Membranes for reverse osmosis desalination by direct casting on porous supports
by Donald Gong-Jong Wang

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:
Reverse osmosis stands out as the one method attracting the most world-wide attention for the desalination of saline water. It is a technically feasible process with high thermodynamic efficiency, flexibility and simplicity.

Cellulose acetate membranes have the most satisfactory desalinized water flux and most adequate desalination ability so far. Unfortunately, the hydrolysis of the acetate group in the cellulose acetate causes a short membrane life problem, This is the major problem at the current stage of development. It was believed that the membranes cast directly onto porous supports could reduce the high labor cost of membrane replacement as a shorter time and simpler procedure would be required to replace the membrane.

The purpose of this research was to investigate the membranes fabricated by direct casting onto porous supports. This is one of the most effective methods of attacking the membrane life problem indirectly by reducing the membrane replacement cost and to attack the membrane life problem directly by preventing the mechanical failures. The membranes were tested in test cells. Salt water under pressure was circulated through the cells on the upper side; product water was withdrawn on the other side. Enough circulation was maintained to reduce polarization effect.

Eighteen different kinds of porous materials were tested and two-hundred and eighty-four runs were made. Two simple practical fabrication techniques were developed. Also the process variables and the relationships of each variable as concerned with membrane fabrication by direct casting were determined. The optimum fabrication conditions for 1% NaC1 feed concentration were found.

Membranes cast from dilute cellulose acetate-acetone binary solution need the support structure similar to the cellulose acetate. Under the standard test conditions of this research, membranes cast on cellulose and cellulose triacetate porous materials gave a range of water flux from 3.1 to 8.15 gal/ft2 day and salt rejection from 91.8 to 82.5%• The difficulties of improving the membrane performance by this technique are discussed.

Membranes cast from acetone-formamide-cellulose acetate ternary solution on rigid porous epoxy supports showed definite promise. By using the standard test conditions of this study, the membranes gave an average water flux of 21 gal/ft2 day with 95% salt rejection while certain commercial membranes under the same test conditions can only give an average water flux of 11 gal/ft2 day with 95% salt rejection. Also, membranes showed an excellent reproducibility. The reasons for its high performance are discussed.

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ABSTRACT

Reverse osmosis stands out as the one method attracting the most world-wide attention for the desalination of saline water. It is a technically feasible process with high thermodynamic efficiency, flexibility and simplicity.

Cellulose acetate membranes have the most satisfactory desalinized water flux and most adequate desalination ability so far. Unfortunately, the hydrolysis of the acetate group in the cellulose acetate causes a short membrane life problem. This is the major problem at the current stage of development. It was believed that the membranes cast directly onto porous supports could reduce the high labor cost of membrane replacement as a shorter time and simpler procedure would be required to replace the membrane.

The purpose of this research was to investigate the membranes fabricated by direct casting onto porous supports. This is one of the most effective methods of attacking the membrane life problem indirectly by reducing the membrane replacement cost and to attack the membrane life problem directly by preventing the mechanical failures. The membranes were tested in test cells. Salt water under pressure was circulated through the cells on the upper side; product water was withdrawn on the other side. Enough circulation was maintained to reduce polarization effect.

Eighteen different kinds of porous materials were tested and two-hundred and eighty-four runs were made. Two simple practical fabrication techniques were developed. Also the process variables and the relationships of each variable as concerned with membrane fabrication by direct casting were determined. The optimum fabrication conditions for 1% NaCl feed concentration were found.

Membranes cast from dilute cellulose acetate-acetone binary solution need the support structure similar to the cellulose acetate. Under the standard test conditions of this research, membranes cast on cellulose and cellulose triacetate porous materials gave a range of water flux from 3.1 to 8.15 gal/ft^2 day and salt rejection from 91.8 to 82.5%. The difficulties of improving the membrane performance by this technique are discussed.

Membranes cast from acetone-formamide-cellulose acetate ternary solution on rigid porous epoxy supports showed definite promise. By using the standard test conditions of this study, the membranes gave an average water flux of 21 gal/ft^2 day with 95% salt rejection while certain commercial membranes under the same test conditions can only give an average water flux of 11 gal/ft^2 day with 95% salt rejection. Also, membranes showed an excellent reproducibility. The reasons for its high performance are discussed.

INTRODUCTION

In 1952, when the United States began its formal desalting program, thermal distillation was the only one of nature's approaches which had been transformed into a well-established desalting technique. Recently, a variety of processes, such as: multistage flash distillation, long-tube vertical distillation, electrodialysis, reverse osmosis, etc., are being developed and perfected for the conversion of saline water. Reverse osmosis is one of these processes and stands out as the one attracting the most world-wide attention among desalting enthusiasts.

The basic principles underlying reverse osmosis have been understood for decades, and considerable work was done in the early part of this century with membranes that showed some ability to differentiate between water and dissolved salts. No effort was directed at developing reverse osmosis for the desalination of saline water until shortly after the federal desalination program was established. In early 1957 Breton[3] reported that cellulose acetate film can be applied as a semipermeable membrane for sodium chloride solution and showed that reverse osmosis is a technically feasible process.

The principle of reverse osmosis is relatively simple. For example, when a sodium chloride solution is separated from water by a semipermeable membrane as in osmosis, water will flow through the membrane into the solution, as in Figure 1(a), until it reaches the osmotic equilibrium of that solution. At equilibrium, there is no net flow of water through the membrane, as in Figure 1(b). However if we apply an external pressure

which is greater than osmotic pressure (for example, a solution containing 1% NaCl has approximately 115 psi. osmotic pressure) the flow will be reversed, as in Figure 1(c). Since the membrane is impermeable to the salt, pure water is obtained from the saline solution. This is the principle of the reverse osmosis desalination process.

There are three factors which make this process appealing. First, in the view point of thermodynamics study, this process can be operated near the minimum work of separation. It was reported by Reid[16] that the minimum energy requirement for producing 1000 gallons of water from sea water is only 2.63 Kw-Hr. Second, the process is not highly dependent on large scale plants to make it economical and small installations could be expected to produce water at a cost only slightly higher than large ones. Therefore, plant size is more flexible. Third, the process can be operated at ambient temperature, corrosion problems are less critical than distillation processes and insulation cost may be eliminated.

In 1957 Breton[3] reported that cellulose acetate acts as semi-permeable membrane for sodium chloride solutions. Reid, Trautmann[19,23] and other workers have tried a wide variety of other materials, including almost all types of existing high polymers (polystyrene, polyethylene, nylon, cellophane, cellulose acetate-butyrate,[9] cellulose propionate,[8] ethyl cellulose, etc.). Also many other new membrane materials are being and have been tested. Graphitic oxide membrane,[6] porous glass membrane,[7] and copolymer systems based on galactose methacrylate[21] are examples of new membrane types. However, none of the materials tried

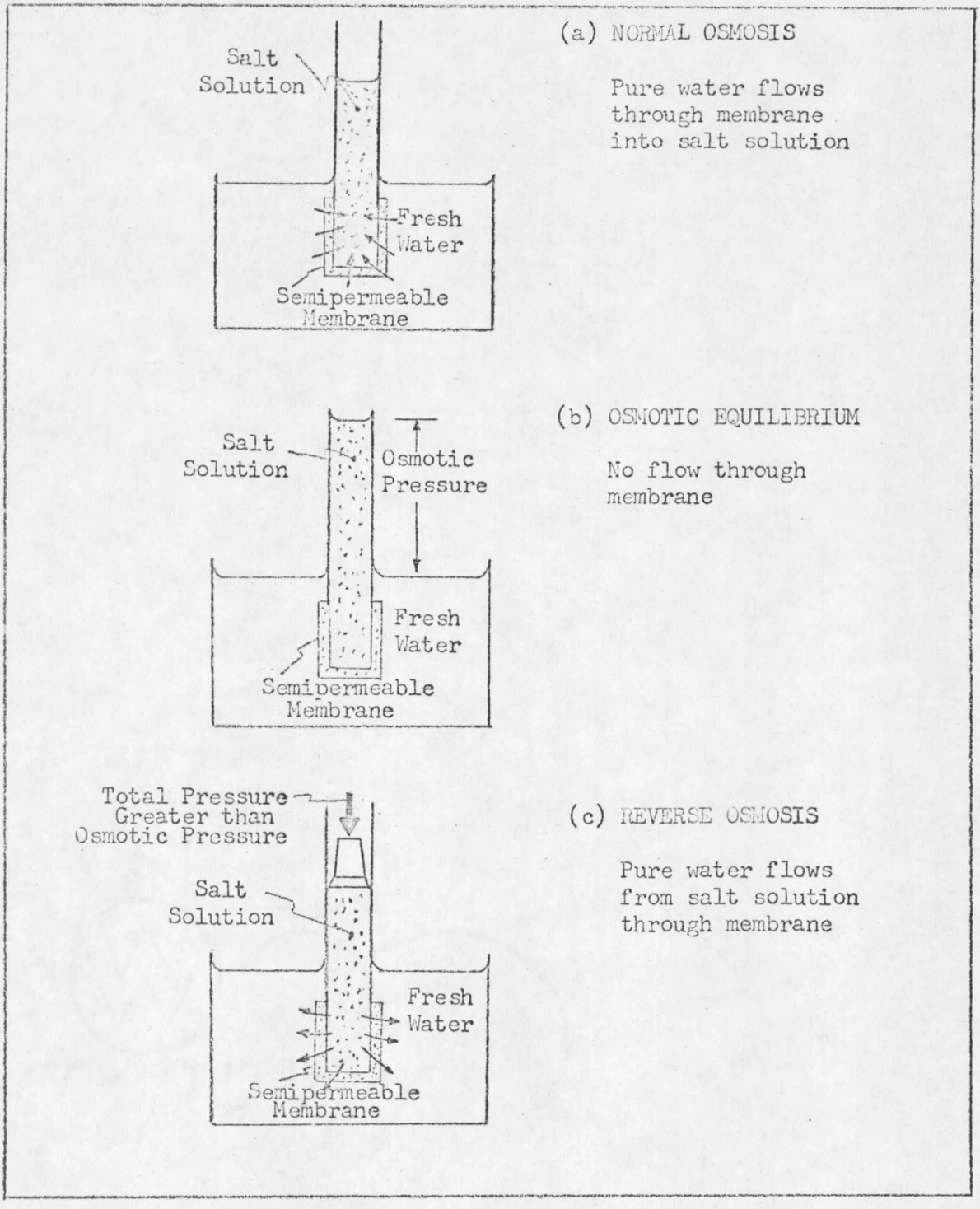

Figure 1. Osmosis Phenomena

have shown as much promise as cellulose acetate.

Reid and Breton,[18] Lonsdale, Merten and Riley,[12] have shown that salt rejection increases and water flux decreases as the degree of acetylation of cellulose acetate is increased. By the proper selection of acetyl content, casting solution composition, fabrication technique, heat treatment and casting conditions, cellulose acetate membranes can be applied for the conversion of saline water.

An early hypothesis proposed by Breton[3] stated that membrane desalination could be explained on the basis of flow through the membrane by two parallel mechanisms. Both water and salt are transported by "hole-type diffusion" with no desalination occurring. In addition, water alone is transported by "alignment-type diffusion". Sourirajan[22] proposed another hypothesis and explained that desalination occurs because of a thin film of pure water at the liquid-membrane interface and depends on the properties of interface. For pores with a diameter less than twice the thickness of the film, only water will flow. For larger pores both pure water and saline water will be transferred. On the basis of these experimentally based criteria, Blunk[2] postulated the following mechanism for the passage or rejection of aqueous solutes by the membrane: "Water is retained in the osmotic-skin part of the membrane in such a way that it still possesses the solubilizing properties attributable to its hydrogen-bonding capacity but has largely lost the solubilizing properties attributable to its high dielectric constant. Therefore small species whose solubilities in water are due partially

(hydrogen-bonding univalent ions) or wholly (nonelectrolytes) to their hydrogen-bonding capacities, tend to pass through the membrane. On the other hand, small species whose water solubilities are due primarily to the high dielectric constant of water tend to be rejected. These species include nonhydrogen-bonding univalent ions, and all ions of valence greater than unity regardless of hydrogen-bonding characteristics."[2]

One of the serious problems with cellulose acetate membranes is the low rate of water transmission through them. Reid and Breton[18] obtained a maximum membrane constant of 8.2×10^{-7} g/cm^2·sec·atm (.945 GSFD* at 800 psi) and a salt reduction factor** of 25 (96% salt rejection***) for a membrane six microns thick, cast from acetone solution. Mahon[13] attacked the low flux problem indirectly by making very fine tubes of cellulose triacetate to increase surface area per unit volume which can give a membrane constant, 5×10^{-8} g/cm^2·sec·atm (.0575 GSFD at 800 psi) and a salt reduction factor between 100 and 25 (99%-95% salt rejection) for 10 microns wall thickness of the fine tubes. Based on his reported flux of 7×10^{-7} g/cm^{2}sec, each cubic foot would produce 200 gallons per day. Loeb and Sourirajan[11] attempted to increase the flux through the shrinking of commercially available cellulose acetate membranes in hot water. They obtained a membrane constant of 1.1×10^{-6} g/cm^2·sec·atm,

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*GSFD: gal/ft^2 day.

**Salt reduction factor: 100/(100-percent salt rejection).

***Percent salt rejection: 100x[(feed conc.-product conc.)/feed conc.]

(1.265 GSFD at 800 psi) and a salt reduction factor of 100 (99% salt rejection) for a membrane 100 microns thick.

As a result of experience gained with this porous cellulose acetate membrane shrinking technique, Loeb and Sourirajan initiated the development of high-flux semipermeable membranes. They encountered an article by Mlle. Dobry[5] in which she suggested the use of saturated aqueous magnesium perchlorate as a solvent for cellulose acetate in the preparation of ultrafiltration membranes. They developed the first casting solutions containing electrolytes. The typical casting solution is a quaternary mixture of cellulose acetate - magnesium perchlorate - water-acetone in the proportion 22.2 - 1.1 - 10.0 - 66.7 wt %. They got the best results with a membrane constant of 4.7×10^{-6} $g/cm^2 \cdot sec \cdot atm$ (5.4 GSFD at 800 psi and 10.2 GSFD at 1500 psi) and a salt reduction factor of 105 (99.8% salt rejection) for a membrane 250 microns thick. To obtain this performance, they found it is necessary to control rigidly the composition of the casting solution, the sequence and timing of the various steps of the membrane preparation and the temperature of the casting solution between $-5^{\circ}C$ to $-10^{\circ}C$. "The sensitivity of the membrane to seemingly insignificant factors in its preparation is one of the most striking aspects of this problem."[1] Using casting solutions which contained nonelectrolytes, Manjikian, Loeb and McCutchan[14] described a number of useful membrane casting solutions. In these, the number of components may be four, three or even two. Of the composition tested, the ternary mixture cellulose acetate-formamide-acetone, was

found to be the most useful. Membranes made from this mixture are equal to or better than those fabricated from casting solution containing electrolytes, and are simpler to produce. Today this type of cellulose acetate membrane has been increasingly developed and perfected for the conversion of both sea water and brackish water.

Unfortunately the hydrolysis of acetate group of this high polymer causes a most serious problem -- short membrane life as reported by Reid, Breton[18] and Vos.[24] The decrease of both water flux and salt rejection as a function of operation time forces one to replace the membrane after a certain period of time and increases the over-all cost of this process. It has been reported that the labor cost of membrane replacement would be much higher than the cost of membrane itself. It is thought that by directly casting the membranes on porous supports, one can eliminate many of these problems.

The purpose of the author's research is to investigate a membrane which can cut down the high labor cost of membrane replacement and can increase the dependability, reproducibility and durability of the membrane itself. The over-all objectives of the research work are: (1) to devlop the fabrication methods for membranes by direct casting; (2) to determine the process variables and the relationship of each variable as concerned with membrane fabrication by direct casting onto porous supports; and (3) to optimize the conditions of fabrication that will produce the highest quality reverse osmosis desalination membranes which can be easily handled.

The structure of high flux membranes containing electrolytes or non-electrolytes has been examined by Riley, Gardner, and Merten[25] using electron microscope techniques. They found that the membrane consists of a fine-pored matrix with a very thin dense layer (active layer) of cellulose acetate on the surface identifiable as the air-dried surface. For an original formulation of Loeb and Sourirajan[11] membrane, the dense surface layer (active layer) was estimated from the electron micrographs to be about .2 - .25 microns thick when the total membrane thickness was about 100 microns; the porous sub-structure was estimated to have a pore size on the order of .1 - .4 microns. The dense surface layer thickness would be a strong function of membrane fabrication conditions and a function of total membrane thickness. Furthermore, they indicated that the resistance to both flow of water and salt is in the dense surface layer.

The polarization effect due to concentration build-up on the membrane-brine interface for a high flux membrane has a significant effect on membrane performance. The concentration build-up in the boundary layer increases the salt flux due to the high concentration gradient and decreases the water flux because of effective applied pressure is reduced. In the case of turbulent flow, if we assume that the boundary layer is idealized as a thin film and eddy motion is negligible, a simplest model for the concentration boundary layer -- film-theory model may be applied. The film-theory model contains a number of simplifying assumptions known to be incorrect, but the effect of these assumptions upon the film-theory

predictions on the significance of the variables are rather small. For this thin film model, Brian[16] gave the following equation to describe the salt concentration build-up at the membrane surface in terms of the permeation flux, the fluid mechanical parameter, and the Schmidt number N_{sc} for salt diffusion:

$$\frac{C_2'}{C_2^b} = \frac{\exp\left[\left(\frac{v'}{j_D \bar{U}}\right) N_{sc}^{2/3}\right]}{r + (1-r)\exp\left[\left(\frac{v'}{j_D \bar{U}}\right) N_{sc}^{2/3}\right]}$$

where C_2' = salt concentration at membrane interface, g/cm^3

C_2^b = salt concentration in bulk solution, g/cm^3

v' = product water flow velocity through the membrane, cm/sec

j_D = Chilton-Coburn mass transfer j-factor

N_{sc} = Schmidt number for salt diffusion; kinematic visosity of solution, cm^2/sec/molecular-diffusion coefficient in salt, cm^2/sec

$\bar{U}$ = average velocity over the cell, cm/sec

r = salt rejection.

For high salt rejection membrane $r \doteq$ unity, the above equation can be simplified to:

$$\frac{C_2'}{C_2^b} = \exp\left[\left(\frac{v'}{j_D \bar{U}}\right) N_{sc}^{2/3}\right]$$

The above equation shows that the concentration build-up in the boundary layer is a strong function of desalinized water flux and feed flow velocity, even if the bulk solution concentration is nearly unchanged. The high flux membrane with a low feed flow velocity will usually cause a serious polarization effect.

EQUIPMENT AND PROCEDURE

Test Cell

The test cell shown on Figure A1 was used for testing all reverse osmosis desalination membranes. Four identical cells were used. The test cells were made of stainless steel 304 blank flanges with 4.5" outside diameter and a 2" diameter test area. The membrane was mounted between the two halves of the cell, and salt water under pressure was circulated through the upper half. With the cone shape of the upper half surface, as shown on Figure A1, an even flow distribution across the test cell was obtained. This was studied by placing a glass plate over the test cell and injecting potassium permanganate solution into the incoming water stream. The concentration of potassium permanganate (indicated by color intensity) as it flowed across the cell showed that the flow distribution was quite good with no short-circuiting or stagnation areas.

The membrane was supported by a 1/8-inch porous stainless steel plate (Grade H, pore size 5 microns, Pall Corp.). A 4.5" OD x 2" ID x 1/16" Neoprene rubber gasket was used between the membrane and the high pressure side of the cell. The two halves were held together by eight 5/16-inch stainless steel bolts, which were tightened stepwise to a perfect seal.

Membrane Test System and Flow Diagram

The test system consisted of the four test cells, a pre-filter and a filter (5 microns), two parallel test lines which could be operated at the same time or independently and a plastic feed tank with a heater, stirrer, cooler and a thermo-probe connected to a temperature controller. The whole system was constructed of stainless steel and plastic to eliminate the corrosion problem. Circulation of salt water through the upper half of the test cells was provided by a stainless steel pump (Jaeco Model 753 S-8).

The flow diagram as used in typical runs with a 5 microns filter at high pressure side is shown on Figure A2. The pressure of one back pressure regulator was kept at 1200 psi and the other was kept at 800 psi. In this way, one test line merely served as a safety device. In many runs to avoid the leakage of the filter, the back pressure regulators were both kept at same pressure and the filter was connected at low pressure side of one of the two lines. The feed tank could be maintained as clean as when the filter was connected at high pressure side.

The pressure on the system was controlled by a regulator on the nitrogen cylinder and measured by a pressure gauge near the inlet of test cell. The product was withdrawn from the cell under its own pressure through a 1/4-inch Swagelok male connector and returned to the feed tank except when samples were taken. The product was collected in a graduated cylinder when sampling. After taking salt concentration measurements the product water was returned to the tank to maintain the feed concentration

constant at 10,000 ppm. sodium chloride.

In order to get meaningful data on desalination membranes, it is necessary to take account of the possible effects of liquid boundary layers on the membrane-salt water interface and to control the temperature in the test cell. A maximum feed flow rate 11.4 ml/sec was used. The average volume of the test cells was 8.3 ml., so that the feed in the cell was replaced every .73 seconds and the average feed flow velocity across the cell was 7.0 cm/sec. The temperature in the feed tank containing 10,000 ml. 1% NaCl, was controlled at 24.5 ± .2°C by an electronic temperature controller and the salt water in test cell was about 25 ± .5°C. The temperature increase between tank and test cell was due to pumping and flow conditions. The operating pressure was 800 ± 35 psi in most runs unless otherwise specified.

