The fluidized bed as a turbulence promoter in the reverse osmosis desalination process

by Juin-yih Lai

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:
The reverse osmosis process is characterized by the use of pressure in excess of osmotic pressure to force fresh water at ambient temperature through a selective membrane capable of rejecting dissolved salts. It is a technically feasible process with good thermodynamic efficiency, flexibility, and simplicity.

At this time, total cost for desalinated water by the reverse osmosis process is still high, mainly due to the low flux obtained and the short membrane life. The purpose of this research was to determine the feasibility of using a fluidized bed to improve the performance and hence to decrease the product cost of reverse osmosis desalination. Five different sizes of glass beads and six different kinds of membranes' have been tested under a variety of conditions in l4l runs. A brief economic study was also made.

A glass bead size of approximately 0.018,5-inch diameter appears best for this fluidized bed in the brine flow velocity range between 0.57 and 0.97 cm/sec. The significance of using the fluidized bed with these glass beads was to increase the salt rejection and to increase the water flux by 21.7 to 35.8% for nylon supported membranes. The most significant effects were on membranes where concentration polarization was the greatest.

It was determined that different membrane positions and cell geometry affected the performance of the membranes.. The flux decline with time for cellulose acetate membranes on nylon supports was greatly decreased.

A study conducted on scale formation shows that by employing a fluidized bed system with a scale-forming feed, both the water flux and membrane life are significantly improved. In view of the economics, the most significant effect of using the fluidized bed is to decrease the considerable cost of membrane replacement.

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ABSTRACT

The reverse osmosis process is characterized by the use of pressure in excess of osmotic pressure to force fresh water at ambient temperature through a selective membrane capable of rejecting dissolved salts. It is a technically feasible process with good thermodynamic efficiency, flexibility, and simplicity.

At this time, total cost for desalinated water by the reverse osmosis process is still high, mainly due to the low flux obtained and the short membrane life. The purpose of this research was to determine the feasibility of using a fluidized bed to improve the performance and hence to decrease the product cost of reverse osmosis desalination. Five different sizes of glass beads and six different kinds of membranes have been tested under a variety of conditions in 141 runs. A brief economic study was also made.

A glass bead size of approximately 0.0185-inch diameter appears best for this fluidized bed in the brine flow velocity range between 0.57 and 0.97 cm/sec. The significance of using the fluidized bed with these glass beads was to increase the salt rejection and to increase the water flux by 21.7 to 35.8% for nylon supported membranes. The most significant effects were on membranes where concentration polarization was the greatest.

It was determined that different membrane positions and cell geometry affected the performance of the membranes. The flux decline with time for cellulose acetate membranes on nylon supports was greatly decreased.

A study conducted on scale formation shows that by employing a fluidized bed system with a scale-forming feed, both the water flux and membrane life are significantly improved. In view of the economics, the most significant effect of using the fluidized bed is to decrease the considerable cost of membrane replacement.

I. INTRODUCTION

The water problem--the problem of how to have water in adequate quantity and of adequate quality, available at a reasonable cost, when and where needed--is one of worldwide importance.

A new conventional source of water may be developed today for a cost of 13 cents to 70 cents per thousand gallons. It is estimated that by 1980 this cost will have risen to 20 cents to 90 cents per thousand gallons (7). In terms of improvements in technology and/or equipment for conventional sources of water, there is little potential for cost reduction. Clearly, desalination will be a part of the solution of the total water problem.

Many processes have been tried for desalination. Some of them have been used in actual large desalination plants in many countries. Those are: multistage flash distillation, electrodialysis (brackish water only), vapor compression distillation, direct freezing, and reverse osmosis.

Saline water conversion is still in its infancy; therefore the cost of desalination is still relatively high. However, in some areas where the conventional water supplies are very meager, desalination is even now competitive with other means of obtaining usable water.

It was reported that the cost of fresh water obtained by a small desalination plant (multistage flash evaporation) was $0.80 to $1.10 per thousand gallons, and for a large plant the cost was $0.20 to $0.40 per thousand gallons (50 million gallons per day product or more) with present technology (7).

Recently, reverse osmosis has become one of the most interesting processes. Possibly the most important reason is the development of membranes which combine good salt rejection with moderately high water flux. Second, is the appealing conceptual simplicity of the method, which essentially consists of removal of salt by filtering it away from water under pressure.

