AN INVESTIGATION OF THE PURIFICATION OF SYNTHETIC BRINE BY REVERSE OSMOSIS

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ABSTRACT

AN INVESTIGATION OF THE PURIFICATION OF SYNTHETIC BRINE BY REVERSE OSMOSIS

By

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A study was made of the use of reverse osmosis to purify brackish water. The reverse osmosis system including the hollow fiber membrane cartridges was provided by Dow Chemical Company. The feed brine used was of 8700 ppm concentration, closely resembling the Marshall formation, underground water in the Michigan area.

Two hollow fiber membrane cartridges (Model No. J-267 and L6J2) were used, one at a time. The ion rejections of SO_4^{-2}, Ca^{+2}, Na^+ and K^+ were determined at different water recoveries over a period of time. Water recovery and flux were also calculated. The accuracy of the result was tested by using a CA ratio.

Analysis was done by injecting a radioisotope of the ion studied into the feed stream. Then the radioactivity was detected with liquid scintillation techniques.

Kesara Bhuntumkomol

The average total ion rejection was found to be 90% at steady state. The rejection decreased with increase of water recovery. Ions with larger charge and mass (SO_4^{-2}, Ca^{+2}) were rejected more easily than smaller ions (Na^+, K^+). Water recovery of 30% is recommended for use with the brine to prevent chemical precipitation.

Higher feed rates and system pressures should be tried using the Marshall formation. Further cost studies to determine the most feasible process for the brine should be done.

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By

Kesara Bhuntumkomol

A THESIS

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To my parents

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1. INTRODUCTION

1.1 Recent Development and Use

During the past 20 years, the reverse osmosis (RO) process has progressed rapidly as a promising method to recover water from saline solutions. Its advantages are simplicity and, theoretically, low energy requirements--no energy-wasting phase change takes place. All that is needed is a strong, corrosion resistant, reliable, cheap, selective membrane (1).

The RO process is achieved by forcing a salt solution under high pressure past a semi-permeable membrane, which passes water more readily than other organic or inorganic materials.

Interest in reverse osmosis first started in 1953 when C. E. Reid at the University of Florida found that secondary cellulose acetate (CA) may be used as a semipermeable membrane to separate water from saline solution by RO (2). However, CA had disappointingly low water transport and a very short productive life. During the 1950's, Loeb and Sourirajan at the University of California found that by heat treating the film and adding swelling agents to the casting formulation, they could make CA membranes which not only had excellent selectivity but also had water permeabilities sufficiently high to be of real practical interest (3).

From that point on, the major advances have been the development, engineering and marketing of RO systems. Most of the research and development is sponsored by the Office of Saline Water, U.S. Department of Interior. Today, RO systems for water treatment are commercially available for any moderate need, ranging from a 2.5 gal./day unit for a home drinking supply to a 150,000 gal./day auxiliary source for municipal water, a 350,000 gal./day plant for vacation resorts and 800,000 gal./day plants for industrial water (1).

The scope of RO systems is being extended to seawater desalting. Some other applications of RO are:

<u>Food processing</u>.--recovery of protein from cheese whey; concentration of maple sap, fruit juices, coffee and tea; concentration of drugs and biological products.

<u>Pollution control</u>.--removing chromate from cooling tower blowdowns; removal of sulfates from acid mine drainage; retrieval of gold, silver, platinum and other precious metals from electroplating solutions and rinses.

Water reclaimation.--treating of secondary sewage effluent; reducing phosphate in the discharge (1).

1.2 Purpose of Study

The purpose of the present study is to obtain data to determine the efficienty of the RO membrane by determining its ion rejection, flux, etc. (see Appendix A) using synthetic brine as feed solution.

The composition of the synthetic brine used in this study closely resembles that from the Marshall formation, a brackish water source below the fresh water table in the central region of Michigan. The Marshall formation is found at a depth of about 600 feet (4). A U.S. Geological Survey of 1900 showed its salt concentration to be about 8768 ppm, including Ca^{+2}, Na^{+}, K^{+}, SO_4^{-2}, Cl^{-}, HCO_3^{-} ions (see Appendix C). It was once hoped that this high concentration of salts could be separated and sold for profit. Now, thought is being given to this brackish source as potential municipal water. RO is looked upon as one of the best means to purify water from the Marshall formation.