Membrane Fabrication Equipment

A level glass surface table with the dimension of 12" x 11" was used for membrane casting. This was used to produce even membrane thicknesses. A constant temperature and humidity chamber was used for membrane casting after run No. TS-44. The chamber was constructed with a fiber glass body, a safety glass window (10½" x 32") in front of the chamber, and two 6" diameter rubber plate covered working holes on the front chamber door (40" x 10"). The chamber contains lights, a heater, cooler, fan, two salt solution containers and a thermoprobe connected to an electronic temperature controller. In the most cases, the temperature

was kept at 24.5 ± .2°C by temperature controller and humidity was kept at about 50% humidity by using saturated $Ca(NO_3)_2 \cdot 4H_2O$ salt solution. Several 7" long and 3/8" diameter glass rods were used for spreading the casting solution. Vacuum insulated containers and stainless steel beakers were used for membrane heat treatments and gelations.

Membrane Test Procedure

After fabrication the membranes were immersed in distilled water overnight and allowed to equilibrate in distilled water. A membrane with a 3-1/16" diameter was cut from a water absorbed membrane. This was larger than the stainless porous support (2-3/4" diameter) to eliminate possible leakage. The membrane was then firmly mounted in the test cell.

After the test cell was assembled, the system was filled with about 10,000 ml. of salt water. The salt water feed was made of reagent grade sodium chloride dissolved in distilled water. For most runs a 10,000 ppm sodium chloride solution was used. After the temperature of the feed reached 24.5°C in the tank, the pump was started and the pressure on the system was raised stepwise (usually 50 psi steps) at intervals of one-minute until the selected operating pressure was reached. This was usually 800 psi. At intervals thereafter the feed flow velocity was checked and adjusted to 11.4 ml/sec, the temperature and pressure were recorded, and the collected product water was analyzed. The feed concentration was also checked and maintained constant. The change in

feed concentration during a run was seldom more than 1% and never more than 2%.

Salt Water Analysis

The analysis of the salt water and product water was done by electrical conductivity measurements of the solutions. A conductivity bridge (Industrial Instruments Model RC-16 B2) was used in conjunction with a conductivity cell requiring a sample of about 1.0 ml. The resistance readings at a given concentration were reproducible, so the concentration of both feed and product were converted from the reading of resistance by using the calibration curve presented in Figure A3. On this figure, a concentration range .001 to .32 moles/liter versus resistance at 23, 25, and 27°C were plotted. The data are shown on Table I. Within the range of interest, the relationship between concentration and resistance can be approximately expressed as:

$$C_t = \frac{6.4 - (t - 25.) \times .1}{(R_t)^{1.0496}}$$

where C_t = salt water concentration, Moles/Liter.

t = temperature of conductivity measurement, °C.

R_t = resistance at temperature t, Ohms.

RESULTS

Two hundred and eighty-four runs were made and eighteen different kinds of porous support were tested. The work was done mainly involving two phases: (1) Membranes cast on porous materials with dilute cellulose acetate-acetone casting solution; (2) Membranes cast on porous materials with cellulose acetate-formamide-acetone ternary casting solution.

MEMBRANES CAST ON POROUS MATERIALS WITH DILUTE CASTING SOLUTION

Porous Supports

Eighteen different kinds of commercially available porous supports such as: cellulose, nylon, cellulose triacetate, filter paper, glass fiber, poly-vinyl chloride, fluorinated vinyl, epoxy, teflon, (as shown on Table II) etc., were tested. Only cellulose and cellulose triacetate showed promise. Filter paper is a cheap porous material and is relatively easy to handle. However, its poorly defined pore size may cause reproducibility problems and its durability is poor. Epoxy porous support is also a most promising porous material candidate. This support can not be wetted by water using the usual procedures, and the surface roughness may cause some other difficulties concerned with membrane fabrication by using dilute casting solutions. Hence, no further attempts were made to cast membranes onto this support with dilute casting solutions.

Membrane Fabrication Technique

The membrane fabrication technique used for this phase was that of applying a thin layer of cellulose acetate (E398-10,3) -acetone (mass ratio = 3:100) casting solution onto a predampened porous support. The water filling the pores of the dampened support serves a two-fold purpose. First it prevents the casting solution from flowing into the porous supports. Second it forms a high porosity structure on the bottom part of casting film. By this technique, it appeared that a higher casting solution viscosity on a smaller pore size supports was easier to cast. The results for membranes cast on cellulose (Gelman, ∝-6 .45 microns; ∝-8 .2 microns) and cellulose triacetate (Gelman, GA-10 .05 microns) are summarized in Table III.

Results and Results Analysis

Twelve runs were made by using membranes cast on cellulose and cellulose triacetate porous supports with dilute casting solution. The results are shown on Table III. Membranes cast on cellulose porous materials gave a highest salt rejection of 90.6% with 4.14 GSFD water flux and a highest water flux of 7.12 GSFD with 82.5% salt rejection. Membranes cast on cellulose triacetate porous materials gave a highest salt rejection of 91.8% with 3.1 GSFD water flux and a highest water flux of 8.15 GSFD with 84.5% salt rejection.

The results from examination of many porous supports had indicated the need for a support structure similar to the cellulose acetate.

However, the series of membranes listed in Table III were fabricated under a set of standard conditions and still show a lack of reproducicility. Much of this comes from difficulty in controlling the water content and water distribution in the dampened support. Since the membranes were not very promising, the use of dilute acetone-cellulose acetate solutions on porous supports was discontinued in 1967.

If a new fabrication technique or a perfect pore filling agent is found the results may be improved. The membranes cast directly on flexible porous supports can not cut down the labor cost and can not decrease the time of membrane replacement. It can only slightly prevent mechanical failures of the membrane. However, the short membrane life which is mostly caused by the hydrolysis of the acetate group of cellulose acetate and only partially caused by mechanical deformation cannot be improved to any great extent by direct casting on supports. In other words, the membranes cast on flexible porous supports are worth developing only under the condition that a new high polymer having a long membrane life is found.

The results which were obtained were similar to Riley and Lonsdale's[20] recent reverse osmosis results for cellulose-triacetate coated Millipore VFWP filter supports and better than their osmosis results for cross-limked E398-10 cellulose acetate thin films with porous CN/CA supports cast on the thin film.

MEMBRANES CAST ON POROUS MATERIALS WITH TERNARY CASTING SOLUTIONS

Casting Solutions and Porous Supports

Casting solutions were made of formamide, Fisher certified reagent grade, Fisher Scientific Company; acetone, reagent grade, Fisher Scientific Company; and cellulose acetate of different grades such as: E394-45, E394-60, E398-3, E398-10, E400-25, Eastman Chemical Products, Inc. The mass ratio of acetone to formamide was kept constant at 1.5:1.0. Manjikian, White and Allen[15] reported that aging of the casting solution for acetone-cellulose acetate-formamide ternary solution has no detectable effect. Therefore, the aging of casting solution in this research was kept as constant, 24 hours. Three different kinds of commercially available porous supports were tested: epoxy (Versapor 6429, .9 microns, Gelman), cellulose (α-6, .45 microns, Gelman), and S.S. 316 porous plate (Grade H, 5 microns, Pall Corp.). The water fluxes and percent salt rejections of membranes cast on these three different porous materials are shown on Table IV.

Preliminary Tests

Forty-four runs were made for preliminary tests. The water fluxes and salt rejections are shown on Table IV. A wide variety of process variables were used. Several methods of heat treatment were tried as follows: (1) immerse membrane and glass plate or porous S.S. 316 plate in hot water and maintain at a predetermined temperature for a

certain period of time by heating; (2) set membrane in test cell and maintain at a predetermined temperature for a certain period of time by heating in hot water; (3) immerse membrane and glass plate or Porous S.S. 316 plate in an insulated container having a constant volume of hot water at a predetermined temperature for a certain period of time; (4) immerse membrane and glass plate or Porous S.S. 316 plate in hot water at a certain temperature and let it cool down gradually; and (5) pump hot water through the test cell. Methods (4) and (5) were unsatisfactory because it was difficult to precisely maintain the heat treatment time and temperature. Only the first three methods showed promise. An examination of the results shows that the heat treatment temperature and time are most important and only minor variations in performance with changes in percent cellulose acetate, solvent evaporation time, and grades of cellulose acetate. Since the casting was done without temperature and humidity control for preliminary tests, an analysis of these effects was not attempted. But it was believed that there are several process variables, such as: heat treatment time and temperature, solvent evaporating time, gelation temperature, grades of cellulose acetate, casting solution composition, etc. Also, from the preliminary tests, results showed that the rigid epoxy porous support was the best. This porous support is easiest to work with (easy to maintain an even thickness of casting solution layer, easy to cast, no expansion and shrinkage during gelation and heat treatment). Also, this support is most inexpensive and the most promising for further

application in a commercial desalination unit.

For the further studies of each process variable, most membranes were cast directly onto Versapor 6429, Gelman (Epoxy, .9 microns pore size).

Membrane Fabrication Technique

The technique used for most of this phase was that of applying a layer of cellulose acetate, acetone and formamide ternary solution onto a porous support under various conditions. The casting procedures were: (1) set the porous support on a flat glass plate; (2) use one layer of masking tape to maintain a clearance of about .005 ± .001"; (3) use a glass rod to spread casting solution onto the support, Versapor 6429, Gelman (Epoxy, .9 micron), unless otherwise specified; (4) let the solvent partly evaporate; and (5) gelation in cold water or ice water for an hour. The casting and solvent evaporation environment for the membranes was at 24.5 ± .2°C and approximately 50% humidity.

Heat Treatment Methods

The several methods of heat treatment used in this phase were: (1) immerse membrane and glass plate in hot water and maintain at a predetermined temperature for a certain period of time by heating; (2) set membrane in test cell and maintain at a predetermined temperature for a certain period of time by heating in hot water; (3) immerse membrane and glass plate in an insulated container having a constant volume of hot

water at a predetermined temperature for a certain period of time.

Type of Cellulose Acetate Effect

Five different grades of cellulose acetate, with the range of viscosities 3 - 60 sec. and percent acetyl content 39.4 - 39.9%, such as: E394-45, E394-60, E398-3, E398-10, E400-24, Eastman Chemical Company, Inc., were studied. Twelve membranes were tested for a period of 45 hours. The membranes were fabricated under the following conditions: cast on Versapor 6429, Gelman (Epoxy, .9 microns); casting solution composition, cellulose acetate 21.9%, formamide 31.2%, acetone 46.9%; casting environment, 24.5°C, 50% humidity; solvent evaporating time, 25 sec.; gelation, 4-5°C, 1 hour in water; heat treatment, 85\83°C*, 5 min. by using heat treatment method (3).

The results are shown on Table V and Figures 2, 3, and 4. There are no correlations between water flux and percent acetyl content or water flux and viscosity, as shown on Figure 2. Also there are no correlations between salt rejection and percent acetyl content or salt rejection and viscosity, as shown on Figure 3. This may be due to the test range of percent acetyl content is too small and the viscosity of each grade of cellulose acetate is different. The higher viscosity as well as higher

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*85\83°C: The initial temperature in an insulated container was 85°C, and at the end of heat treatment the temperature in container was 83°C.

acetyl content gives a higher melting point. Under the same heat treatment conditions, the higher melting point cellulose acetate membrane may have higher porosity and thinner active layer and thus gives lower salt rejection but higher water flux. On the other hand, the higher acetyl content cellulose acetate gives higher salt rejection but lower water flux. Hence, there are difficulties in finding correlations. Also, under the same test conditions for a test period of 45 hours, the results did not show any difference in the slope of each curve, as shown in Figures 2 and 3, which indicates no difference in membrane life with respect to each different grade of cellulose acetate. This is because the difference of membrane performance within a small range of acetyl content would be very small which may be less than the experimental error.

The overall results, a plot of salt flux factor* versus water flux, GSFD, in Figure 4 showed that E400-25 and E394-60 would be better than other grades cellulose acetate (E394-45, E398-3, E398-10) when using the above fabrication conditions. As can be seen, the points of E400-25 are closer to the lower-right corner on this plot which indicates that E400-25 has higher salt rejection and higher water flux performance. If we consider the effect of both melting point and acetyl content on the membrane performance, the obtained results, as shown on Figure 4, are

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*Salt Flux Factor: 1 - (% salt rejection/100).

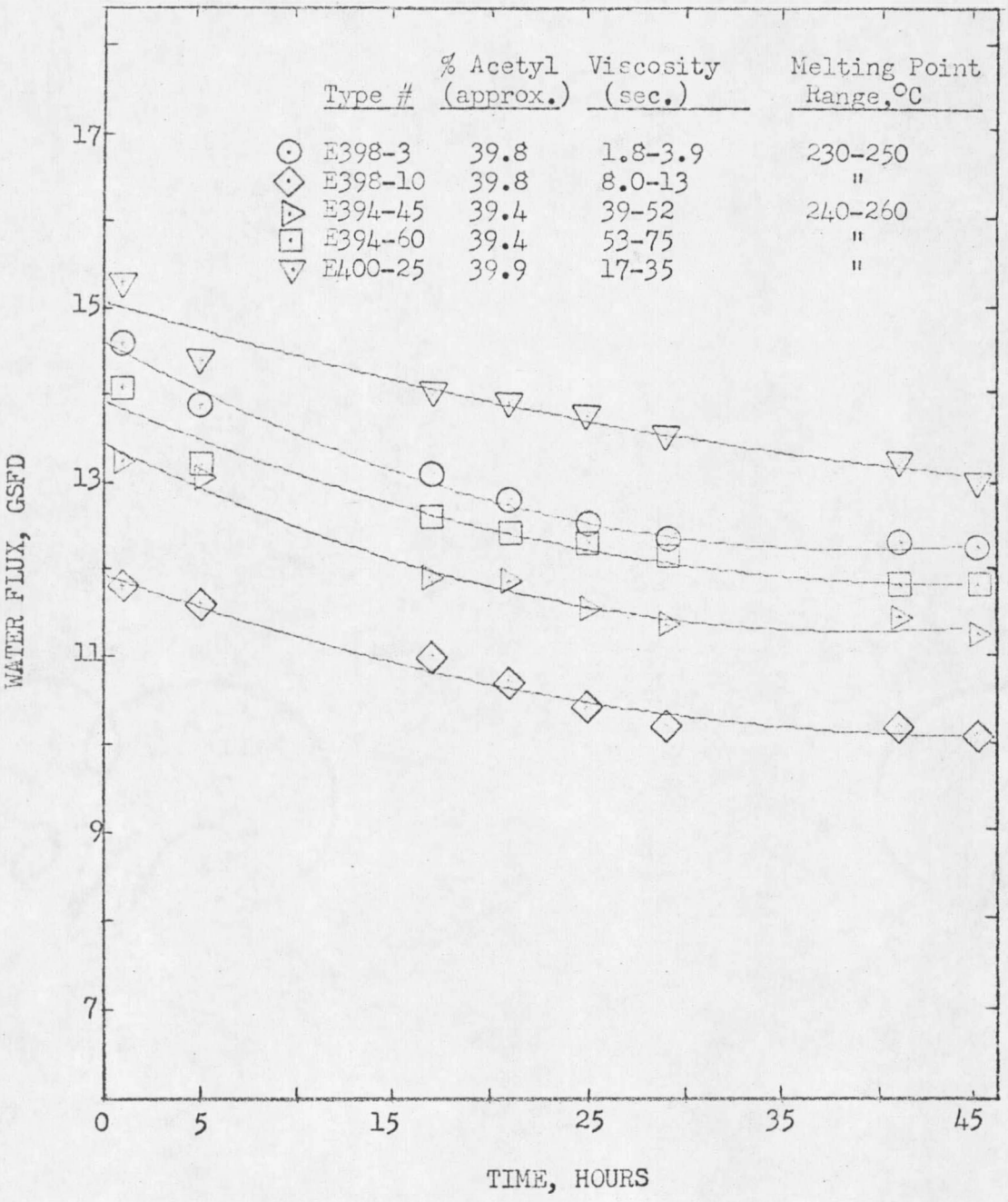

Figure 2. Effect of Type of Cellulose Acetate on Water Flux

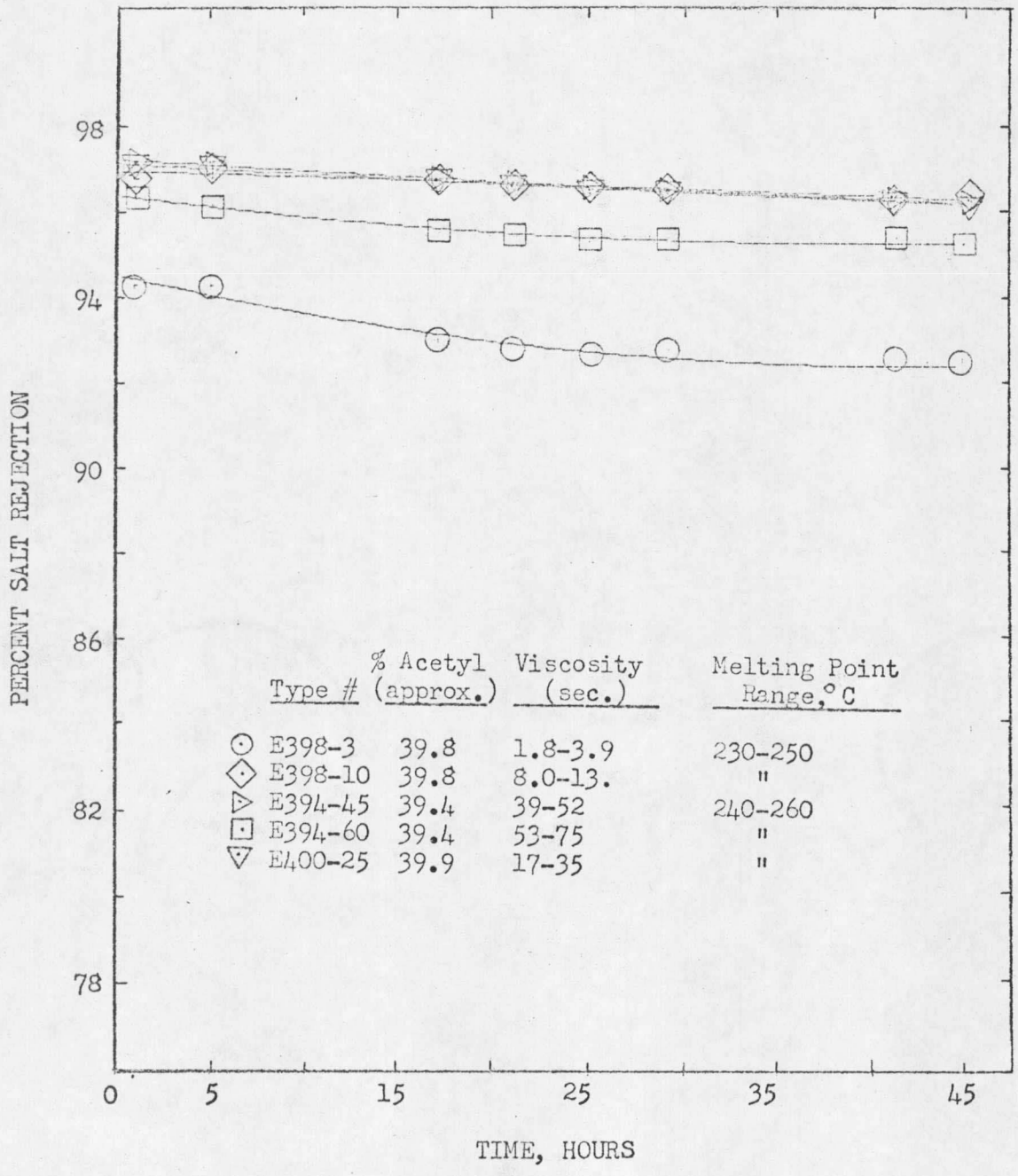

Figure 3. Effect of Type of Cellulose Acetate on Salt Rejection

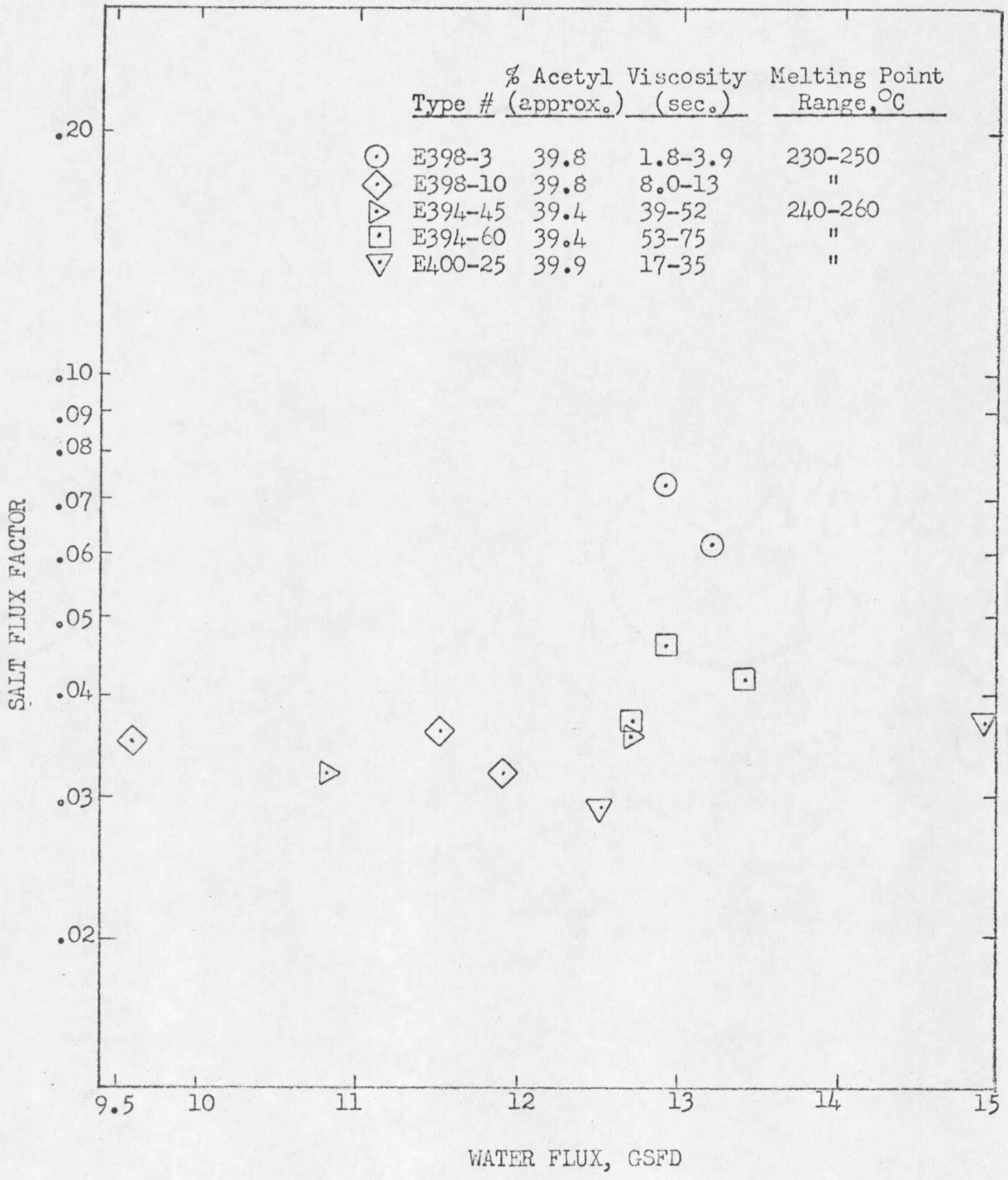

Figure 4. Effect of Type of Cellulose Acetate on Overall Results

consistent with the results of others. Reid and Breton[18] reported that the higher acetyl content cellulose acetate gives higher salt rejection and lower water flux. Lonsdale, Merten and Riley[12] showed that the semipermeability of cellulose acetate should increase with acetyl content.