Third, this process tends to avoid scaling problems and to minimize corrosion since it always operates at ambient temperature. Fourth, the theoretical work for desalting sea water by reverse osmosis at 25°C is 2.65 kilowatt-hours per thousand gallons. The energy consumption of multistage flash distillation and long-tube vertical evaporator distillation, for example, is six times that of the reverse osmosis process (26).

The reverse osmosis process is characterized by the use of pressure in excess of the osmotic pressure to force fresh water at ambient temperature through a selective membrane capable of rejecting dissolved salts. The process name is derived from the phenomenon

whereby water under an applied pressure driving force flows in a reverse direction to the flow in an osmotic experiment where the driving force is the concentration gradient.

Many theories have been proposed for the mechanism of water transport through the membrane. According to Reid and Breton (18), the semipermeability of cellulose acetate is caused by regions of bound water within the membrane, and the transfer of water and ions through the membrane is governed by two different mechanisms. Those ions and molecules which can associate with the membrane through hydrogen bonding actually combine with the membrane and are transported through it by alignment-type diffusion; those which can not enter into hydrogen bonding with the membrane are transported by hole-type diffusion with no desalting.

A solution-diffusion mechanism is favored by Riley et al. (19), whose transport equations are apparently limited to their concept of perfect membranes, which are presumably those which have a completely nonporous surface structure. Banks and Sharples (3) also consider that the mechanism of reverse osmosis is one of diffusive flow through the pore-free layer on the membrane surface. Sherwood et al. (22) proposed that water and solute cross the membrane by parallel processes of diffusion and pore flow.

According to Sourirajan's (24) preferential sorption-capillary flow mechanism, reverse osmosis separation is the combined result of an interfacial phenomenon and fluid transport under pressure through capillary pores. He proposed that a thin film of pure water exists at the liquid-membrane interface. For pores with diameters greater than twice the film thickness, both pure water and saline water will flow. Through the smaller pores, only pure water will pass.

The most important part of reverse osmosis equipment is the membrane. The important membrane properties are water flux, salt rejection, and membrane life. Flux is usually given in gallons/ft^2-day (GSFD) and salt rejection is usually given as percent salt rejection or salt reduction factor = 100/(100-percent rejection). Many kinds of membranes have been tried for reverse osmosis, some of them with high rejection but very low flux, such as ethyl cellulose-poly-acrylic acid membranes, and some of them with high flux but low rejection, such as poly-acrylonitrile membranes.

Cellulose acetate is the most promising membrane which provides high rejection and moderately low flux. The first recognition that salt rejection by membranes might be useful in desalination seems to have been by Reid at the University of Florida (26). Reid and Breton (18) obtained a maximum water flux of 0.945 GSFD and salt

reduction factor of 25 (96% salt rejection) from their cellulose acetate membranes. Since then, cellulose acetate membranes have been improved quite rapidly. A ternary casting solution of cellulose acetate, formamide, and acetone was found to produce good membranes. Membranes from this casting solution gave fluxes of 20 GSFD, salt rejections of 95% and membrane life of six months (1). Today this type of cellulose acetate membrane is the most widely used.

Total cost for products by the reverse osmosis process, using cellulose acetate membranes, is still high. It is mainly caused by the low flux and short membrane life.

General Atomic Division of General Dynamics has proposed a design for a one million gallon per day reverse osmosis pilot plant. The minimum cost of fresh water produced by this pilot plant was estimated to be 75.5 cents per thousand gallons from sea water. The water flux of their membranes is about 10 GSFD under 1440 psi pressure. If the flux can be increased to 20 GSFD keeping the other conditions the same, for example, the cost of fresh water obtained from this pilot plant could be reduced to about 50 cents per thousand gallons (26).

In this pilot plant the cost of membrane replacement is about one third of the total cost. It is reported that the labor

cost of membrane replacement would be much higher than the cost of the membrane itself. It is believed that the membranes cast directly onto porous supports could reduce the high labor cost of membrane replacement, as a shorter time and more simple procedure would be required to replace the membrane.

Wang (28) has investigated a membrane formed by using direct casting on porous supports. His membrane, cast from cellulose acetate (E-400-25, 21.9%), formamide (31.2%), acetone (46.9%), ternary solution on rigid porous epoxy filled fiberglass supports (Gelman Versapor, 0.9 micron), can provide an average water flux of 21 GSFD and 95% salt rejection.