The equipment was provided by Dow Chemical Company. This RO study using a hollow fine fiber module consisted of 2 parts. First, the experiments were repeated using the cartridge Model J-267, which was used by Tucker in his M.S. Thesis (5). In the second part, the new cartridge Model L6J2 was used. The analysis was accomplished by using radioactive tracer technique and liquid scintillation.

2. THEORY

2.1 Principles of Reverse Osmosis

Osmosis is the tendency of a solvent to flow through a semipermeable membrane from a dilute solution (water) to a concentrated one (saline) as depicted in Figure 1a. The driving potential for the flow of pure water is known as osmotic pressure ($\Delta\pi$). The actual flow of fluid is related to the chemical potential of the solution. This chemical potential is a function of the solution pressure, temperature and the number and types of molecules in the solution (6) or,

$$\Delta\mu = \bar{v}\,(\Delta P - \Delta\pi) \qquad \ldots\ldots\ldots \quad (1)$$

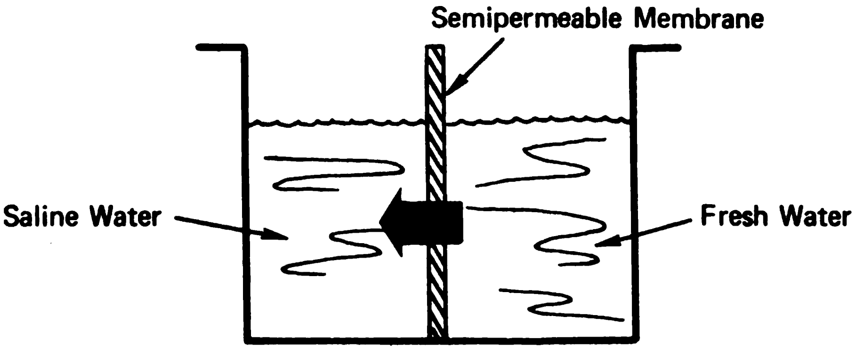
where:

$\bar{v}$ = partial molar volume of water (pressure independent)

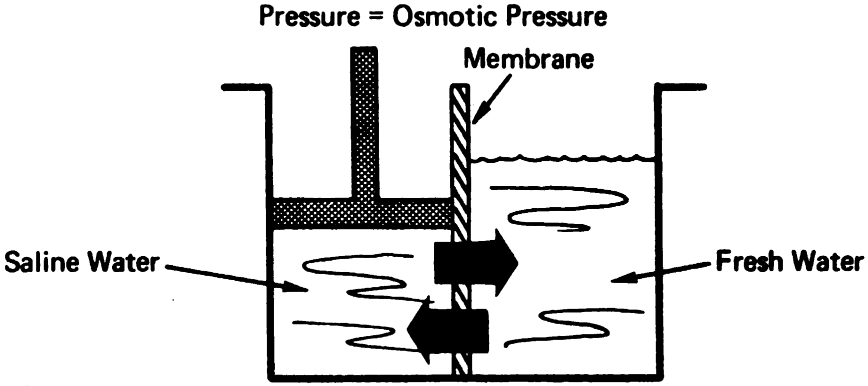
$\Delta\mu$ = chemical potential difference for water across the membrane

ΔP = pressure difference between the two solutions

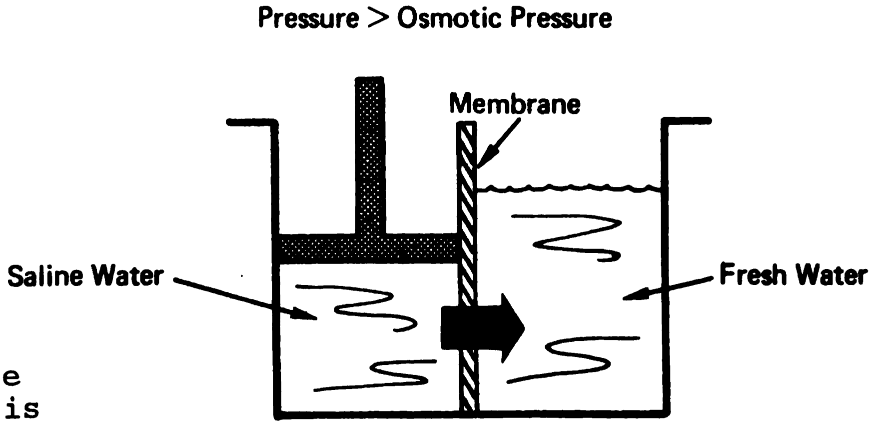
$\Delta\pi$ = osmotic pressure difference between the two solutions