The test conditions were as indicated in "Membrane Test System and Flow Diagram" except that during the first 30 min. the pressure was kept at 1000 psi to eliminate the membrane compression problem. By using the high initial pressure, it is thought that most of the compression would have taken place before data were taken.

The curves of Figures 2 and 3 were fitted by second order polynomial by using least square error method and plotted by computer, IBM 1620.

Type of Cellulose Acetate and Operating Pressure Effect

Three different grades of cellulose acetate, E400-24, E394-45, E394-60, with viscosities: 25, 45, 60 sec. and percent acetyl contents, 39.4 - 39.9%, were tested. Twelve membranes were made for this study under operating pressures: 600, 900, 1200, and 1500 psi. Each grade of cellulose acetate was applied to make four membranes. Two of these four membranes were made under solvent evaporating time 25 sec., heat treatment temperature 85\83°C, 5 min. by using heat treatment method (3), and the other two membranes were made under solvent evaporating time, 5 sec. initial heat treatment temperature 83\81°C, 5 min. by using heat treatment method (3), second heat treatment temperature, 86°C, 4 min. by

using heat treatment method (2). The other casting variables and results were shown on Table V. The results showed that higher operating pressure can give higher water flux and salt rejection. When increasing operating pressure, the increase in water flux of E400-25 was larger than E394-45, and E394-60. This showed that higher acetyl content cellulose acetate has a higher degree of crystallinity and is less compressible.

Theoretically, water flux versus operating pressure or effective applied pressure should give a linear relationship; yet, this nonlinear relationship, as shown on Figure 5, may be caused by the compressibility of membrane itself. Water flux versus applied pressure data of Lonsdale, et al.[12] gave the same relationship. Additional evidence of membrane compaction can be derived from the results of Michaels, et al.[17] They measured water flux as a function of net pressure by maintaining a fixed osmotic pressure while varying the applied pressure. The apparent water permeability decreased by perhaps 20% as the applied pressure was increased from 25 to 80 atm.

When increasing operating pressure, the salt rejection of E400-25 showed more improvement than E394-60 and E394-45, as shown on Figure 6. This may indicate that salt flux is nearly unchanged and the relative salt rejection increases as water flux increases due to the increasing operating pressure. A mathematical expression showing that salt rejection improves with increasing pressure has been pointed out by Clark[4] by assuming solution-diffusion transport model only, and neglecting the leakage term. Therefore the calculated value showed

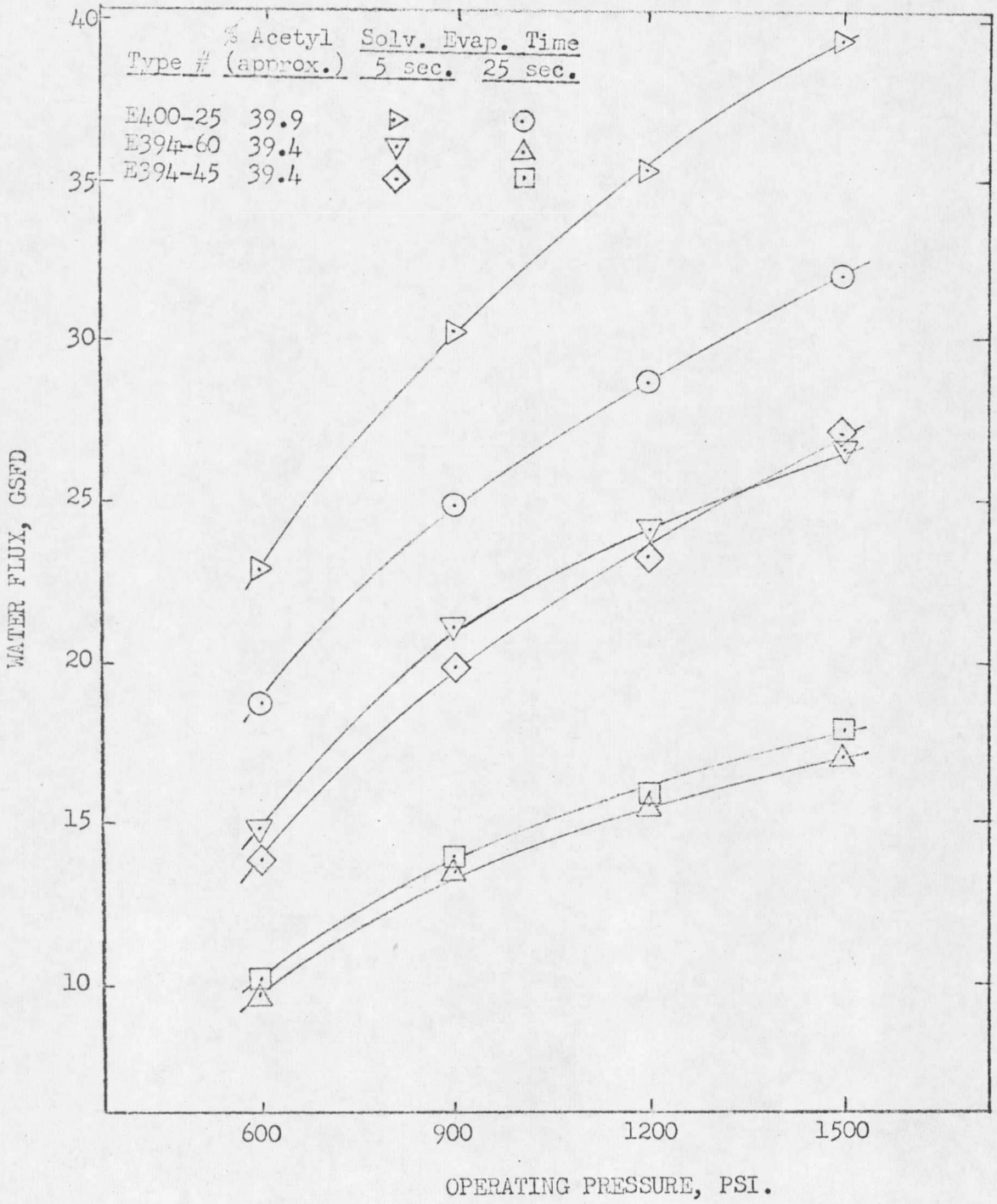

Figure 5. Effect of Type of Cellulose Acetate and Operating Pressure on Water Flux

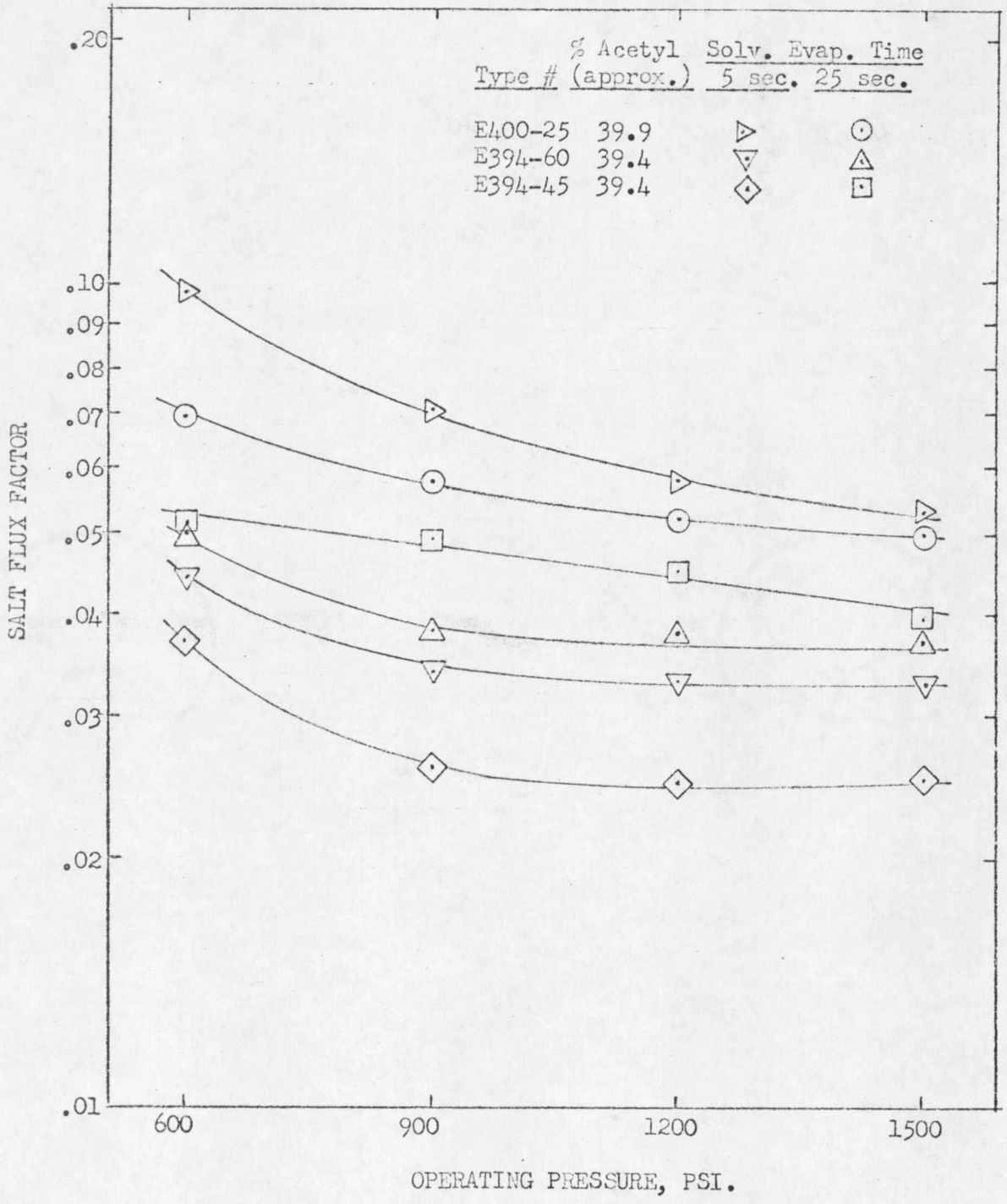

Figure 6. Effect of Type of Cellulose Acetate and Operating Pressure on Salt Flux

higher than the experimental data of Breton.[3]

Percent Cellulose Acetate Content Effect

The previously discussed results showed that E400-25 and E394-60 would be better than other grades of cellulose acetate. During this investigation, these two different grades of cellulose acetate with a wide range of percent cellulose acetate content: 16.7, 19.4, 20.6, 21.9, and 24.2%, were studied. Twenty-one membranes were tested. The membranes were fabricated under heat treatment temperature 85~83°C, 5 min. by using heat treatment method (3). The other process variables and results are indicated in Table VII, Figures 7, 8 and 9.

Figure 8 shows that for lower cellulose acetate content solutions, E394-60 can give higher percent salt rejection, but for higher percent cellulose acetate content solutions, E400-25 can give higher percent salt rejection. Within the range of cellulose acetate content of 16.7-24.2%, results indicate that E400-25 can give water flux higher than E394-60 as shown on Figure 7.

Figure 9 showed that E400-25 can give higher quality membranes because the E400-25 curve is closer to the lower-right corner on this salt flux factor versus water flux plot.

The standard test conditions were used except that during the first 30 min. the operating pressure was kept at 1000 psi to eliminate the effect of compression.

