mil channels

3.2.8 Ultrafiltration in sugar processing[10]

Although UF cannot be used to concentrate or purify sucrose without appreciable losses, there are significant areas for application in modern sugar refineries.

Beet or cane sugar extracts contain, in addition to sucrose, objectionable amounts of polysaccharides, lignins, proteins, starches, gums, and other colloidal impurities that contribute color or taste to the crystalline product and reduce the protein yield. Raw sugar juice has a pH of 6, and in order to avoid inversion during evaporation of water the juice must be neutralized. As a consequence of neutralization and heating, some proteins and other colloidal material precipitate and contaminate the suclose during crystallization. These impurities result in a poor strike of sugar crystals (low product yield) and connot be washed off the crystals with the molasses (mother liquor). Thus, impure sucrose crystals are formed with a substantial amount of the remaining in the molasses. "Defecation" be accomplished by chemical precipitation processes along with fitration or sedimentation, but only at considerable cost and limited efficiency. UF offers a more attractive alternative.

Dorr-Oliver, as early as 1966, demonstrated that UF of raw sugar juice yields a clear, colloid-free filtrate from which sucrose can be directly crystallized in high yield and purity. The work can be done on the very first production scale membrane (about 60 square feet) made by Dorr-Oliver.

Thus, UF has potential for improving yields and purity of sucrose, it is also possible that recovered by product protein would be saleable.

Sugar processing applications for UF may also extend to the recovery of xylose (wood sugar) from spent pulping liquors. Recent federal action against cyclamate sweeteners could open a market for xylose since it is sweet but low in calories. Ultrafiltration membranes can remove the lignins, gums, and other colloidal material present in pulp mill wastes while passing xylose (molecular weight of 150) and other low nolecular weight materials.