1a. Osmosis



1b. Osmotic Equilibrium



1c. Reverse Osmosis

Figure 1. Reverse Osmosis Principle

Using Raoult's law for dilute solutions, van't Hoff formulated an equation to calculate osmotic pressure:

$$\pi \simeq RT/V \simeq nRT/v \qquad \ldots\ldots\ldots \quad (2)$$

where:

π = osmotic pressure

$\frac{v}{n} = V$ = molar volume

T = temperature

R = proportionality factor

When an external pressure equal to the osmotic pressure is applied to the concentrated salt solution, the flow of fluid will be in equilibrium as seen in Figure 1b. This condition is known as osmotic equilibrium. If the external pressure on the salt is continued beyond the osmotic pressure, a reversal of flow will take place. Pure water will be separated from the concentrated salt solution as shown in Figure 1c. This last phenomenon is the basis of the RO method of desalination.

The following equations approximately describe the flow of water and salt through most current RO membranes (7).

$$J_1 = K_1(\Delta P - \Delta\pi) = K_1 \, P_{eff} \qquad \ldots \quad (3)$$

$$J_2 \simeq KB\Delta C \qquad = KB(C_W - C_P) \qquad \ldots \quad (4)$$

where:

J_1 = product water flux (gal./day - ft^2)

K_1 = membrane permeability constant (gal./day - ft^2 - psi)

ΔP = pressure difference measured between the feed and the product stream (psi)

$\Delta\pi$ = osmotic pressure difference between the feed and the product stream (psi)

P_{eff} = effective membrane driving pressure (psi) (see equation 5)

J_2 = salt transfer flux (lb/hr.)

K = proportionality constant

B = salt permeation constant

C_W = feed stream salinity measured at membrane wall

C_P = product salinity

Equation 1 indicates the significance of high fluid pressure on the water production rate. Acting in opposition to the pressurized fluid is the osmotic pressure of the saline solution. Osmotic pressure associated with typical brackish water feeds are in the range of 30 to 150 psi., where seawater may be as high as 450 to 600 psi. To assure a reasonable flow of product water through current high salt rejecting CA membranes, fluid system pressures in the range of 600 to 800 psi are required for brackish water feeds and up to 1500 psi for seawater feeds (7).

2.2 Osmotic Membrane

The most important part of the RO system is the membrane. An ideal membrane is one which would allow only water molecules to pass through its structure (semipermeable). A number of substances such as collodion, cellophanes, porous glass frits, finely cracked glass, inorganic precipitates and CA polymers have been used in fabricating semipermeable membrane films. A modified CA material has proven to be most satisfactory in demineralization studies. It has good selectivity, dope formulations amenable to variation, good availability of raw materials and relatively low cost.

There are 4 different basic membrane configurations currently being evaluated for use with RO units (7). They are:

2.2.1. Plate and Frame

The plate and frame configuration (see Figure 2) was the first type explored in early RO development and appears to be losing favor now. The advantages and disadvantages of the configuration are:

Advantages:

(a) Design simplicity

(b) Physical ruggedness

(c) Only the membrane is replaced in the event of membrane failure.

Disadvantages:

(a) Difficult brine flow patterns

(b) High labor requirements for membrane assembly and replacement

(c) High equipment cost

2.2.2. Tubular

The tubular configuration is similar to a typical shell and tube heat exchanger. Figure 3 shows a schematic of a typical design. This configuration has the following advantages and disadvantages:

Advantages:

(a) Well defined flow passages

(b) Filtration requirements are small

(c) Porous tubes can be utilized as both the porous structure and the membrane support.

(d) Ease of cleaning

Disadvantages:

(a) Large number of tubes and fittings required per unit surface area

(b) Low packing density

(c) Moderately high initial cost

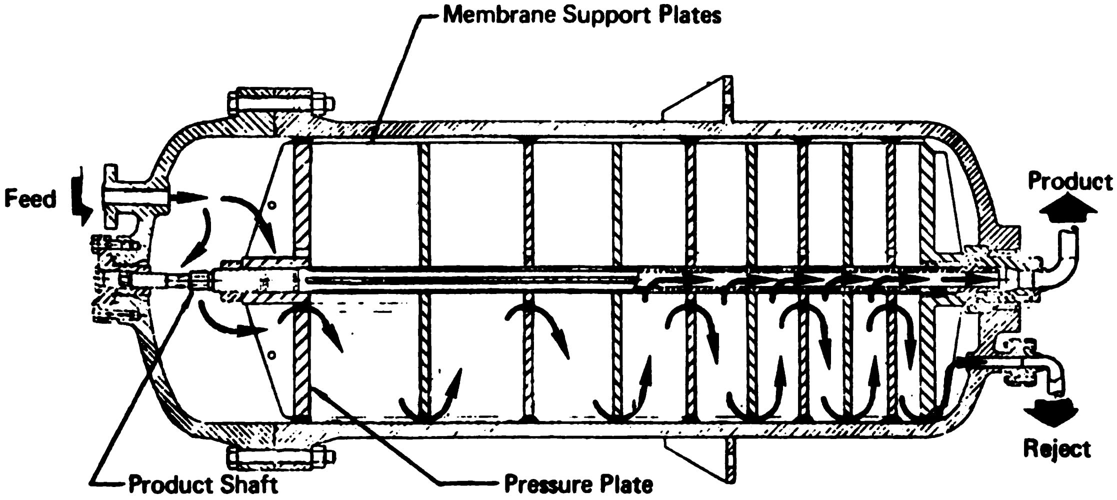


Figure 2. Plate and Frame Module Configuration (7)

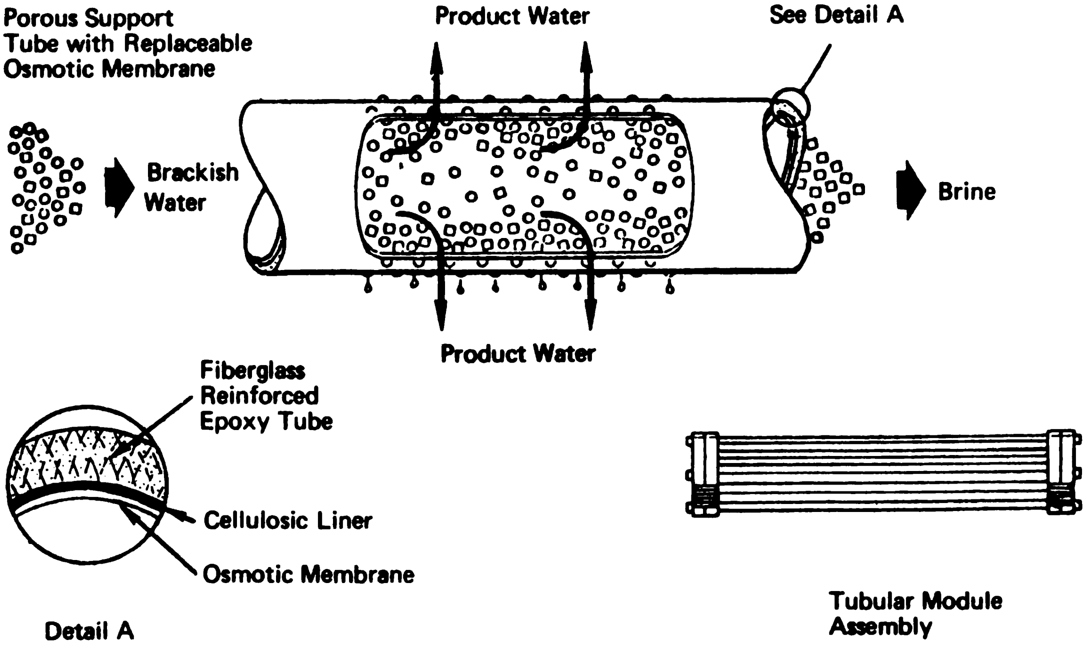


Figure 3. Tubular Module Configuration (7)

2.2.3. Spiral Wound

Figure 4 depicts the configuration of a spiral wound membrane module. The advantages and disadvantages of the module are as follows:

Advantages:

(a) High membrane packing density possible

(b) Adaptable to factory fabrication and simple field replacement of module

Disadvantages:

(a) Product flow path is long

(b) A high level of feedwater filtration is required to prevent plugging of the brine side spacer