The results this far showed that E400-25 can give better results

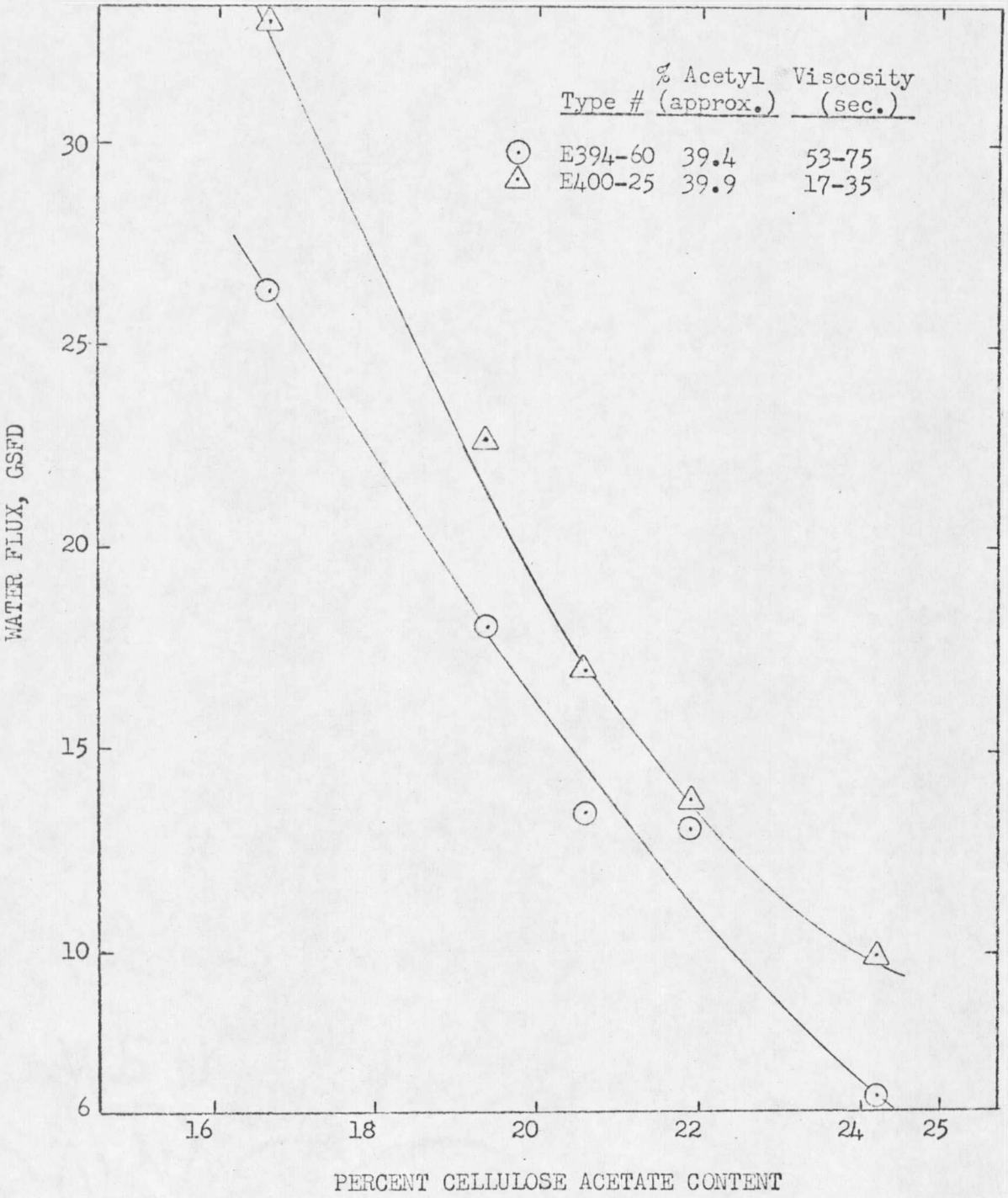

Figure 7. Effect of Percent Cellulose Acetate Content on Water Flux

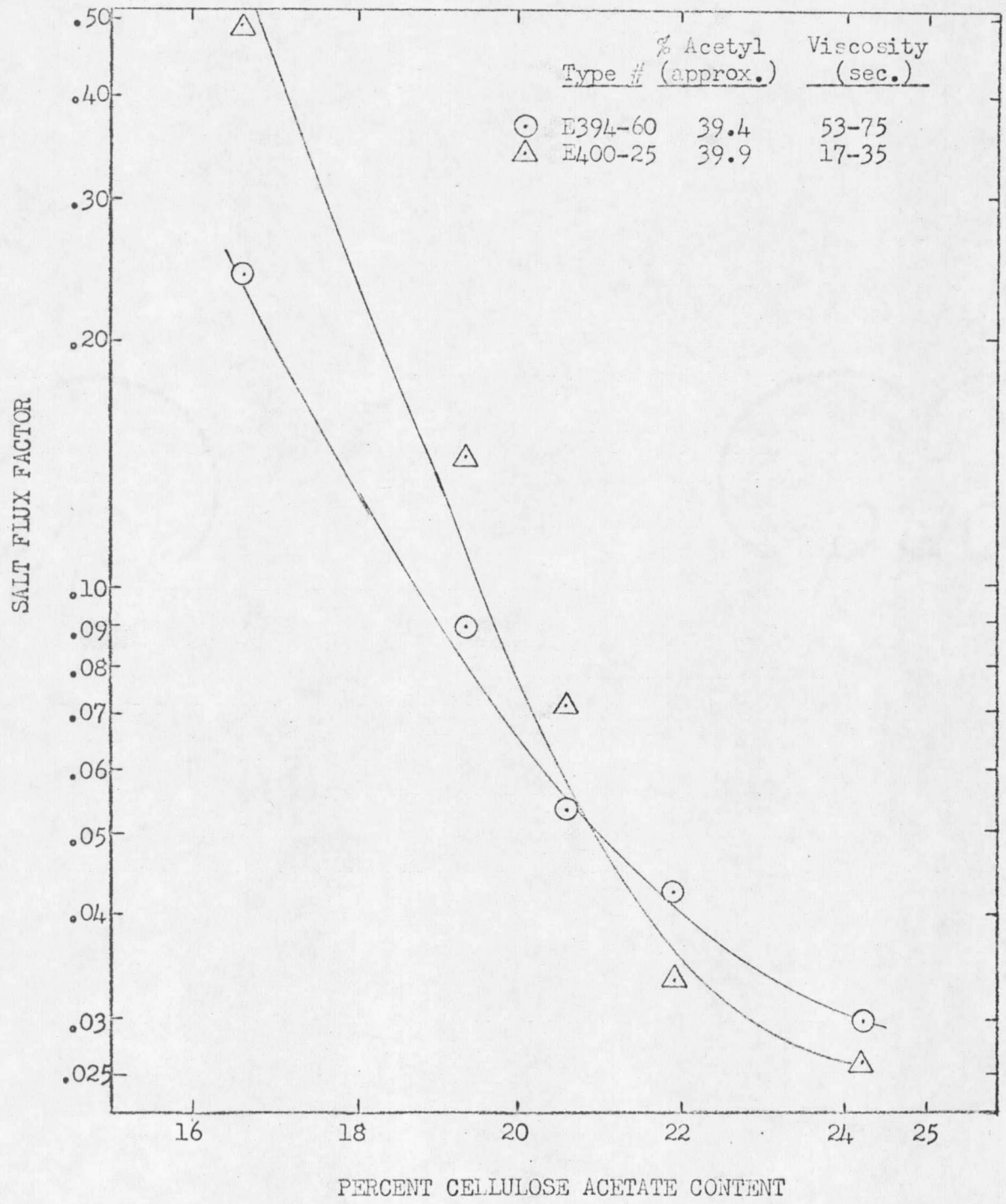

Figure 8. Effect of Percent Cellulose Acetate Content on Salt Flux

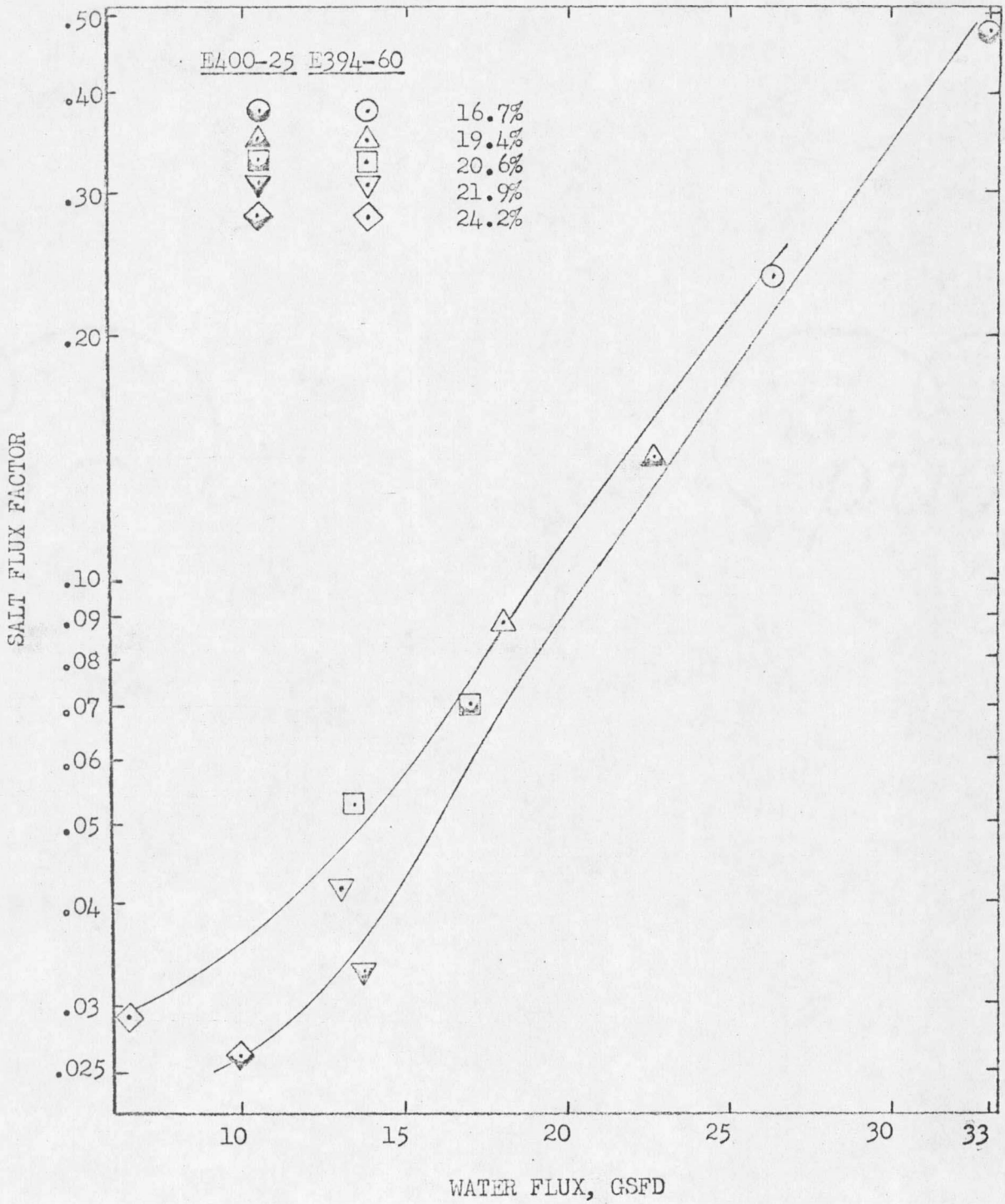

Figure 9. Effect of Percent Cellulose Acetate Content on Overall Results

(better overall results and less compressibility) than E394-60. Therefore, for the further study E400-25 (acetyl content 39.9%, viscosity 25 sec.) was chosen which is the highest acetyl content of the five grades cellulose acetate. Also, a cellulose acetate of higher acetyl content may give longer membrane life. Breton[3] reported that a membrane with 43% acetyl content was not degraded after forty days, while one with an acetyl content of 37% was completely degraded after seven days.

Heat Treatment Temperature Effect

Three different percent cellulose acetate content casting solutions (19.4, 20.6 and 21.9%) of E400-25 cellulose acetate were tested under five different heat treatment temperatures (83⅛81, 83, 85, 87, and 89°C). The initial heat treatment utilized a temperature of 83⅛81°C for 5 min. by using heat treatment method (3). After two hours of operation the second heat treatment at 83°C for 5 min. using heat treatment method (2) was applied to the same membrane. Then every two hours an increment of 2°C was applied using the same procedure. The results showed that where higher percent salt rejections are required, higher percent E400-25 content would be better; and where lower percent salt rejection are required, lower percent E400-25 content would be better, as indicated on Figure 10.

In each case, two membranes were tested. The standard test conditions were used except that during the first 30 min. the pressure was

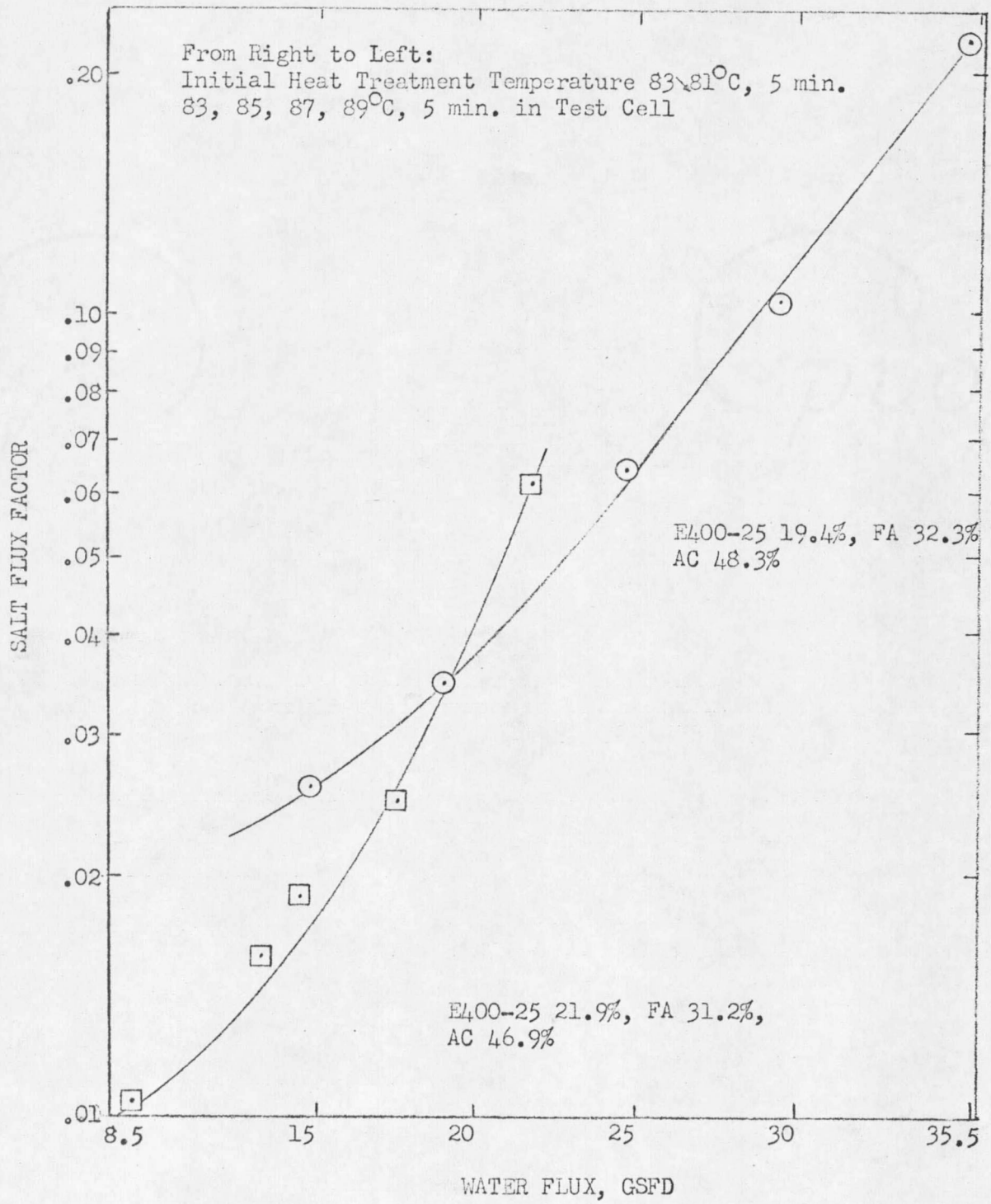

Figure 10. Effect of Heat Treatment Temperature on Overall Results

kept at 1000 psi to eliminate the membrane compression problem. The results and process variables were shown on Table VIII and Figure 10.

Heat Treatment Time and Temperature Effect

Ten membranes were made from a casting solution containing E400-25 21.9%, formamide 31.2% and acetone 46.9%, under the casting conditions: casting environment, 24.5°C and 50% humidity; solvent evaporating time, 5 sec.; gelation at 0°C, 1 hr. in water. A series of successive heat treatments repeated at the same temperature were applied to a given membrane. Different membranes were given these treatments at different temperature levels. This was done to determine the time and temperature effects on membrane performance.

The results are presented in Table IX and Figure 11 is a plot of salt flux factor versus water flux. Heat treatments at 80°C are indicated by the dotted line starting with a 4 min. treatment followed by three more 4 min. treatments. At each temperature level the first treatment was by method (1) and the rest by method (2). This sequence was repeated for membranes at 82, 84, and 86°C. In addition a single 2 min. treatment at 86°C and a double 2 min. treatment at 88°C are shown. The results showed that membrane properties are more sensitive to heat treatment temperature and less sensitive to heat treatment time, especially when the heat treatment time is longer than 4 minutes. By increasing the heat treatment time, the water flux decreases and salt rejection increases slightly.

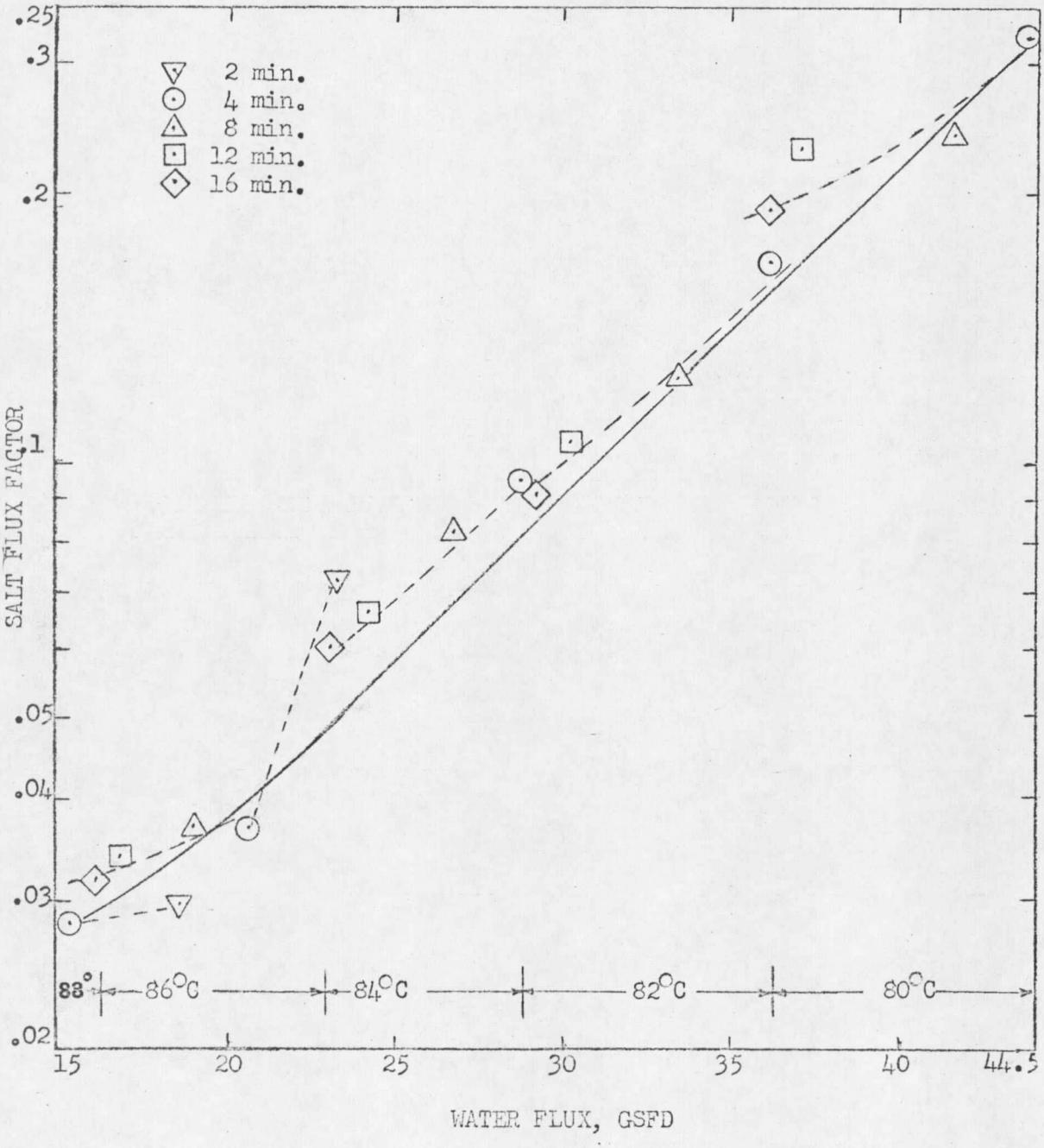

Figure 11. Effect of Heat Treatment Time and Temperature on Overall Results

The overall results showed for heat treatment temperatures, from 80 to 86°C, 4 min. would be better; while at 88°C a heat treatment time of 2 min. can give better results, but the reproducibility would be lower. This is due to the difficulty in precisely controlling the short heat treatment time.

Solvent Evaporating Time Effect

Two different percent cellulose acetate content casting solutions were studied in this investigation. Six membranes were made with E400-25 19.4%; solvent evaporating time 10, 25, 40 sec. and eight membranes were made with E400-25 23.1%; solvent evaporating time 10, 25, and 40 sec. The initial heat treatment was at temperatures of 80\78°C for 5 min. using heat treatment method (3) and additional heat treatment at temperature increments of 5°C after every 2 hours operation by using heat treatment method (2), as shown on Table X, Figures 12 and 13.

The overall results were plotted as salt flux factor vs. water flux, GSFD, on Figure 13 for E400-25 19.4% with 10, 25, 40 sec. solvent evaporating time and Figure 12 for E400-25 23.1% with 10, 25, 40 sec. solvent evaporating time. The results showed that solvent evaporating times were more sensitive with respect to water flux, but less sensitive with respect to salt rejection. In other words, shorter solvent evaporating times will give higher water fluxes with nearly the same salt rejection as longer solvent evaporating times. Also, it can be believed that a solvent evaporating time of 5 sec. would be better, considering the overall results.

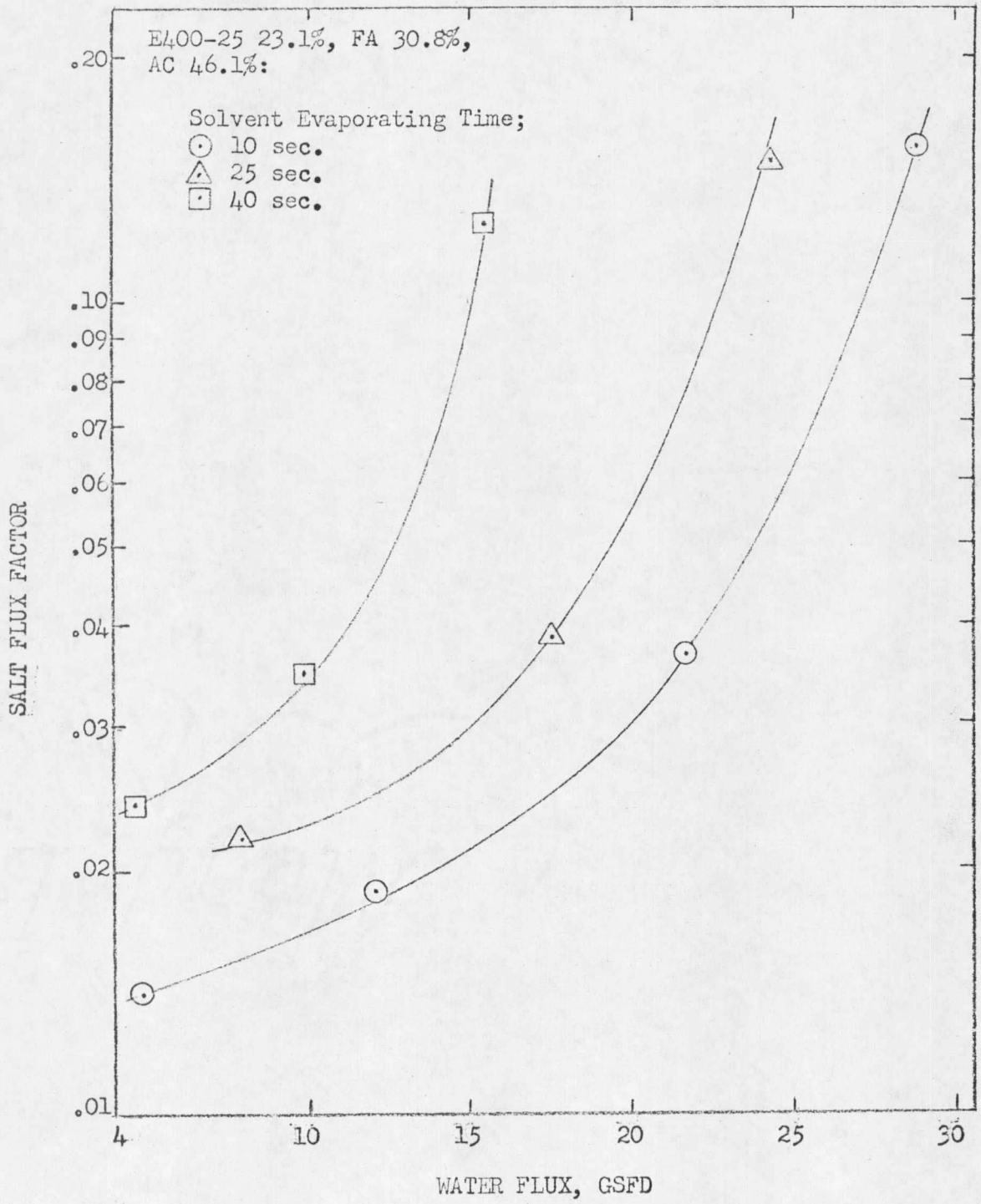

Figure 12. Effect of Solvent Evaporating Time

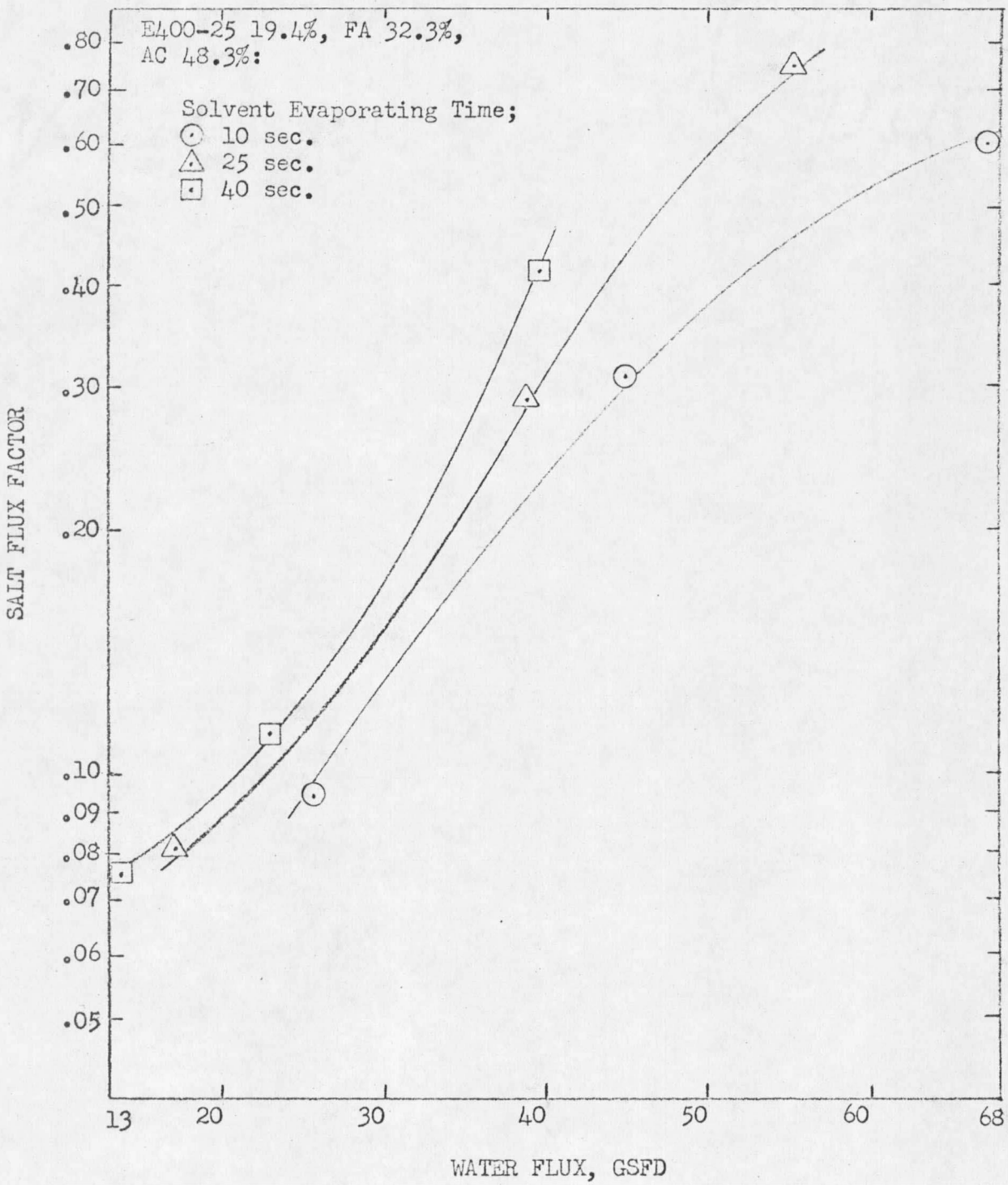

Figure 13. Effect of Solvent Evaporating Time

The standard test conditions were used except that during the first 30 min. the operating pressure was kept at 1000 psi to eliminate the effect of compression.