Lai (15) showed that other porous materials also have promise as supports. Polyvinyl chloride was most promising. The average water flux and salt rejection based on a 124-hour-long run were 23.5 GSFD and 95.7%, respectively. Casting conditions were the same as those used by Wang except heat treatment temperature was 84°C instead of 86°C.

Coverdell (6) used small diameter cylindrical porous media as supports to provide a high membrane area per unit volume of equipment. His was one of the approaches to decrease the total cost for products by the reverse osmosis process.

When brine is pumped through a salt-rejection membrane, the salt held back concentrates in the layer adjacent to the membrane surface. This salt build-up in the boundary layer is called 'concentration polarization'. The concentration polarization has been an important problem of high water flux membranes in reverse osmosis desalination. The salt concentration polarization has several effects which are detrimental to the desalination process. First of all, concentration polarization results in the effective osmotic pressure at the membrane surface exceeding the osmotic pressure of the bulk saline water and hence lowers the water flux. In addition, the concentration polarization has a detrimental effect by increasing the salinity of the product water. The useful life of the osmotic membrane is often shortened by increased salinity of the saline water and concentration polarization will aggravate this effect.

Several analytical studies of concentration polarization have been reported with particular reference to saline water conversion (5,8,23). These studies assume that the membrane exhibits either complete salt rejection or incomplete salt rejection at a constant level. A more desirable approach to the subject is given by Sherwood et al. (22), who have coupled the equations of solute and solvent transport through the membrane to the theory of concentration

polarization. A similar approach is offered by the Kimura-Sourirajan (14) analysis, which is based on a generalized pore diffusion model applicable for the entire possible range of solute separation.

In view of the detrimental effects of concentration polarization, it is logical to consider ways by which the effect of salt build-up can be reduced. Tien (28) proposed a system consisting of impermeable relaxation sections placed alternately between semi-permeable membrane sections. The high concentration at the boundary of the impermeable section can be attenuated by molecular diffusion and convection which redistributes salt more uniformly across the flow channel. It is possible that by proper arrangement of the impermeable sections and membrane sections, one could obtain greater production capacity in a reverse osmosis system even though a fraction of the conduit is nonproductive.

Spiral turbulence promoters positioned away from the membrane surface by small wire runners were used by Thomas and Watson (27) to get reduction of concentration polarization.

The semi-empirical analyses of Brian (5) and Sherwood (22) show that the polarization effect is a function of desalinized water flux and axial velocity. Sheppard and Thomas (20) maintained a very high axial velocity (24 ft/sec) which provided a high turbulence to decrease the polarization problem.

In order to provide a combination of higher axial velocity and greater turbulence, Hamer (11) used movable glass spheres in a tubular membrane unit.

A cavitational method to increase turbulence was investigated by Harvey (12). He used ultrasonic transducers close to the membrane to generate a high frequency vibration. Huff (13) proposed an infrasonic activation to avoid the destructive effects that are associated with high frequency vibration and cavitation.

The reason for trying the glass-bead fluidized bed approach to reverse osmosis by the author was to establish high turbulence at low feed velocity. The high turbulence was expected to increase the water flux and salt rejection through the membrane by decreasing the concentration polarization effect. A longer membrane life would be expected due to the fact that the fluidized bed decreases the salinity of the product water.

The object of the author's thesis was to determine the feasibility of using a fluidized bed to improve the performance of reverse osmosis desalination. Five different sizes of glass beads and six different kinds of membranes have been tested under a variety of operating conditions in 141 runs. A brief economic study was also made.

II. EQUIPMENT AND PROCEDURE

A. Membrane Fabrication Equipment

A constant temperature and humidity chamber was used for membrane casting of all runs. The chamber was constructed with a fiber glass body, a safety glass window (10-1/2+ 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 contained lights, a heater, cooler, fan, two salt solution containers, and a thermoprobe connected to an electronic temperature controller. The temperature was kept at 70°F and humidity was kept at 50% by using saturated $Ca(NO_3)_2 \cdot 4H_2O$ salt solution. A level aluminum surface with the dimensions of 8 inches by 5 inches was used for membrane casting in order to produce even membrane thicknesses.