(c) Module telescoping must be prevented

2.2.4. Hollow Fine Fiber

The hollow fine fiber module which was used in this study was developed by the Dow, DuPont and Monsanto Companies. The configuration is similar to a shell and tube heat exchanger with a large number of hollow fibers (CA or nylon) serving as tubes. The fiber sizes are in the range 25 to 250μ O.D. with wall thickness of 5 to 50μ. The brine flows external to the fiber and the product flows through the fiber (see Figure 5). The advantages and disadvantages of this configuration are:

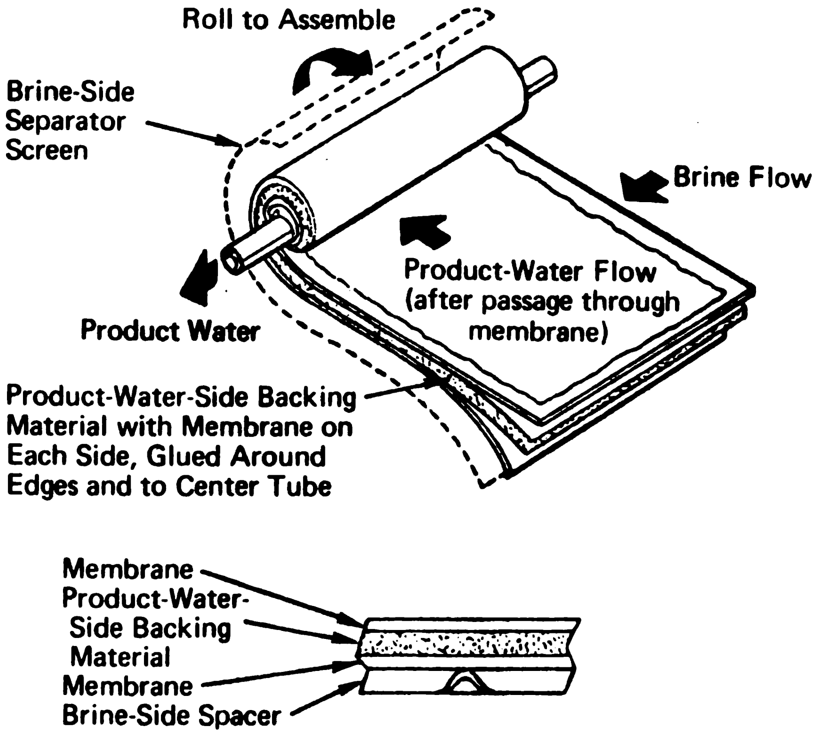
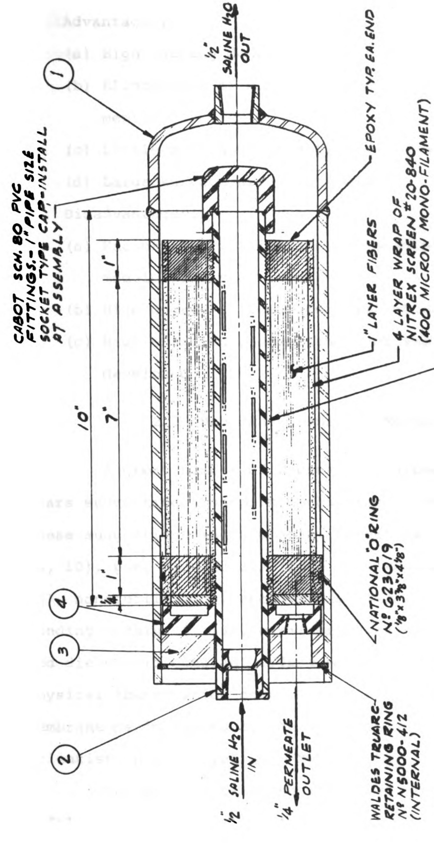


Figure 4. Spiral Wound Module Configuration (7)



① Pressure Case

② Slotted Saline Water Distribution Core

③ End Plate

④ Channel Cover

Figure 5. Hollow Fiber Module Configuration (8)
(Single Cartridge - Single Pass)

Advantages:

(a) High packing density

(b) Elimination of membrane support material requirements

(c) Little membrane compaction (with nylon fibers)

(d) Large surface area/unit volume

Disadvantages:

(a) Factory fabrication and replacement of membrane module required

(b) High degree of feedwater filtration required

(c) High efficiency desalting membrane has not been developed

2.3 Membrane Transport Mechanism

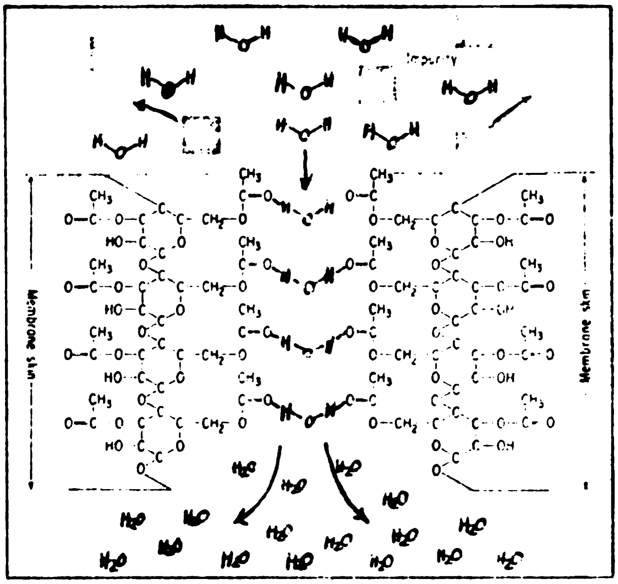
A great number of papers have appeared in recent years suggesting transport mechanisms in RO desalination. These suggestions include solution-diffusion models (9, 10), pore flow models (11), free volume models (12-14), nonequilibrium thermodynamics (15-17), hydrogen bonding models (2, 18), capillary sorption models (19) and dielectric constant effect models (20). However, a physical theory which completely and accurately describes membrane performances to the satisfaction of all involved scientists has not yet been formulated.

The most outstanding theory is the pore flow model, whose explanation of the transport of water and salts across CA membrane is given in the following passages (1).

Chemically, CA is a hydroxylic polymer made up of long chains of β-glucoside units (30,000-60,000) that have been acetylated with acetic anhydride and then hydrolyzed to reduce acetylation to about 40%. Most often, the CA powder supplied for RO membrane casting is in this partially acetylated form, which is known as 2.5 cellulose acetate. RO membranes are also cast from the fully acetylated form (triacetate).

When cast as RO membranes, CA is a film about 4 mils thick. It is asymmetric--that is, the film has a thin, dense layer of about 0.25μ above a thick, porous layer. Water passes easily from the dense layer through to the porous one, but with difficulty the other way. Unlike the thick, amorphous underlayer, the dense layer on top of the membrane is made up of tightly packed and organized chains of CA polymer that attract and hold water. Thus, water and solute are separated because the water molecules can form hydrogen bonds with the acetyl groups on the polymer, while many other species cannot (see Figure 6).

The CA polymer chains within the dense layer are highly organized because the membrane receives an annealing treatment that shrinks the film and crystallizes the polymer. The long molecules are somewhat separated



Eastman Chemical Products, Inc.

Figure 6. Water Transfer in CA Membrane (21)

and relatively immobile because of the interplay of van der Waals' forces. In this state, the polymer chains are close enough to crosslink with water molecules in the casting formulations and the annealing media.

These water molecules bridge across adjacent chains by forming strong hydrogen bonds with the acetyl groups. In this way, the voids between chains are filled with bound-water molecules and no foreign substances can pass. If the polymer chains were not densely packed, water molecules would bond to acetyls on the same chain and leave voids through which foreign ions could pass.

Water molecules move through the membrane by an applied pressure that pushes the water from a bond with one acetyl group to the next. Only a moderate force is necessary because the bonds are transferred, not broken. Dissolved ions or molecules that do not hydrogen bond cannot enter into attachments with bonding sites (acetyl groups) and are left to concentrate at the membrane surface.

2.4. RO System Parameters

There are 2 important parameters which characterize an RO system:

2.4.1. Water Flux

Product per unit area of membrane or water flux is defined as the amount of product recovered per day from a unit area of membrane. This flux is determined by physical characteristics of the membrane (e.g., thickness, chemical composition, porosity) and by the conditions of the system (e.g., temperature, differential pressure across the membrane, salt concentration of solution touching the membrane and velocity of the feed moving across the membrane). In practice, the properties of the membrane and the solutions are relatively constant, and water flux becomes a simple function of pressure, as described by equation 3.

Flux declines with time for several reasons:

- Membrane fouling or temporary flux reduction is caused when foreign or nonhydrogen bonding materials (such as calcium carbonates, sulfate scales, hydrates of iron oxides and aluminum, silicates, miscellaneous particulates and biological growths) coat the membrane surface and interfere with inward movement of water.