Gelation Temperature Effect

Two different grades of cellulose acetate were made in studying gelation temperatures, 0°C and 24.5°C. Eight membranes were made with casting solution compositions, E398-10 or E400-25, 21.9%, formamide 31.2%, acetone 46.9%; casting environment, 24.5°C and 50% humidity; solvent evaporating time 5 sec.; gelation at 0°C or 24.5°C, 1 hr. in water; heat treatment at 86°C for 4 min. by using heat treatment method (1).

In each case two membranes were made to be tested under operating pressures 600, 900, 1200 and 1500 psi. The results showed that lower gelation temperatures will give higher salt rejection but lower water flux. Also, at lower gelation temperatures, one can get a slightly more linear relationship, when plotting water flux versus operating pressure. This may indicate that at lower gelation temperature one can get slightly lower porosity in sub-layer structure and thus less compressibility. For high NaCl concentration feed, a lower gelation temperature may be needed, but for low NaCl concentration feed, higher gelation temperature may be better.

The results are shown on Table XI, Figures 14 and 15. Manijikian, Loeb and McCutchan[14] pointed out that the gelation temperature should

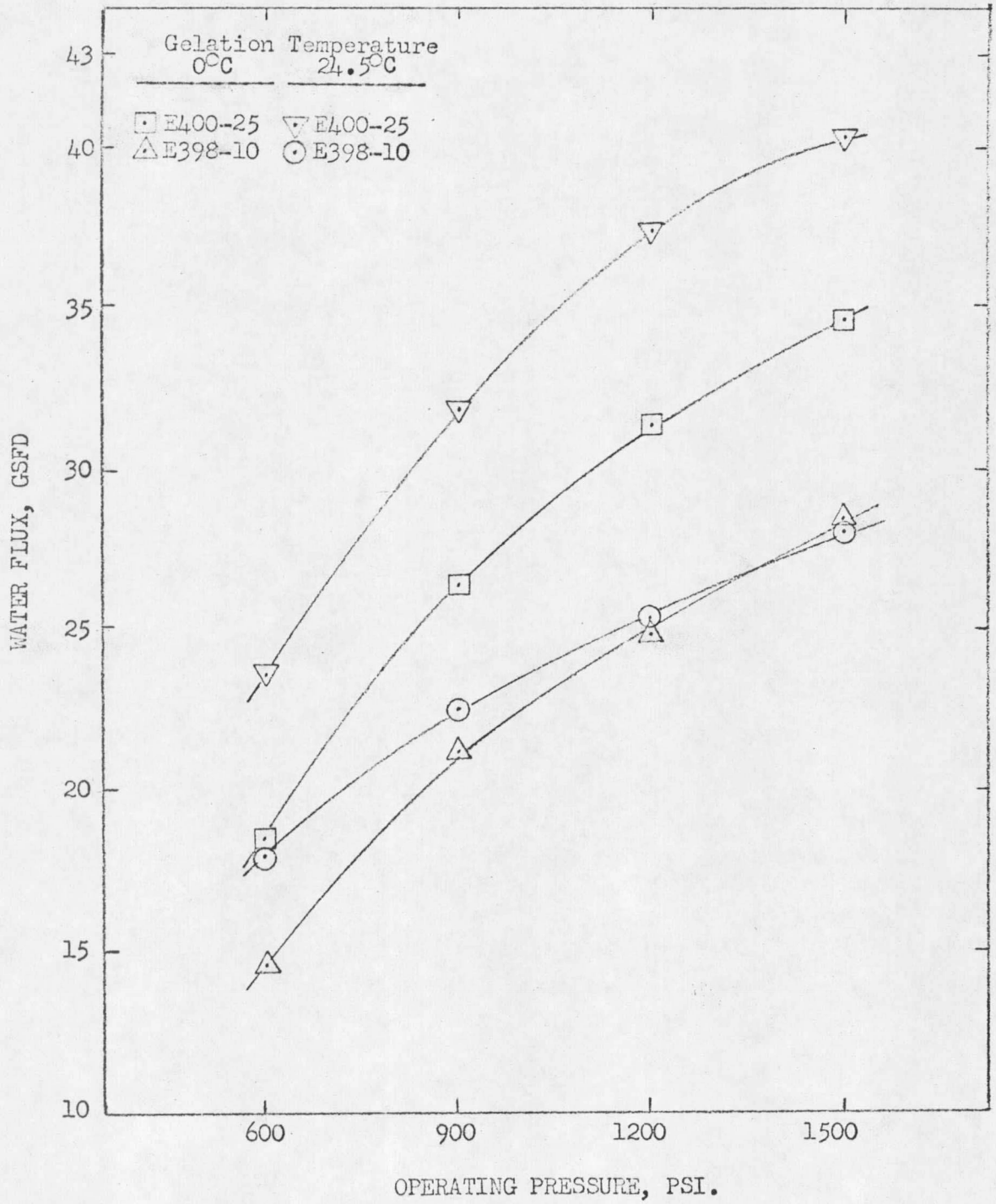

Figure 14. Effect of Gelation Temperature on Water Flux

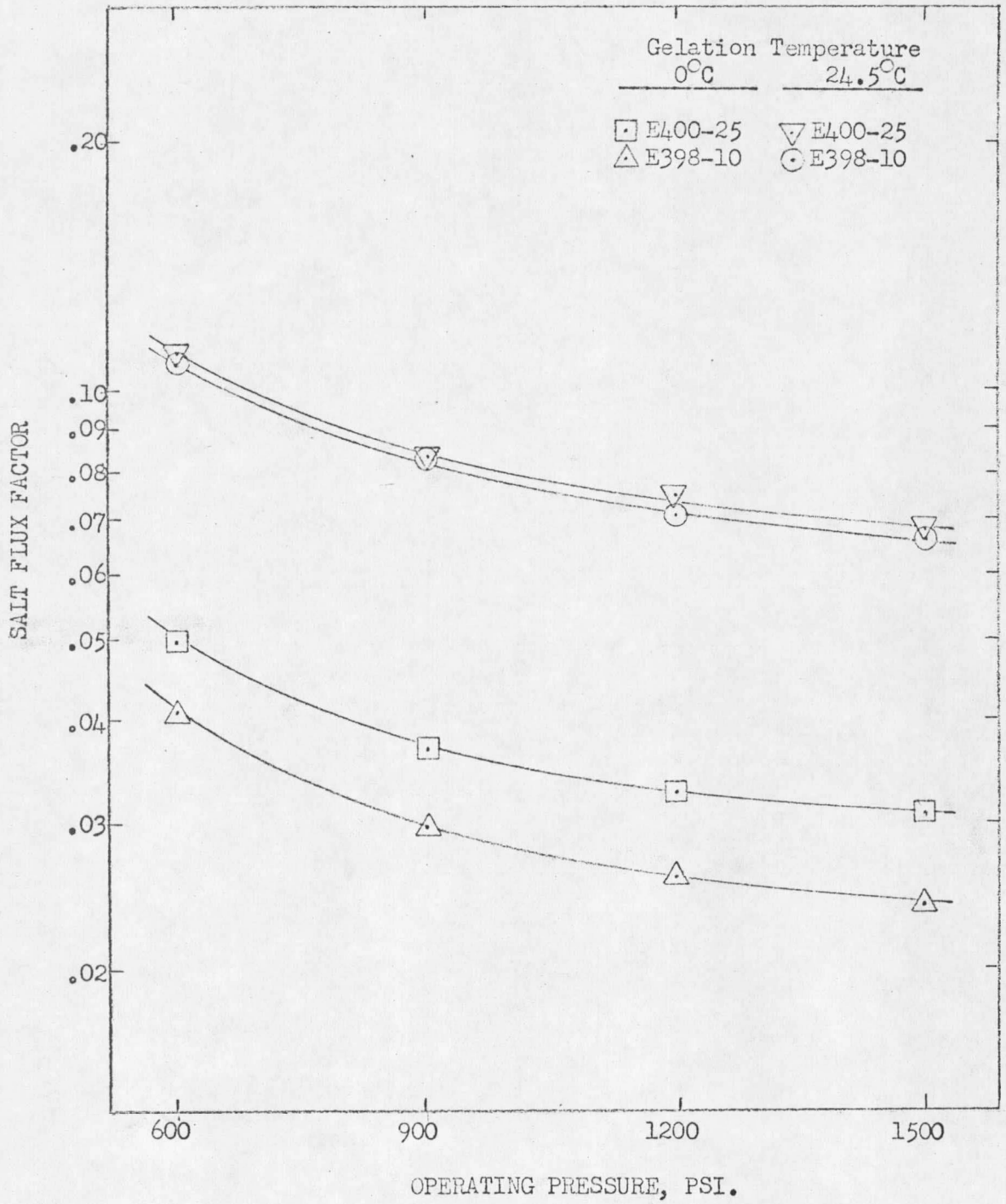

Figure 15. Effect of Gelation Temperature on Salt Flux

be in the range 0° to 5°C. The results showed it was not necessary to be in that range, if where a lower salt rejection is required (low salt content feed available) a slightly higher gelation temperature would be better.

Epoxy Porous Support Properties

Twenty-five membranes were tested to study the epoxy porous support properties. The membrane casting variables and results are indicated on Table XII and Table XIII. In run #TS-124, the membrane was made by casting onto a reused porous epoxy support and in run #TS-125 the membrane was cast on a new porous epoxy support with a solvent exaporating time less then 5 sec. The initial heat treatment was made at 84\82°C by using heat treatment method (3) for 5 min. and an additional heat treatment was given before testing at a temperature of 84°C for 5 min. by using heat treatment method (2). In run #TS-128 and 129 the membranes were cast on reused epoxy porous supports and in run #TS-105 and 103, the membranes were cast on the new supports with a solvent evaporating time of 5 sec. The initial heat treatment was at 83\81°C for 5 min. by using heat treatment method (3), and a second heat treatment was made at 83°C for 5 min. by using heat treatment method (2). The results showed that the epoxy porous support can be reused, as shown on Table XII.

At four different operating pressures (600, 900, 1200, 1500 psi) the results of commercial membranes (Desalination System, Inc.) with

porous epoxy as support (TS-136, 137, 138, 139), membranes cast on glass (TS-191, 192, 193, 194) and membranes cast on epoxy porous support (TS-167, 170, 171, 174, 141, 146) showed the same type of nonlinear relationship as water flux increased due to pressure increase. The commercial membranes without epoxy supports (set directly on 5 microns SS316 porous plate) leaked when tested. When plotting log water flux, GSFD, versus inverse pressure, psi^{-1}, straight lines are obtained, as shown on Figure 16. This non-linear relationship is caused by the compressibility of the membrane itself. The results show that Versapor 6429, Gelman (Epoxy, .9 micron) is a promising commercially available porous support at present. The support can be used for pressures up to 1500 psi, or higher.

Run #TS-191, 192 membranes were cast on glass plate but the edges were not fixed during heat treatment procedure. Run #TS-193, 194, the membranes were fabricated under same conditions except the edges were fixed during heat treatment. The results showed that the fixed edge membranes gave higher water flux but lower salt rejection. This result may be caused by the fact that during the heat treatment procedure, the fixed edge membranes shrink less.

The water flux of membranes cast directly onto porous epoxy support was higher than those cast on glass plates because the epoxy porous support is a rigid support and prevents shrinkage of the membrane during the heat treatment. Results of this effect are shown in Table XIII and Figure 16.

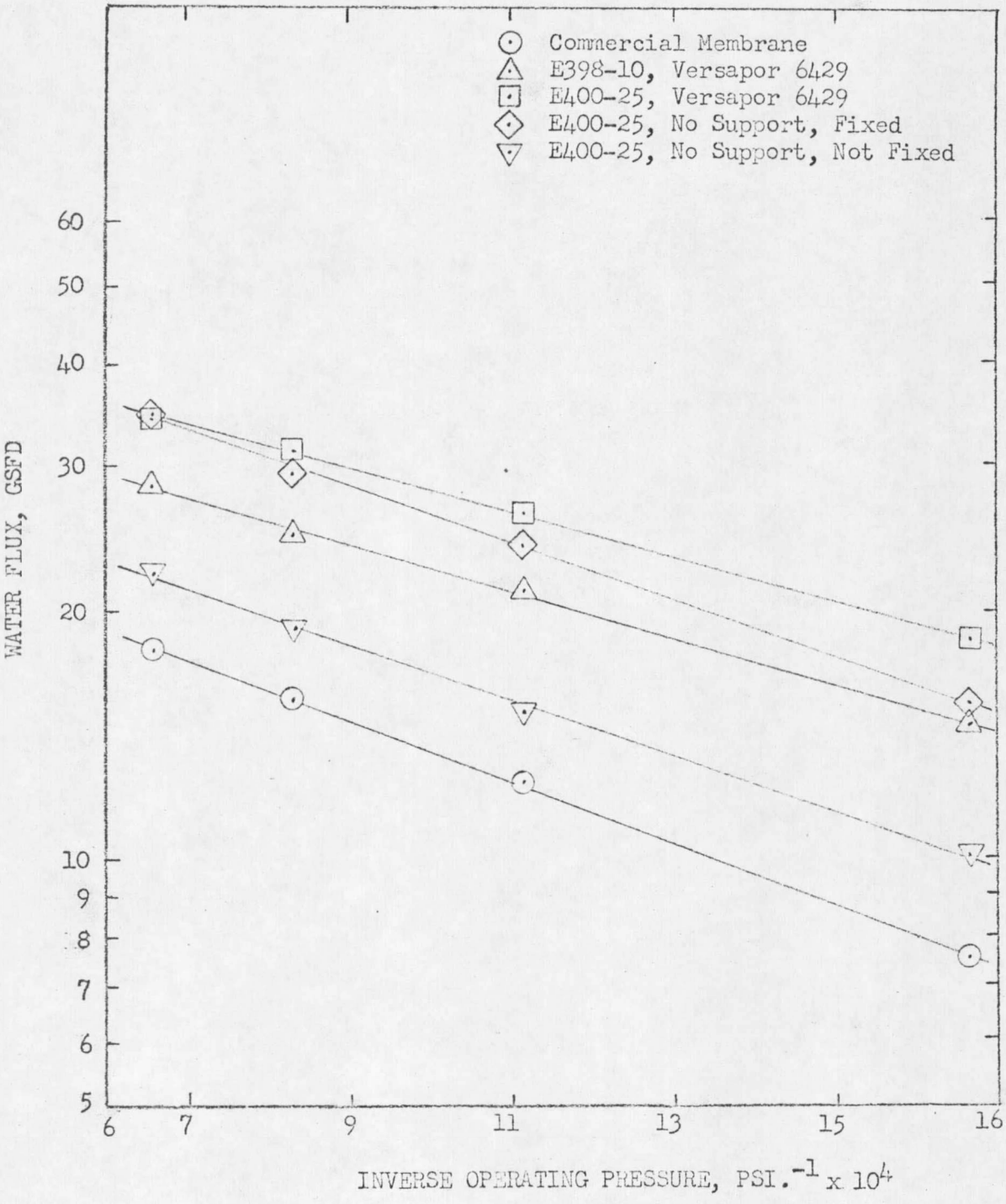

Figure 16. Relationship of Operating Pressure and Water Flux

Comparison of Commercial Membranes and Membranes By Direct Casting onto Porous Support

The results reported above showed that optimum membrane fabrication conditions for 10,000 ppm feed brine, under the casting environments of 24.5°C and 50% humidity are: casting solution, E400-25, 21.9%, formamide 31.2%, acetone 46.9%; solvent evaporating time, 5 sec; gelation at 0°C in water for an hour; heat treatment, at 86°C for 4 min. in water; membrane cast on Versapor 6429, Gelman (Epoxy, .9 mocron).

The results of TS-175, 176, 177, 178 showed that membranes fabricated by this optimum condition can give a water flux of 21 GSFD and a salt rejection 95% (115 hours average) with excellent reproducibility. The commercial membranes (Desalination System, Inc., California) tested in this study only give 11 GSFD water flux and 95% salt rejection (25 hours average) with poor reproducibility as shown on Table XIV.

A plot of water flux versus salt flux factor indicating the membrane properties of commercial membranes and the membranes fabricated by direct casting onto porous supports is shown on Figure 17. This plot also shows that a membrane gelation temperature of 0°C will give slightly higher reproducibility than a gelation temperature of 4-5°C.

The results of four representative runs (TS-175, 176, 177, 178) were plotted with water flux versus time and salt rejection versus time using the IBM 1620 computer as shown in Figures 18 and 19. The water flux versus time curves were fitted by a third order polynomial and salt rejection versus time curves were fitted by a second order polynomial by using least square error method.

This study shows that membranes fabricated by direct casting onto rigid epoxy porous materials are definitely promising. The results showed that under the standard test conditions of this study, the membranes cast on Versapor 6429, Gelman (Epoxy, .9 microns) by using above said process variables can give a high water flux of about twice that of the commercial membranes with an equally good salt rejection ability and an excellent reproducibility. Since the membrane is directly cast on a rigid porous support, by a proper design, the high labor cost of membrane replacement can be significantly decreased as a shorter time and simpler procedure is required to replace the membrane. On the other hand, this can definitely reduce the plant shut-down time. Also, membranes fabricated by direct casting on a rigid porous support, can prevent the membrane mechanical deformation to a great extent. Therefore, this is one of the most effective ways to attack the short membrane life problem indirectly by reducing the membrane replacement cost and directly by decreasing the possibility of membrane mechanical failures. Furthermore, the rigid solvent-insoluble porous support can be reused. The overall cost would not be increased by direct casting on porous supports.