B. Test Cells

The test cell shown in Figure 8 was made of stainless steel 304 blank flanges with 4.5" outside diameter and a 2" diameter test area. The membrane was supported by a 1/8-inch porous stainless steel plate (Grade H, pore size 5 microns, Pall Corp.) which was mounted between the two halves of the cell. This cell was originally designed for use without a fluidized bed and was used only for the preliminary study.

The test cell shown in Figure 9 was used for testing all membranes after Run 6 with or without a fluidized bed. The body of the

test cell, which was made of stainless steel 316, consisted of three parts: namely, front plate, frame, and back plate. These three parts were held together by twelve 5/16-inch stainless steel bolts, which were tightened stepwise to obtain a good seal. The space (3-3/4" x 1-3/4" x 7/8") inside the frame sandwiched between the front plate and the back plate was used as a fluidizing bed.

The porous stainless steel plates (pore size 40 microns, Mott Metallurgical Corp.) on the bottom entrance and the top exit were used to give uniform flow distribution and to prevent the glass beads from escaping, respectively. The membrane was supported by a porous stainless steel plate (pore size 5 microns, Pall Corp.) with the dimension 1-3/4 inches by 1-3/4 inches, which was glued in the back plate.

In order to increase the linear fluid velocities across the space without the fluidized bed, plexi-glass plates (3-3/4" x 1-3/4") of various thicknesses can be inserted inside the cell. These fillers were located against the front plate and served to reduce the volume of the cell.

As shown in Figure 10, glass beads were introduced into the fluidized bed through a hole on one side of the frame. The salt water under pressure was circulated through the entrance on the bot-

tom of the frame, and left through the top. The product water flowed through the membrane and its supporting porous steel plate into the receiver.

C. Membrane Test System

As shown in Figure 11, the test system consisted of a pump (Jaeco Model 753 S-8), surge tank, filter, test line, test cell, and a plastic feed tank with stirrer and cooler. All equipment was of plastic or stainless steel construction to eliminate corrosion.

The surge tank was used to keep a stable brine feed rate and the filter was used to maintain a clean system. The brine feed rate was controlled by a needle valve which was connected to the exit stream of the filter. Two pressure gauges were connected to the test cell to detect the pressure drop across the cell.

The system pressure was controlled with two back pressure regulators located at the filter and after the test cell. A high-pressure nitrogen cylinder was used to load the regulators. The temperature of the feed solution (1% NaCl) was kept at 25°C. The heat added by the pump and brine circulation was removed by cooling water. The pressure used for all runs was 800 psi.

A conductivity bridge (Industrial Instruments Model RC-16 B-2) was used in conjunction with a conductivity cell to analyze the con-

centration of salt water and product water. The relationship between concentration and resistance can be approximately expressed as:

$$C_t = \frac{6.4 - (t-25) \times 0.1}{(R_t)^{1.0496}}$$

where C_t = salt water concentration, moles/liter

t = temperature of conductivity measurement, °C

R_t = resistance at temperature t, ohms

This equation was used to calculate concentration from different temperature and resistance to make a plot of concentration versus resistance at different temperatures. This plot, Figure 12, was used to convert the resistance of every sample to concentration. Periodically this curve was checked against standard NaCl solutions.

D. Chemicals and Materials

Five kinds of glass beads with a density of 156 lb/ft^3 have been used. Three spherical glass beads made by 3M Company were tried first. Those with 0.0185-inch diameter were called No. 1 for this study; those with 0.011-inch diameter were designated No. 2, and those with 0.008-inch diameter, No. 3. A bigger size of spherical glass beads with 0.0394-inch diameter (called No. 4) made by Van Water & Rogers Company was used later. The irregular shaped glass beads with diameters between 0.0232 and 0.0328-inch (called No. 5)

which were obtained by washing and screening the developer for a Xerox machine were also considered.

The membranes used for all runs were cast on porous supports, nylon (#5055, Travis Mill Co.) or dacron (#601, Travis Mill Co.) materials.

The composition of the casting solution used in this study was cellulose acetate 21.9%, formamide 31.2%, and acetone 26.9% by weight. The E 398-10 cellulose acetate, containing 39.8% acetyl from lot No. AC-1466, was from Eastman Chemical Company. "Baker grade" formamide and "Baker analyzed" reagent grade acetone, both from Baker Chemical Company, were used.

E. Test Procedure

The following is the membrane fabrication procedure used for this study. The support was fixed on the aluminum plate with masking tape which was about 0.005 thick. A glass rod was used to spread the solution smoothly onto the support, with the tape as a thickness guide, in a constant temperature and humidity chamber. The cast solution was evaporated as long as needed. The aluminum plate was immersed with the membrane in ice water for one hour. Then the membrane was heat treated with the aluminum plate in hot water which had been heated to the required temperature. The heat treatment time

used was four minutes. The membrane was immersed in cold water until it was tested. It was cut to the dimension to fit the test cell when it was tested.

The membranes were firmly mounted in the test cells with the cellulose acetate film facing the high pressure side. The pump was started and the pressure gradually increased until 800 psi was reached. Cold water to the cooler was adjusted to keep the temperature of the feed solution at 25°C. The feed concentration was checked every day. A product water sample was taken once every hour or two and most tests were run two to four hours.

III. RESULTS

One hundred and forty-one runs have been made to determine the feasibility of using a fluidized bed to improve the performance of reverse osmosis desalination. The results of all these tests are tabulated in Table XIII.

PRELIMINARY TESTS

Several runs were made for preliminary tests with the cell shown in Figure 8, which was designed for use without a fluidized bed. With the cell positioned vertically, the salt water entered through the lower entrance and left through the upper hole. Most of these runs showed that by using a fluidized bed both the water flux and salt rejection were improved. At the end of a 124-hour run with a fluidized bed, the salt rejection decreased only slightly from the original value. It appeared that there was no destruction caused by glass beads on the membrane surface after a long running time. The geometry of this cell was improper to achieve a uniform fluidized bed. When a plexi-glass plate was used instead of one stainless steel plate, the fluidization could be visually observed. Even at high brine flow velocities approximately 1/4 of the bed was not fluidized. To improve the flow distribution, a new experimental cell was deemed necessary.

MINIMUM FLUIDIZED BED VELOCITY

A plexi-glass plate was used instead of a front steel plate as shown in Figure 9 in order to visually observe the minimum fluidized bed velocity. The brine (1 wt.%) was pumped through the cell at atmospheric pressure. This velocity for glass bead No. 1 was 0.385 cm/sec; No. 2, 0.254; No. 3, 0.152; No. 4, 0.86; No. 5, 0.515.

THE BASIS FOR COMPARISON BETWEEN RESULTS WITH FLUIDIZED BED AND WITHOUT FLUIDIZED BED

Increasing brine flow velocity resulted in increased water flux and salt rejection without a fluidized bed although it increased only slightly for a brine flow rate above 6 cm/sec. This is also true for a fluidized bed in the brine flow velocity range between 0.57 and 2.0 cm/sec. Figure 1 shows the effect of brine flow velocity on water flux and salt rejection of a typical run for both cases. Because of this condition it is important to determine a suitable basis for comparing the results of these two situations.

The pure water permeability constant (A) was used to help determine a basis. This constant is a membrane permeability (GSFD/psi) determined with pure water in the cell. Constant A with fluidized bed and without fluidized bed at varied velocities with feed containing 150 ppm salt was determined in Runs 50, 53, 58, 59, 60,