Run #TS-195, 196, 197 and 198, the membranes were made under the same conditions as the above said four representative runs, except the membranes were cast on Versapor 6424, Gelman (Epoxy, 5 microns). The results showed that the membrane cast on larger pore size porous supports gives higher water flux but lower salt rejection than the

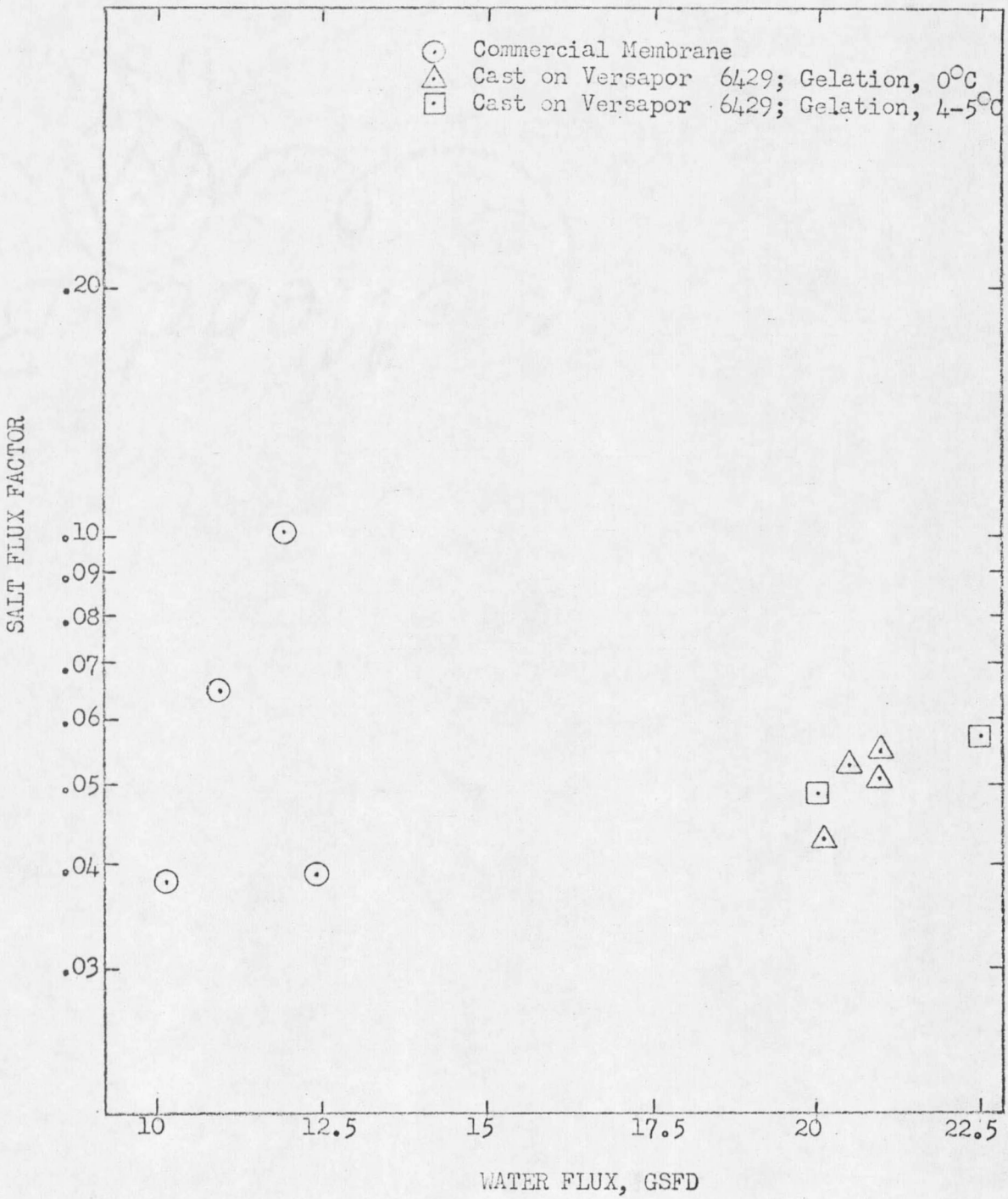

Figure 17. Comparison of Commercial Membranes and Membranes by Direct Casting on Porous Supports

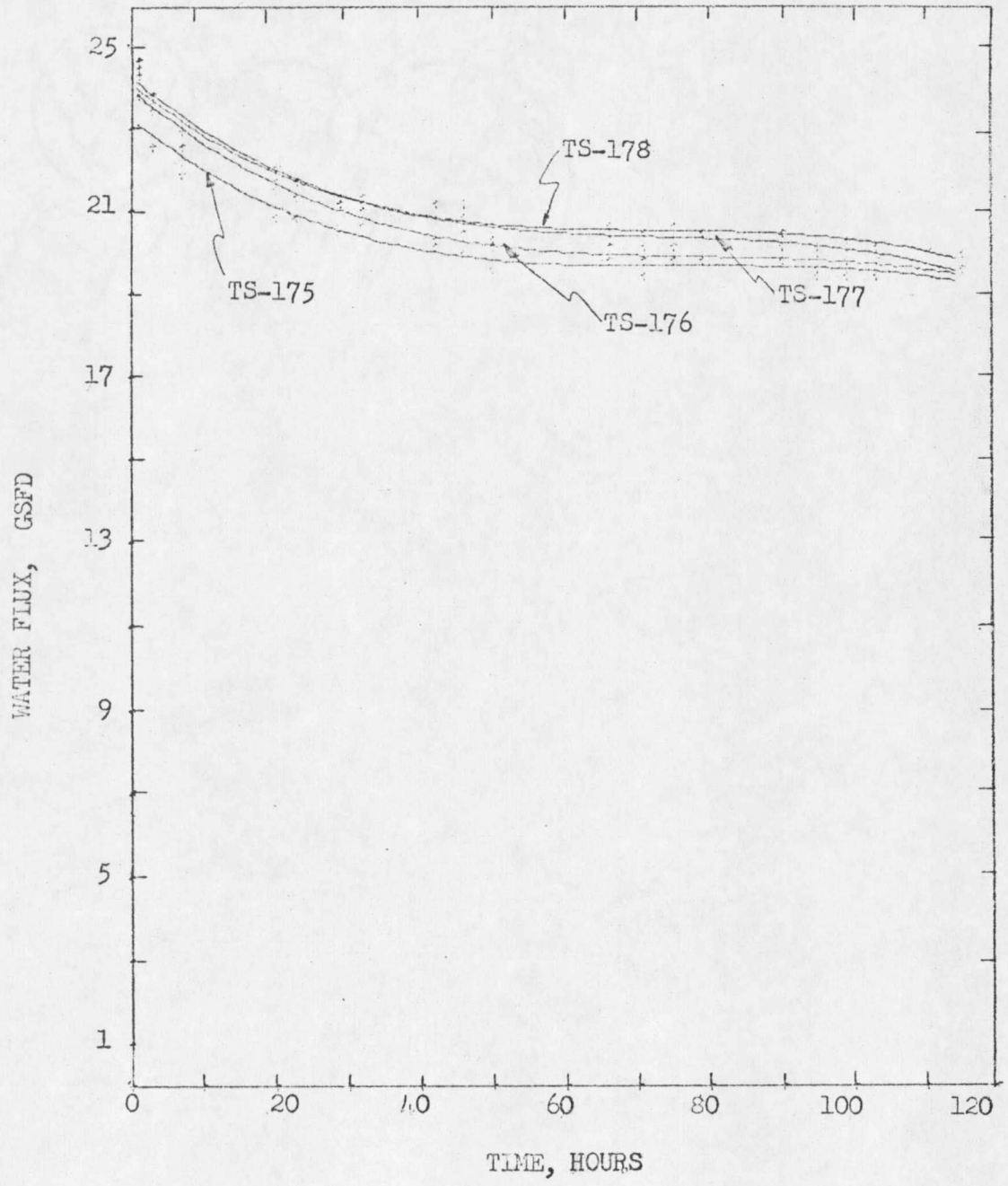

Figure 18. Water Fluxes of Representative Runs

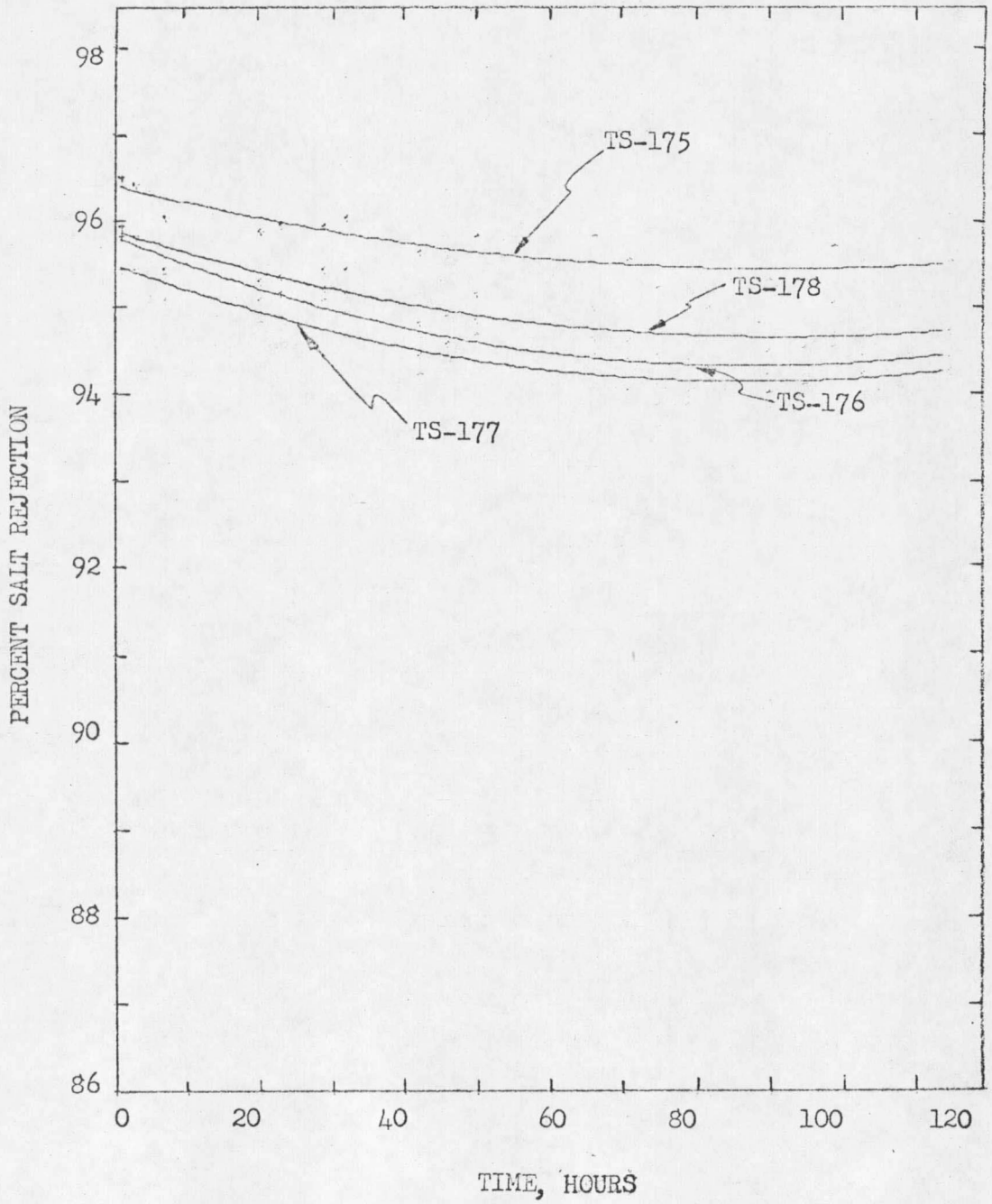

Figure 19. Salt Rejections of Representative Runs

membrane cast on smaller pore size supports. This may be mainly due to membrane cast on larger pore size support having higher mechanical deformation possibility. Also, this may be partly due to easier penetration of casting solution into a larger pore size support and forms a thinner membrane thus a thinner active layer.

Run #TS-204 and 205, the membranes were made under the above said optimum membrane fabrication conditions, except that a thicker layer of casting solution was spread on the support with two layers of masking tape to maintain the clearance. Results showed that the water flux decreases about 15% and salt rejection increases slightly as the casting solution layer is doubled, as shown on Table XIV. If we assume that the resistance to both flow of water and salt is in the active layer as reported by Loeb and Sourirajan[10,11] is correct this may indicate that active layer thickness increases slightly as the total membrane thickness is increased. But, if we compare the water flux of membranes prepared by Breton[3] and by Loeb and Sourirajan[10,11] it may indicate that the active layer is a strong function of membrane fabrication variables.

The results above indicate that using a masking tape to maintain a casting solution layer thickness of .005 ± .001" in most runs of this research is quite acceptable. In other words, if the fabrication variables, such as: casting solution, solvent evaporating time, heat treatment time and temperature, gelation temperature, casting environments, etc., are maintained constant, the deviation of casting solution layer thickness in that range will not effect the membrane performance

to any great extent. This is because the active layer thickness is more sensitive to casting variables and less sensitive to total membrane thickness.

Effect of Feed Flow Rate on Membrane Performance

The study of feed flow rate effect on membrane performance was done by using four runs operating under the test range of average feed flow velocity .67 cm/sec. to 12.3 cm/sec.

Four membranes were made under the fabrication conditions: casting solution composition, E400-25, 21.9%, formamide 31.2%, acetone 46.9%; casting environment, 24.5°C and 50% humidity; solvent evaporating time, 5 sec.; gelation at 0°C for an hour in water; heat treatment at 86°C for 4 min. in water. Two of the four membranes were cast on Versapor 6424, Gelman (Epoxy, 5 microns) and the other two membranes were cast on Versapor 6429, Gelman (Epoxy, .9 microns). The results are shown on Table XV and Figure 20.

The results indicated that the feed flow velocity 7.0 cm/sec. for most runs is quantitatively acceptable. This feed flow velocity is much lower than the Office of Saline Water's specification of 100 cm/sec. The surging of the reciprocating pump can serve to reduce the concentration build-up. If a high feed flow rate of 100 cm/sec., as specified by the Office of Saline Water, is applied it would be expected to increase slightly the membrane performance. For high water flux and salt rejection membranes a feed velocity less than 3.3 cm/sec. may cause serious

polarization effects using the test equipment of this study, as shown on Figure 20.

Since the test system of this investigation is a discontinuous flow system in the cells (change in flow direction) and in addition there is surging of the reciprocating pump, there is no way to define the flow pattern in terms of Reynolds number. There are several indications that the higher water flux and salt rejection causes higher salt concentration at the boundary layers, although the bulk salt concentrations are nearly unchanged. Therefore, for a high water flux and salt rejection membrane, the membrane performance is a stronger function of feed flow rate than a low semipermeability membrane. Birkhimer[1] reported that he found no detectable change of membrane performance when the feed rate is increased to 4.5 ml/sec. through $2\frac{1}{2}$" diameter test cell with 8 ml. cell volume (average feed flow velocity across cell, 3.6 cm/sec.). This is due to his low membrane water flux which causes less concentration build-up on the membrane-salt water interface and less polarization effect.

The equations given by Brian[16] as mentioned in the "Introduction" can also be quantitatively applied in this test system to explain the effect of feed flow velocity on membrane performance. The equations show for the high salt rejection case that we get higher product water flow velocity through the membrane (higher value of v'). This increases the value of numerator and gives a larger ratio of C_2'/C_2^b (salt conc. at membrane interface/salt conc. in bulk solution). If we use higher feed flow velocity over the cell (Larger $\bar{U}$), the value of denominator increases

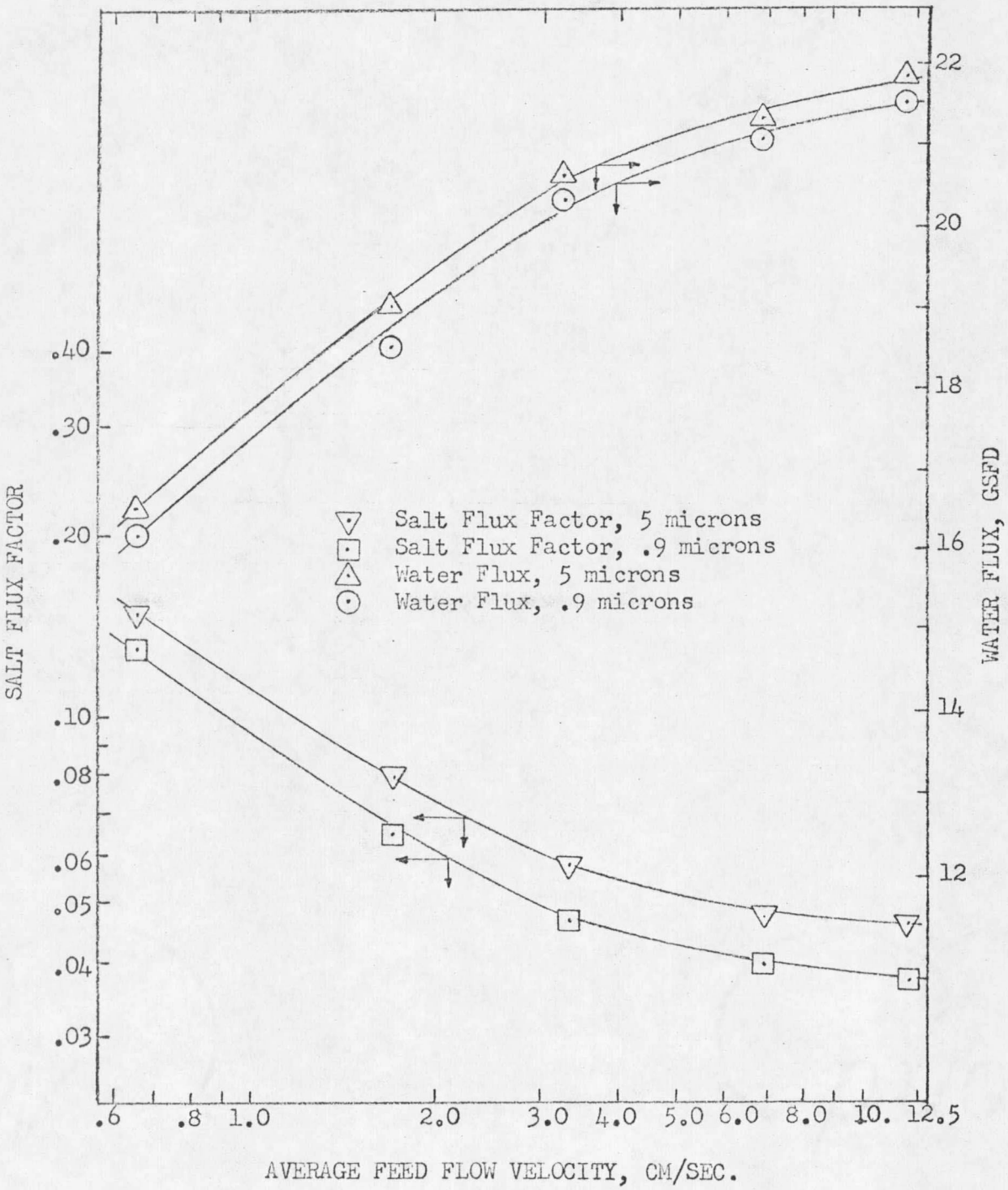

Figure 20. The Effect of Feed Flow Rate on Membrane Performance.

and gives smaller ratio of C_2'/C_2^b. In other words, a high salt rejection membrane with a higher water flux gives a higher salt concentration build-up and has higher polarization effect. On the other hand, if we increase the feed flow rate we can obtain a less salt concentration build-up in the boundary layer and obtain a less polarization effect.

CONCLUSIONS

This study shows that by a proper selection of casting solution composition, percent acetyl content of cellulose acetate, fabrication technique, membrane casting conditions and porous support materials the cellulose acetate membrane (the best high polymer for reverse osmosis desalination, thus far) can be directly cast onto porous material and gives the desired membrane performance.

The results of membrane fabrication by direct casting on porous materials with dilute casting solution was not very promising. It was discontinued in the second year of this research due to the following reasons: (1) the porous supports found promising were not rigid supports; (2) a lack of reproducibility comes from difficulty in controlling the water (pore filling agent) content and the water distribution in the dampened support; (3) water fluxes and salt rejections were low so as to make the technique doubtful for commercial use.

The porous epoxy support, Versapor 6429, Gelman (Epoxy, .9 microns) was the most promising among those commercially available porous supports that were tested. This is a rigid, high strength and relatively cheap porous material. The membranes fabricated by direct casting on this support give the highest performance. Its virtues were high water flux (about twice that of commercial membranes), high salt rejection, high reproducibility, dependability and durability. The fabrication procedure of this type membrane is relatively simple and the quality can be adjusted by changing process variables to meet the market requirements

for minimal desalination cost.

The process variables, such as: casting solution composition, type of cellulose acetate, solvent evaporation time, gelation temperature, heat treatment temperature, heat treatment time, etc., have been discussed in a previous section. These results showed that there are no definite optimum process conditions and one can use different combinations of the said variables to get the same quality membranes. Also the optimum condition will depend upon the requrements of the market. For example, different saline water areas require different membrane specifications to get potable water at the lowest cost.

Using the Office of Saline Water's specification that the feed salt concentration be 10,000 ppm, the author found the optimum conditions for membranes by direct casting on rigid epoxy porous support (Gelman, Versapor 6429, .9 microns) to be as follows when cast at 24.5°C and 50% humidity:

Casting solution: Cellulose acetate E400-25 (acetyl content 39.9%, viscosity 25 sec.) 21.9%, formamide 31.2%, acetone 46.9% by weight.

Casting solution layer thickness: .005 ± .001".

Solvent evaporating time: 5 sec.

Gelation: 0°C, 1 hour in water.

Heat treatment: 86°C, 4 min. in water.

The results were compared with commercial membrane (Desalination System Inc., California) as shown on Figure 17.

The high reproducibility of membranes cast on rigid porous supports may be due to the even strength distribution as the membrane shrinks during the heat treatment. The high water flux may be also due to less shrinkage during the heat treatment. On the other hand, the membranes cast on a glass plate or flexible porous supports usually give lower reproducibility and lower water flux. Membrane performance for those cast on glass plates or flexible porous support is highly dependent on how the membrane shrinks during the heat treatment.

RECOMMENDATIONS

It is believed that cellulose acetate membranes for reverse osmosis desalination by direct casting onto rigid solvent insoluble porous supports (Versapor 6429, Gelman, is one of the most promising supports so far), are definitely promising for application in commercial desalination units. For example, as a possible method one can cast membranes on small diameter porous epoxy rods, porous tubes or thin flat rectangular ducts to give high surface area or by using this idea to design a equipment one can obtain higher effective surface areas per unit volume. Thus, one can get a high desalinized water production rate from moderate size equipment. This development not only gives a high product rate but also is one of the most effective methods to attack the membrane life problem indirectly by reducing the membrane replacement cost and to attack the membrane life problem directly by preventing the mechanical failures, which increasing the dependability, reliability, and durability of the membrane itself. Yet, the said expected methods to increase surface area per unit volume and to simplify the membrane replacement procedure will also have some difficult aspects. The economical and effective ends sealing method in this equipment design as concerned with membranes by direct casting onto porous rods, tubes or porous thin flat rectangular ducts is one of the most striking aspects of this development.

Another striking aspect is how to effectively and economically decrease the concentration build-up in the boundary layer for a high performance membrane. For a high recovery ratio (the ratio of product

water to exit salt water) equipment, the bulk salt solution concentration would be also significantly increased. Therefore, the optimization of operation conditions, such as: recovery ratio, membrane specification, operating pressure, operation temperature, stages of the desalting system and the connection of the stages, is also an important aspect.

Since the epoxy porous material can be applied under high pressure up to 1,500 psi or higher, this type of design can be hopefully applied for the conversion of both brackish water and sea water. If for sea water conversion by using single stage, it may be necessary to change the casting solution composition and casting process variables. A cellulose-acetone-formamide-pyridine quaternary casting solution may be applied for the conversion of sea water as reported by Manjikian, Allen and White.[15] This quarternary casting solution could also be directly cast on rigid epoxy porous supports.

APPENDIX

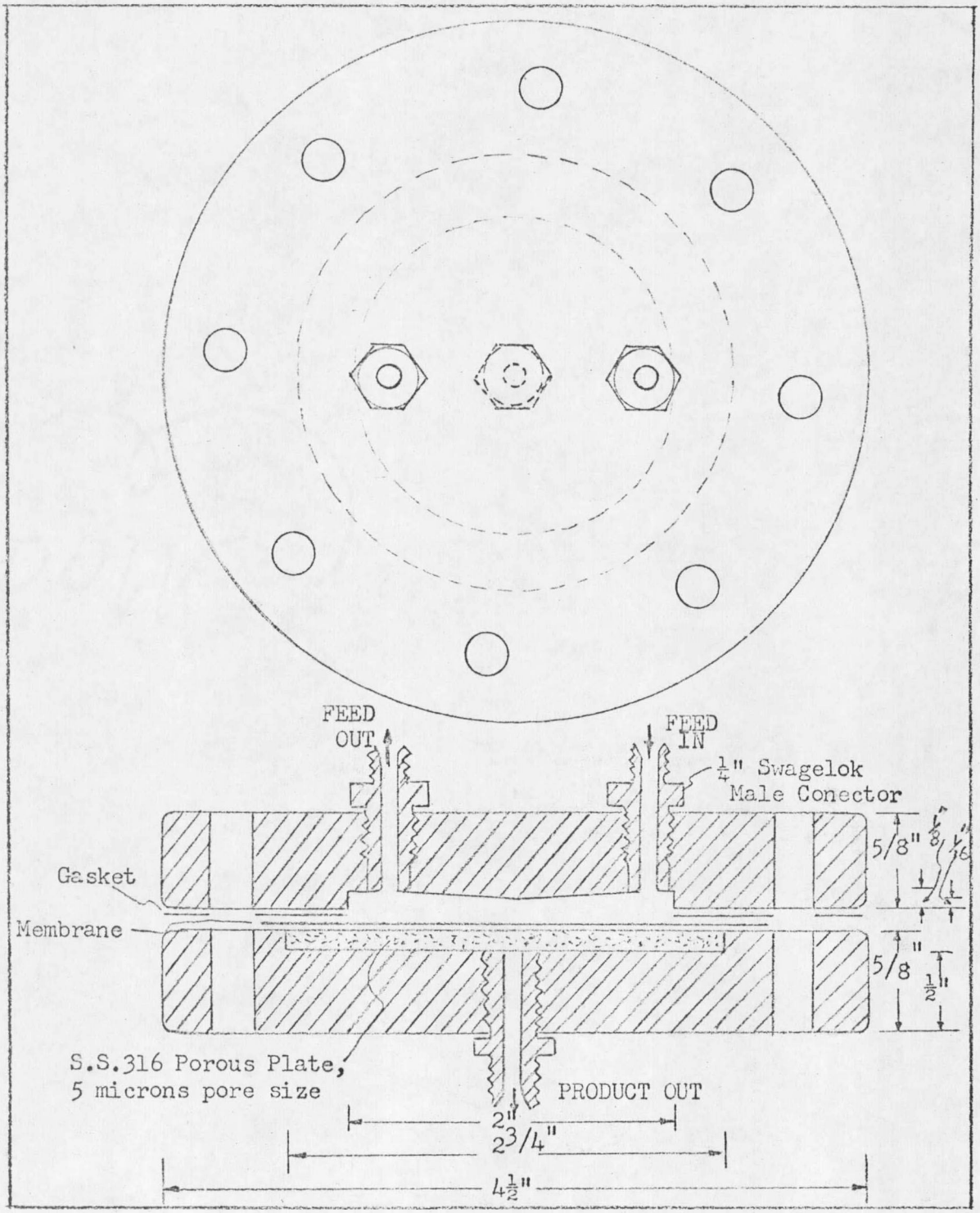

Figure A1. Test Cell

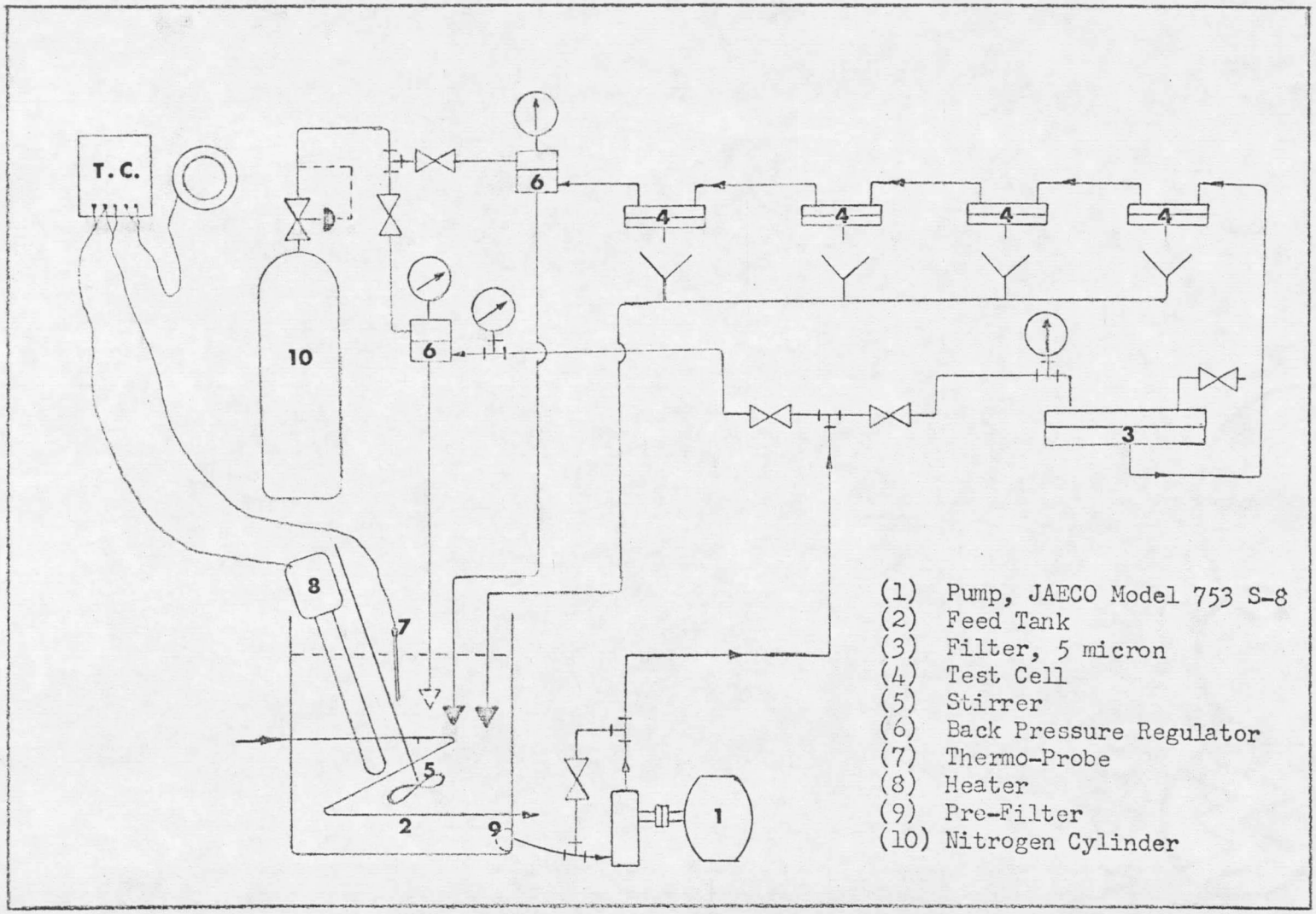

Figure A2. Test System and Flow Diagram

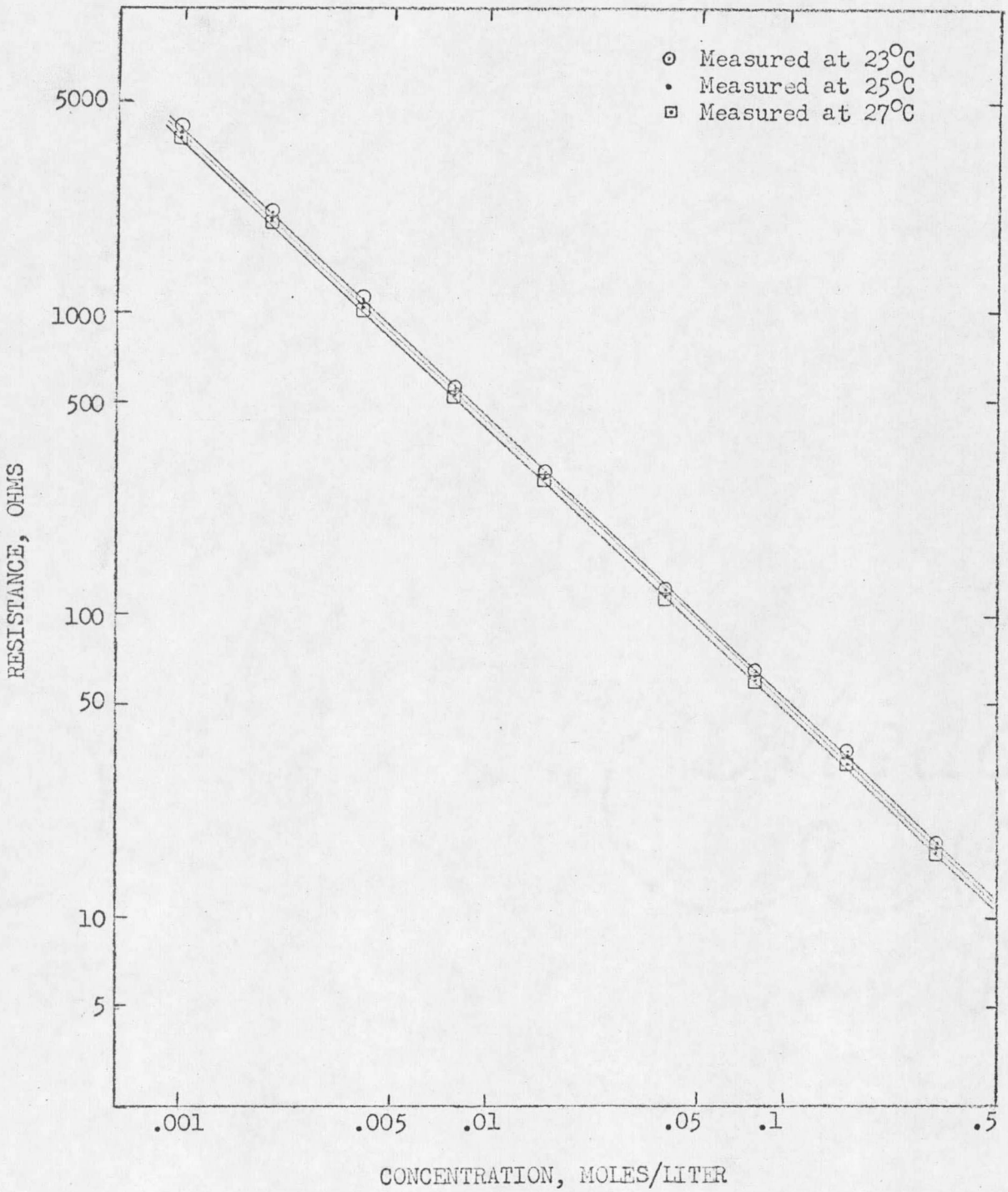

Figure A3. Calibration of Conductivity Cell

TABLE I. CALIBRATION OF CONDUCTIVITY CELL

NaCl Moles/Liter	Resistance, Ohms 23°C	25°C	27°C
.001	4100	3950	3800
.002	2120	2080	2030
.004	1100	1080	1045
.008	550	540	525
.016	290	285	280
.040	120	117	115
.080	62	61	60
.160	35	34	32
.320	17.5	17	16.4

TABLE II. POROUS SUPPORTS

Manufacturer	Material	Commercial Name	Pore Size (Microns)	Solvent Resistance *	Remarks
Gelman	Cellulose Triacetate	GA-4	.8	Good	Good Membrane Formation
		GA-6	.45	"	
		GA-8	.2	"	
		GA-10	.05	"	
	Cellulose	∝-6	.45	Excellent	Good Membrane Formation
		∝-8	.2	"	
	Epoxy	Versapor 6429	.9	"	Supports cannot be Wetted by Water
	Epoxy	Versapor 6424	5.	"	
	Fluorinated Vinyl	VF-6	.45	Fair	Support, Low Strength
	Polyvinyl-Chloride	VM-6	.45	Fair	Support, Low Strength
	Glass Fiber	Type E	—	Excellent	Poor Strength
		Type A	—	"	"
Millipore	Nylon	NR, Duralon	1.	Good	Fair Membrane Formation
	Proprietary	UR, Solvinert	.5	"	Hard to Cast
	Teflon	LS, Mitex	5.	Excellent	Broken Under Pressure
Schleicher & Schuell	Filter Paper	No. 576	—	Excellent	Easy to Cast
	Cellulose Derivatives	0-2	.25	Good	Fair Membrane Formation
	Cellulose-Nitrate Coated Filter Paper	BAC-T-KOTE	.35	Poor	Poor Membrane Formation

*Resistance to acetone with respect to water wetted porous support.

TABLE III. RESULTS OF MEMBRANES CAST ON POROUS CELLULOSE AND CELLULOSE TRIACETATE BY USING DILUTE CASTING SOLUTION

Run No.	Support	Pore Size (Microns)	%SR*	WF** GSFD
DS - 67	∝-6	.45	82.5	7.12
DS - 68	∝-8	.2	90.6	4.14
DS - 69	∝-8	.2	56.3	5.75
DS - 70	∝-6	.45	64.	4.52
DS - 71	∝-6	.45	83.	3.12
DS - 72	∝-8	.2	77.5	5.98
DS - 73	∝-6	.45	60.4	6.73
DS - 74	∝-8	.2	71.	1.1
DS - 75	GA-10	.05	84.5	6.35
DS - 76	GA-10	.05	84.5	8.15
DS - 77	GA-10	.05	91.8	3.1
DS - 78	GA-10	.05	89.	4.35

*Percent Salt Rejection.

**Water Flux, gal/ft^2 day.

TABLE IV. RESULT OF MEMBRANES CAST FROM TERNARY SOLUTION ON POROUS SUPPORTS

Run No.	Casting Solution	Solvent Evap. Time (sec.)	Gelation Temp(°C)	Gelation Time (hr)	Heat Treatment Temp (°C)	Heat Treatment Time(min.)	%SR	WF GSFD
(Support: Versapor 6429, Epoxy, Pore size .9 microns)								
TS-1	E 398-3, 25%	22	5	1	85	4	97.4	6.6
TS-2	E 398-3, 25%	22	7	1	85	5	80.5	16.5
TS-3	E 398-3, 25%	22	7	1	85	5	95.8	10.3
TS-7	E 398-3, 25%	25	5	1	85	4	98.4	10.0
TS-14	E 398-3, 25%	23	5	1	83	5	94.5	9.5
TS-28	E 398-10,21%	25	5	1	84	5	91.0	9.2
TS-29	E 394-60,16.5%	25	Room Temp.	1	84	5	90.0	2.2
TS-32	E 398-10,22%	25	4-5	1	82	5	94.0	13.8
					86	5	97.0	8.0
					90	5	95.0	5.6
TS-33	E 398-10,22%	23	4-5	1	82	5	93.5	1.5
					86	5	95.6	8.7
					90	5	88.7	3.2
TS-34	E 394-60,19%	23	4-5	1	82	4	85.5	25.5
TS-35	E 394-60,19%	25	4-5	1	82	4	91.2	19.2
TS-36	E 394-60,19%	25	4-5	1	82	4	91.0	20.0
					86	4	96.0	12.2
					86	4	96.8	9.2
TS-37	E 394-60,19%	23	4-5	1	82	4	87.0	23.0

TABLE IV. Continued

Run No.	Casting Solution	Solvent Evap. Time (sec.)	Gelation Temp(°C)	Gelation Time (hr)	Heat Treatment Temp (°C)	Heat Treatment Time(min.)	%SR	WF GSFD
TS-38	E 394-60,19%	23-25	4-5	1	82	4	87.0	17.5
					86	4	95.2	9.5
TS-39	E 394-60,19%	25	4-5	1	82	4	89.9	20.0
					84	4	95.5	15.7
					86	4	97.0	11.6
					88	4	97.8	8.7
TS-40	E 394-60,19%	27	4-5	1	82	4	88.0	15.2
					88	4	94.0	12.4
TS-41	E 394-60,19%	25	4-5	1	82	6	88.2	22.0
					84	6	95.0	14.8
					86	6	97.2	11.6
					88	6	98.2	7.9
TS-42	E 394-60,19%	25	4-5	1	82	2	77.4	26.0
					84	2	90.0	17.5
TS-43	E 400-25,19%	20	4-5	1	86	5	93.5	27.0
TS-44	E 400-25,19%	25	4-5	1	86	5	95.5	24.2
(Support: Gelman α-6, Cellulose, Pore size 0.45 microns)								
TS-4	E 398-3, 25%	25	5	1	85	Cooling down	96.5	11.5
TS-5	E 398-3, 25%	25	5	1	85	4	98.6	4.55
TS-6	E 398-3, 25%	25	5	1	85	4	98.5	6.19

TABLE IV. Continued

Run No.	Casting Solution	Solvent Evap. Time (sec.)	Gelation Temp(°C)	Gelation Time (hr)	Heat Treatment Temp (°C)	Heat Treatment Time(min.)	%SR	WF GSFD
TS-8	E 398-3, 25%	23	5	1	85	Cooling down	98.0	10.0
TS-10	E 394-45,14%	23	5	1	85	4	90.0	20.0
TS-11	E 398-3, 25%	23	5	1	85	4	98.0	7.2
TS-12	E 398-3, 25%	23	5	1	85	Cooling down	99.0	5.6
TS-15	E 398-3, 25%	23	5	1	83	5	97.5	9.6
TS-16	E 398-3, 25%	24	5	1	84	5	97.7	5.0
TS-17	E 398-3, 25%	24	5	1	84	5	98.0	5.1
TS-18	E 398-10,21%	25	5	1	84	4	93.0	12.8
TS-20	E 394-60,16.5%	25	5	1	84	4	83.5	14.5
TS-21	E 398-10,21%	25	5	1	84	4	84.2	7.54
TS-22	E 394-60,16.5%	23	5	1	84	4	71.0	6.7
TS-23	E 394-60,16.5%	27	5	1	84	4	78.6	10.8
TS-24	E 394-60,16.5%	25	5	1	84	4	77.1	9.9
TS-25	E 398-10,21%	25	5	1	84	4	85.5	14.8
TS-26	E 398-10,21%	25	5	1	84	4	97.8	4.98
TS-27	E 398-10,21%	23	5	1	84	4	97.4	6.7
TS-30	E 398-10,21%	22	5	1	84	4	95.9	6.0
(Support: Porous 316 Stainless Steel, Pore size 5 microns)								
TS-9	E 398-3, 25%	23	5	1	83	4	97.3	4.68
TS-13	E 398-3, 25%	24	5	1	84	5	92.5	3.2
TS-19	E 398-10,21%	30	5	1	84	4	97.3	5.4

TABLE V. EFFECT OF TYPE OF CELLULOSE ACETATE

Run #	Type of Cellulose Acetate	WF, GSFD	%SR	Ave. WF, GSFD	Ave. %SR
TS-45	E394-60	12.9	95.4		
TS-46	"	12.7	96.3		
TS-50	"	13.4	95.8	13.0	95.8
TS-51	E394-45	12.7	96.4		
TS-52	"	10.8	96.8	11.8	96.6
TS-47	E398-10	11.9	96.8		
TS-48	"	9.6	96.5		
TS-49	"	11.5	96.4	11.0	96.6
TS-53	E398-3	12.9	92.7		
TS-54	"	13.2	93.8	13.1	93.3
TS-55	E400-25	14.9	96.3		
TS-56	"	12.5	97.1	13.7	96.7

Cast on Versapor 6429, Gelman (Epoxy, .9 microns).