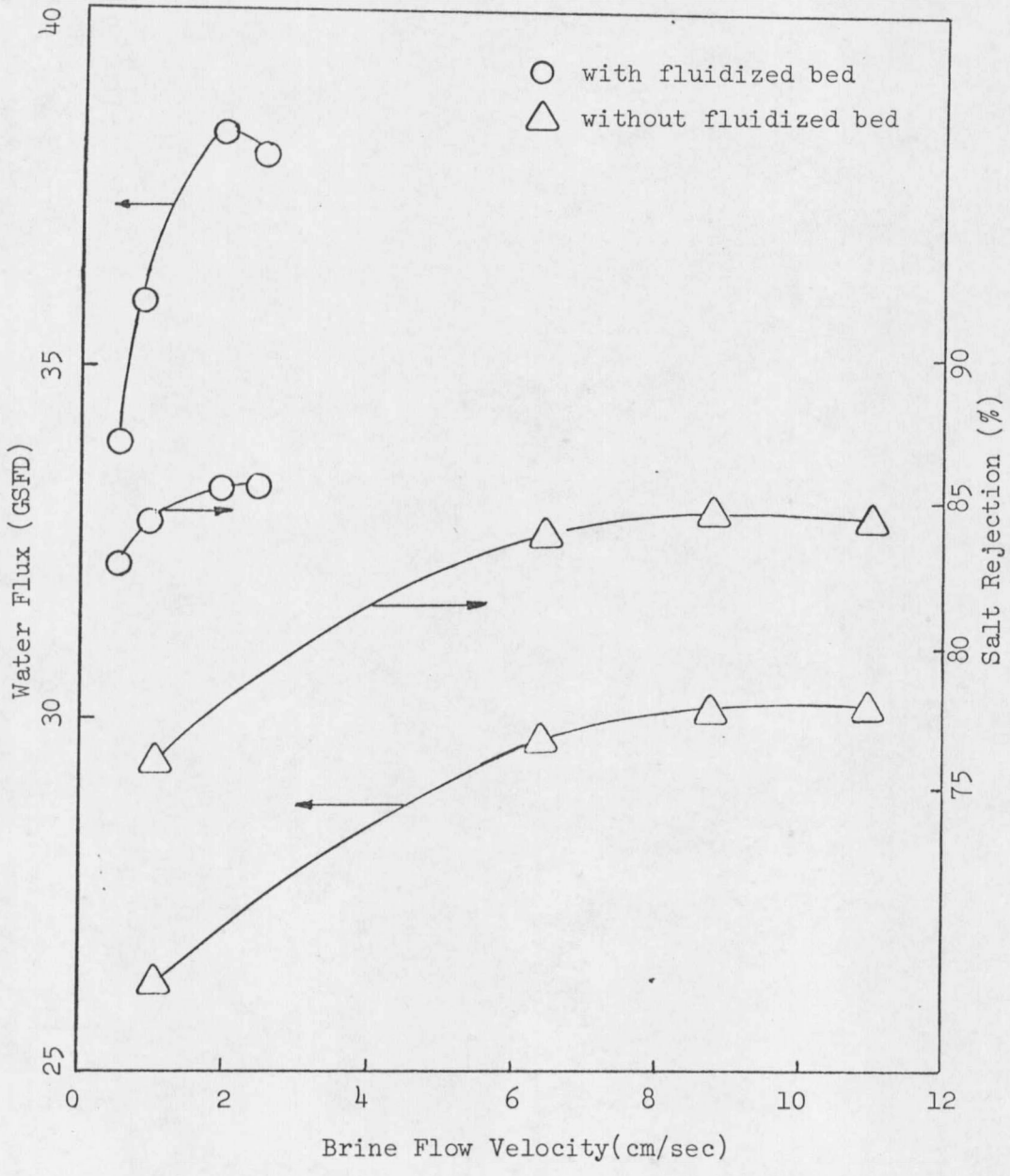

Figure 1 Effect of Brine Flow Velocity on Water Flux and Salt Rejection(398-10-82-nylon membrane)

and 61, all of which employed the 398-10-86 membranes. Figure 2 shows the selected brine flow velocity of 0.97 cm/sec for the fluidized bed was the maximum possible flow without inserting a plastic block to reduce the cell volume. In order to obtain the same value of A, a brine flow velocity of 11.0 cm/sec was needed without the fluidized bed. As also shown in Figure 2, constant A was determined with a feed solution of less salt content (8 ppm) and the same value was obtained at 11.0 cm/sec. The two values for salt content were those of salt residue in the system after washing with pure water. In the determination of another value for constant A using the 398-10-82 membrane at the selected brine flow velocity of 0.97 cm/sec for the fluidized bed, a value of 11.0 cm/sec was obtained without the fluidized bed. Therefore, as a result of these two determinations with the pure water permeability constant as a criterion, it appears that a valid basis for comparison is obtained when using results of a fluidized bed run at a brine flow velocity of 0.97 cm/sec and a run without the fluidized bed at a brine flow velocity of 11.0 cm/sec.

RESULTS FOR DACRON MEMBRANE

Three different kinds of dacron-supported membranes were tested: 398-10-86, 398-10-84, and 398-10-82, which were made of cellulose acetate type 398-10 casting solution with heat treatment