Casting solution composition: Cellulose Acetate 21.9%, Formamide 31.2%, Acetone 46.9%.

Casting environment: 24.5°C, 50% humidity.

Solvent evaporating time: 25 sec.

Gelation: 4-5°C, 1 hr in water.

Heat treatment: 85↘83°C, 5 min.

TABLE VI. EFFECT OF TYPE OF CELLULOSE ACETATE AND OPERATING PRESSURE

Run #	Type of C.A.	Solv. Ev.Time,sec.	Heat Treatment Temp.°C	Time,min.	600 Psi. WF,GSFD	%SR	900 Psi. WF,GSFD	%SR	1200 Psi. WF,GSFD	%SR	1500 Psi. WF,GSFD	%SR
					Operating Pressure							
TS-163	E400-25	25	85\83	5	18.6	93.0	24.9	94.1	28.4	94.6	31.8	94.8
TS-166	"	25	"	5	18.8	93.2	24.7	94.3	28.7	94.9	32.0	95.1
				Ave.	18.7	93.1	24.8	94.2	28.6	94.8	31.9	95.0
TS-164	E400-25	5	83\81,86	5,4,Cell	20.9	92.5	28.2	94.5	32.9	95.4	36.9	95.7
TS-165	"	5	"	"	24.7	87.8	32.2	91.2	37.4	92.9	41.4	93.6
				Ave.	22.8	90.2	30.2	92.9	35.2	94.2	39.2	94.7
TS-155	E394-60	25	85\83	5	9.4	94.6	12.9	95.9	15.0	95.9	16.4	96.1
TS-158	"	25	"	5	10.0	95.3	14.1	96.4	16.0	96.4	17.4	96.5
				Ave.	9.7	95.0	13.5	96.2	15.5	96.2	16.9	96.3
TS-156	E394-60	5	83\81,86	5,4,Cell	14.3	95.6	20.2	96.6	23.0	96.7	25.4	96.7
TS-157	"	5	"	"	15.3	95.5	21.9	96.6	24.9	96.6	27.5	96.6
				Ave.	14.8	95.6	21.1	96.6	24.0	96.7	26.5	96.7
TS-159	E394-45	25	85\83	5	9.2	93.5	11.8	92.9	13.2	93.6	15.3	94.6
TS-162	"	25	"	5	10.8	96.3	16.0	97.3	18.1	97.4	20.2	97.5
				Ave.	10.0	94.9	13.9	95.1	15.7	95.5	17.8	96.1
TS-160	E394-45	5	83\81,86	5,4,Cell	12.9	96.8	18.4	97.7	21.9	97.7	24.4	97.8
TS-161	"	5	"	"	14.8	95.7	21.1	97.0	24.4	97.2	29.6	97.2
				Ave.	13.9	96.3	19.8	97.4	23.2	97.5	27.0	97.5

Casting solution composition: Cellulose Acetate 21.9%, Formamide 31.2%, Acetone 46.9%.

Casting environment: 24.5°C, 50% humidity, Gelation: 4-5°C, 1 hr. in water.

Cast on Versapor 6429, Gelman (Epoxy, .9 microns).

TABLE VII. EFFECT OF PERCENT CELLULOSE ACETATE CONTENT

Run #	Type of Cellulose Acetate	%Cellulose Acetate (Formamide:Acetone=1:1.5)		WF, GSFD	%SR
TS-67	E400-25	19.4		23.2	84.6
TS-68	"	19.4		22.0	86.8
			Ave.	22.6	85.7
TS-55	E400-25	21.9		14.9	96.3
TS-66	"	21.9		12.5	97.1
			Ave.	13.7	96.7
TS-71	E400-25	24.2		9.7	97.5
TS-72	"	24.2		10.1	97.3
			Ave.	9.9	97.4
TS-73	E400-25	20.6		14.9	94.5
TS-74	"	20.6		18.9	91.3
			Ave.	16.9	92.9
TS-65	E400-25	16.7		31.5	54.2
TS-66	"	16.7		34.5	48.4
			Ave.	33.0	51.3
TS-45	E394-60	21.9		12.9	95.4
TS-46	"	21.9		12.7	96.3
TS-50	"	21.9		13.4	95.8
			Ave.	13.0	95.8
TS-57	E394-60	16.7		29.2	71.0
TS-58	"	16.7		23.4	81.2
			Ave.	26.3	76.1
TS-59	E394-60	19.4		17.9	89.6
TS-60	"	19.4		18.1	92.6
			Ave.	18.0	91.1
Ts-61	E394-60	24.2		6.3	96.9
TS-62	"	24.2		6.4	97.3
			Ave.	6.4	97.1
TS-63	E394-60	20.6		13.8	93.8
TS-64	"	20.6		13.0	95.5
			Ave.	13.4	94.7

Casting environment: 24.5°C, 50% humidity.
Solvent evaporating time: 25 sec.
Gelation: 4-5°C, 1 hr in water.
Cast on Versapor 6429, Gelman (Epoxy, .9 microns).

TABLE VIII. EFFECT OF HEAT TREATMENT TEMPERATURE

Run #	% Cellulose Acetate		Heat Treatment Temperature °C 83↘81 WF,GSFD	83↘81 %SR	83 WF,GSFD	83 %SR	85 WF,GSFD	85 %SR	87 WF,GSFD	87 %SR	89 WF,GSFD	89 %SR
TS-69	19.4		35.1	77.5	28.5	89.5	23.3	93.4	18.9	96.4	14.5	96.6
TS-70	19.4		35.1	78.0	30.2	89.5	25.8	93.6	19.0	96.6	15.1	98.2
		Ave.	35.1	77.8	29.4	89.5	24.6	93.5	19.0	96.5	14.8	97.4
TS-75	20.6		18.5	93.0	16.2	97.0	13.0	98.0	10.5	98.5	8.1	98.7
TS-76	20.6		23.0	90.6	20.9	96.0	17.8	97.5	13.9	98.4	10.2	98.6
		Ave.	20.8	91.8	18.6	96.5	15.4	97.8	12.2	98.5	9.2	98.7
TS-77	21.9		21.6	94.3	19.7	97.1	16.0	98.0	14.8	98.2	10.4	98.9
TS-78	21.9		21.6	93.2	15.3	97.8	13.0	98.2	11.7	98.5	8.1	98.8
		Ave.	21.6	93.8	17.5	97.5	14.5	98.1	13.3	98.4	9.3	98.9

Casting solution: E400-25, Formamide:Acetone = 1:1.5

Solvent evaporating Time: 25 sec.

Gelation: 4-5°C, 1 hr. in water.

Heat treatment: initial heat treatment at 83↘81°C, 5 min.; 83, 85, 87, 89°C, 5 min. in test cell by using same membrane.

Cast on Versapor 6429, Gelman (Epoxy, 9. microns)

TABLE IX. EFFECT OF HEAT TREATMENT TIME AND TEMPERATURE

Run #	Heat Treatment Temp.°C	Heat Treatment Time, (min.) 2 WF,GSFD	2 %SR	4 WF,GSFD	4 %SR	8 WF,GSFD	8 %SR	12 WF,GSFD	12 %SR	16 WF,GSFD	16 %SR
TS-182	80			44.7	68.4	41.2	76.0	37.1	78.6	36.2	80.0
TS-183	80			43.3	67.4	41.6	75.0	36.5	77.8	35.7	80.0
			Ave.	44.0	67.9	41.4	75.5	36.8	78.2	36.0	80.0
TS-181	82			36.0	83.8	33.2	88.2	30.8	89.5	29.6	90.6
TS-184	82			35.8	81.3	33.4	87.0	29.4	89.5	28.4	91.2
			Ave.	35.9	82.6	33.3	87.6	30.1	89.5	29.0	90.9
TS-180	84			29.2	90.6	26.4	92.4	24.4	92.9	23.3	93.9
Ts-185	84			27.7	90.3	26.8	91.0	24.0	93.8	22.6	94.1
			Ave.	28.5	90.5	26.6	91.7	24.2	93.4	23.0	94.0
TS-179	86			20.5	96.2	18.4	96.3	16.7	96.5	16.0	96.7
TS-186	86			20.4	96.3	19.1	96.3	16.5	96.6	15.7	96.8
			Ave.	20.5	96.3	18.8	96.3	16.6	96.6	15.9	96.8
TS-189	86	23.8	92.3	21.9	94.6						
TS-190	86	22.4	93.1	20.8	96.4						
	Ave.	23.1	92.7	21.4	95.5						
TS-187	88	19.1	96.9	14.1	97.4						
TS-188	88	17.8	97.1	16.0	97.0						
	Ave.	18.5	97.0	15.1	97.2						

Casting solution composition: E400-25, 21.9%, Formamide 31.2%, Acetone 46.9%.
Casting environment: 24.5°C, 50% humidity. Solvent Evaporating Time: 5 sec.
Gelation: 0°C, 1 hr. Cast on Versapor 6429, Gelman (Epoxy, .9 microns).
Heat treatment: initial heat treatment time, 2 or 4 min. with each increment of heating time, 2 or 4 min. in test cell.

TABLE X. EFFECT OF SOLVENT EVAPORATING TIME

Run #	% Cellulose Acetate	Solvent Ev. Time, Sec.	Heat Treatment Temperature °C 80↘78 WF,GSFD	80↘78 %SR	83 WF,GSFD	83 %SR	88 WF,GSFD	88 %SR	93 WF,GSFD	93 %SR
TS-108	19.4	10	65.3	40.0	43.5	68.4	25.1	89.7		
TS-109	19.4	10	68.4	38.1	45.6	69.4	25.6	91.4	10.3	95.8
		Ave.	66.9	39.1	44.6	68.9	25.4	90.6	10.3	95.8
TS-110	19.4	25	54.5	23.1	38.3	66.6	17.4	90.0		
TS-111	19.4	25	55.2	25.0	38.3	75.0	16.5	93.8		
		Ave.	54.9	24.1	38.3	70.8	17.0	91.9		
TS-116	19.4	40	39.0	58.3	22.3	88.5	14.4	92.1		
TS-117	19.4	40	39.3	57.8	23.0	88.9	13.2	93.0		
		Ave.	39.2	58.1	22.7	88.7	13.8	92.6		
TS-121	21.9	5	36.2	75.0	27.8	92.8	15.3	98.0		
TS-122	21.9	5	35.2	75.0	28.2	92.9	14.6	98.2		
		Ave.	35.7	75.0	28.0	92.9	15.0	98.1		
TS-101	23.1	25	23.7	85.3	17.4	95.8	8.0	97.8		
TS-102	23.1	25	24.4	84.7	17.4	96.4	7.8	97.8		
		Ave.	24.1	85.0	17.4	96.1	7.9	97.8		
TS- 99	23.1	40	14.5	87.5	9.4	96.6	4.5	97.8		
TS-100	23.1	40	15.8	87.5	9.9	96.3	4.4	97.4		
		Ave.	15.2	87.5	9.7	96.5	4.5	97.6		
TS- 97	23.1	10	30.3	82.4	22.3	96.0	12.5	97.8	5.2	98.3
TS- 98	23.1	10	27.1	86.2	20.9	96.6	11.5	98.3	4.4	98.8
		Ave.	28.7	84.3	21.6	96.3	12.0	98.1	4.8	98.6

Casting solution: E400-25, Formamide: Acetone = 1:1.5
Casting environment: 24.5°C, 50% humidity. Gelation: 4-5°C, 1 hr. in water.
Heat treatment: initial heat treatment, 80↘78°C, 5 min., 83, 88 and/or 93°C, 5 min. in test cell by using same membrane.
Cast on Versapor 6429, Gelman (Epoxy, .9 microns).

TABLE XI. EFFECT OF GELATION TEMPERATURE

Run #	Type of Cellulose Acetate	Gelation Temp. °C	Operating Pressure, Psi. 600 WF,GSFD	600 %SR	900 WF,GSFD	900 %SR	1200 WF,GSFD	1200 %SR	1500 WF,GSFD	1500 %SR
TS-167	E398-10	0	14.6	96.6	21.2	97.5	25.1	97.9	28.9	98.0
TS-170	"	0	14.6	95.2	21.2	96.5	24.7	96.9	27.8	97.1
		Ave.	14.6	95.9	21.2	97.0	24.9	97.4	28.4	97.6
TS-168	E398-10	24.5	19.5	87.8	24.7	90.5	27.8	92.0	30.8	92.5
TS-169	"	24.5	16.4	90.5	20.5	92.7	22.8	93.7	25.4	94.1
		Ave.	18.0	89.2	22.6	91.6	25.3	92.9	28.1	93.3
TS-171	E400-25	0	19.1	94.4	27.1	95.9	32.4	96.4	35.3	96.6
TS-174	"	0	17.9	95.5	25.6	96.6	30.3	96.9	33.9	97.1
		Ave.	18.5	95.0	26.4	96.3	31.4	96.7	34.6	96.9
TS-172	E400-25	24.5	23.7	88.5	32.4	91.2	37.6	92.1	40.4	92.7
TS-173	"	24.5	23.5	89.5	31.3	92.1	37.1	92.9	40.2	93.6
		Ave.	23.6	89.0	31.9	91.7	37.4	92.5	40.3	93.2

Casting solution: Cellulose Acetate 21.9%, Formamide 31.2%, Acetone 46.9%.

Casting environment: 24.5°C, 50% humidity.

Solvent evaporating time: 5 sec.

Gelation: 1 hr. in water.

Heat treatment: 86°C, 4 min.

Cast on Versapor 6429, Gelman (Epoxy, .9 microns).

TABLE XII. THE PROPERTIES OF EPOXY POROUS SUPPORT

Run #	Support	Solv.Ev. Time,sec.	Gelation Temp°C	Gelation Time,hr.	Heat Treatment Temp°C	Heat Treatment Time,min.	WF, GSFD	%SR
TS- 79	Ep. .9	25	4-5	1	85↘83	5	13.4	94.5
TS- 80	Ep. 5.	25	4-5	1	85↘83	5	17.4	90.7
TS- 85	—	25	4-5	1	85↘83	5	12.5	95.2
TS- 86	Ep. .9	25	4-5	1	85↘83	5	13.8	95.3
TS-124	Reuse .9	5(less)	4-5	1	84↘82	5	24.4	90.6
					84	5(cell)	21.2	96.2
TS-125	Ep. .9	5	4-5	1	84↘82	5	25.1	89.3
					84	5(cell)	22.3	95.4
TS-128	Reuse .9	5	4-5	1	83↘81	5	26.6	87.6
					83	5(cell)	21.7	88.0
TS-129	Reuse .9	5	4-5	1	83↘81	5	31.0	89.4
					83	5(cell)	24.0	93.0
TS-105	Ep. .9	5	4-5	1	83↘81	5	26.8	87.8
TS-107	Ep. .9	5	4-5	1	83	3	29.2	87.8
TS-103	Ep. .9	5	4-5	1	83↘81	5	26.8	91.8

Casting solution composition: E400-25, 21.9%, Formamide 31.2%, Acetone 46.9%.

Casting environment: 24.5°C, 50% humidity.

TABLE XIII. THE PROPERTIES OF EPOXY POROUS SUPPORT

Run#	Type of Gelation C.A.	Temp.°C	Heat Treatment Temp°C	Time,min.	Operating Pressure, Psi. 600 WF,GSFD	%SR	900 WF,GSFD	%SR	1200 WF,GSFD	%SR	1500 WF,GSFD	%SR
TS-136	Commercial Membrane				8.2	96.1	13.9	96.9	18.6	96.9	21.4	96.8
TS-137	"				7.3	95.8	12.2	96.6	15.8	96.7	18.3	96.6
TS-138	"				8.7	95.1	14.2	96.1	16.9	96.3	19.0	96.0
TS-139	"				6.1	94.1	9.1	95.4	11.5	95.6	13.4	95.7
				Ave.	7.6	95.3	12.4	96.3	15.7	96.4	18.0	96.3
TS-171	E400-25	0	86	4	19.1	94.4	27.1	95.9	32.4	96.4	35.3	96.6
TS-174	"	0	86	4	17.9	95.5	25.6	96.6	30.3	96.9	33.6	97.1
				Ave.	18.5	95.0	26.4	96.3	31.4	96.7	34.5	96.9
TS-167	E398-10	0	86	4	14.6	96.6	21.2	97.5	25.1	97.9	28.9	98.0
TS-170	"	0	86	4	14.6	95.2	21.2	96.5	24.7	96.9	27.8	97.1
				Ave.	14.6	95.9	21.2	97.0	24.9	97.4	28.4	97.6
TS-191*	E400-25	0	86	4	10.4	95.9	15.8	96.6	20.0	97.3	23.5	97.8
TS-192*	E400-25	0	86	4	9.7	96.5	14.4	97.2	18.3	97.8	21.2	98.1
				Ave.	10.1	96.2	15.1	96.9	19.2	97.6	22.4	98.0
TS-193**	E400-25	0	86	4	15.0	93.8	23.5	94.6	29.6	95.8	34.8	96.1
TS-194**	E400-25	0	86	4	16.0	94.2	24.4	95.5	29.8	96.4	35.1	96.9
				Ave.	15.5	94.0	24.0	95.1	29.7	96.1	35.0	96.5
TS-141	E400-25	4-5	84	8	23.0	93.4	31.4	94.7	37.0	95.0	40.7	95.2
TS-146	E400-25	4-5	84	8	18.1	95.3	24.9	96.3	29.2	96.8	31.8	96.9
				Ave.	20.6	94.4	28.2	95.5	33.1	95.9	36.3	96.1

Casting solution composition: Cellulose Acetate 21.9%, Formamide 31.2%, Acetone 46.9%.
Casting environment: 24.5°C, 50% humidity; Gelation: 1 hr. in water.

*Cast on glass, edges, not fixed.

**Cast on glass, edges, fixed.

TABLE XIV. COMPARISON OF COMMERCIAL MEMBRANES AND MEMBRANES BY DIRECT CASTING ON POROUS SUPPORT

Run #	Gelation Temp°C	Gelation Time, hr.	Heat Treatment Temp°C	Heat Treatment Time, min.	WF, GSFD	%SR	Remarks
TS-175	0	1	86	4	20.1	95.7	Opt 115 hrs
TS-176	0	1	86	4	20.5	94.7	"
TS-177	0	1	86	4	20.9	94.5	"
TS-178	0	1	86	4	20.9	94.9	"
TS-147	4-5	1	85	4	24.3	87.4	Opt 92 hrs
TS-149	4-5	1	85	4	24.2	92.1	"
TS-148	4-5	1	86	4	22.5	94.3	Opt 92 hrs
TS-150	4-5	1	86	4	20.0	95.1	"
TS- 81	Commercial Membrane, DSI				10.9	93.5	Opt 25 hrs
TS- 82	"				11.9	89.9	"
TS- 83	"				10.1	96.2	"
TS- 84	"				12.4	96.1	"
TS-195*	0	1	86	4	21.1	91.0	Opt 115 hrs
TS-196*	0	1	86	4	22.4	91.7	"
TS-197*	0	1	86	4	20.1	91.6	"
TS-198*	0	1	86	4	22.9	88.8	".
TS-204**	0	1	86	4	18.2	95.5	Opt 49 hrs
TS-205**	0	1	86	4	16.0	97.2	"

Casting solution composition: E400-25, 21.9%, Formamide 31.2%, Acetone 46.7%.

Casting environment: 24.5°C, 50% humidity.

Solvent evaporating time: 5 sec.

Cast on Versapor 6429, Gelman (Epoxy, .9 microns).

*Cast on Versapor 6424, Gelman (Epoxy, 5 microns).

**Cast on Versapor 6429, Gelman with 2 layer masking tapes clearance.

TABLE XV. EFFECT OF FEED FLOW RATE ON MEMBRANE PERFORMANCE

Run #	Support Pore Size (microns)	Average Feed Flow Velocity, cm/sec. .67 WF,GSFD	.67 %SR	1.75 WF,GSFD	1.75 %SR	3.37 WF,GSFD	3.37 %SR	7.01 WF,GSFD	7.01 %SR	12.3 WF,GSFD	12.3 %SR
TS-199	.9	15.5	89.9	17.7	94.2	19.0	95.7	19.9	96.4	20.4	96.5
TS-201	.9	16.9	84.2	19.3	92.9	21.6	95.0	22.2	95.8	22.8	96.0
	Ave.	16.2	87.1	18.5	93.6	20.3	95.4	21.1	96.1	21.6	96.3
TS-200	5	17.1	83.3	19.5	90.2	21.4	93.0	22.2	94.3	23.0	94.4
TS-202	5	15.8	87.2	18.4	93.7	19.8	95.5	20.4	96.2	20.7	96.3
	Ave.	16.5	85.3	19.0	92.0	20.6	94.3	21.3	95.3	21.9	95.4

Cast on Gelman Epoxy support.

Casting solution composition: Cellulose Acetate, E400-25, 21.9%, Formamide 31.2%, Acetone 46.9%.

Casting environment: 24.5°C, 50% humidity.

Solvent evaporating time: 5 sec.

Gelation: 0°C, 1 hr. in water.

Heat treatment: 86°C, 4 min.

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