  Most fouling can be minimized by pretreating the feed to remove iron and to control pH; by limiting the process to nonscaling concentrations of waste; by filtration and by injection of small amounts of biocide. However, fouling always occurs no matter how thorough the protection. The usual cleaning procedure is to flush the membrane with water and other cleansing agents.

- There is a compaction and compression that slowly reduces the water flux. This results from densification of the thin air-dried membrane layer and crushing of the porous structure of the membrane because of high pressure fluid.

- Another cause of flux decline is the hydrolysis of acetyl groups. The reaction results in a loss of hydrogen bonding sites, which reduces the water transport. This is why RO membranes are limited to a pH operating range of 3 to 7, outside of which rapid hydrolysis and membrane degradation occur. The optimum pH range is 5-6. The reaction is also a source of salt leakage because there are fewer water bridges blocking the passage of foreign materials through the pore.

2.4.2. Product Quality

Product quality is measured by the amount of solute or salt in the product. This depends on selectivity of the membrane and its imperfections. The amount of salt passing through a unit area of membrane is described by equation 4.

The amount of salt in the product depends on the physical characteristics of the membrane, such as thickness, salt diffusion and the distribution of solute between the membrane and the solution. From equation 4, normal salt flux is independent of pressure.

The ability of the membrane to reject salts decreases with time. This is due to the following reasons:

-- Hydrolysis of CA to cellulose as explained in 2.4.1

-- Membrane compaction which may increase the pore size of the membrane and thus reduce the rejection factor

-- Coupling or membrane leakage because of imperfections in the membrane through which the pressurized fluid can flow and contaminate the product water.

Other pertinent parameters to be considered are:

2.4.3. Concentration Polarization

Concentration polarization is a measure of the increase of feed water salinity at the membrane wall beyond that of the bulk solution. The concentration polarization factor (CPF) is defined as the ratio of the salt concentration at the membrane wall relative to that in the bulk of solution. The usual CPF is 1.2 to 2.0 depending on design specifics (1).

The adverse effects of this phenomenon are an increase in product water salinity, an increase in membrane scaling and an increase in osmotic pressure which means higher power requirements. In general, the magnitude of the polarization effect is dependent upon the following parameters:

(a) Brine channel configuration and dimensions
(b) Brine flow velocity
(c) Membrane water permeability

To decrease the CP effects, the boundary layer at the membrane wall should be reduced by higher feed velocities and turbulence. However, there are 2 points which should be emphasized:

I. High membrane water fluxes increase polarization effects.

II. Increasing flow rates decreases polarization effects but increases the pumping power required.

The optimum flow rate should be designed for every application. At present, turbulence promotors (e.g., small plastic balls, waffle-like polyethylene screens) are a more attractive way to reduce the boundary layer.

2.4.4. System Pressure Loss

System pressure loss can be categorized as brine side pressure drop (ΔP_B) and product water side pressure drop (ΔP_p).

The effective system driving pressure is defined by the following equation (7):

$$P_{eff} = (P - P_L - \Delta P_p) - \Delta\pi \qquad \ldots . (5)$$

where:

P = High pressure pump outlet pressure

P_L = Pressure loss associated with the concentrating feed water stream

ΔP_p = Product side pressure drop

$\Delta\pi$ = Osmotic pressure gradient

The brine side pressure loss is due to the friction pressure drop of the brine through the brine channel. Pressure losses are typically 50 to 150 psi or 5 to 15% of the total system pressure.

3. RAW MATERIALS AND EQUIPMENT

3.1 Raw Materials

The synthetic brine used in the experiment resembles that in the Marshall formation, Michigan underground water. The analysis of the top water and brine is shown in Appendices B and C.

For every batch of 50 gallons of synthetic brine made, the amounts of chemicals shown in Table 1 were mixed.

Table 1

Chemical Makeup of Synthetic Brine

Chemical Compound	Amount (gm.)
$NaHCO_3$, Commercial grade	681.0
NaCl, Commercial grade	565.0
$MgCl_2 \cdot 6H_2O$, Purified grade	85.6
KCl, Analytical grade	22.3
Na_2SO_4, Purified grade	124.0
$CaCl_2$, Purified grade	202.2
HCl (conc.), Analytical grade	650 ml.

Radionuclides used:

S^{35}

Ca^{45}

Na^{24}

K^{42}

S^{35} and Ca^{45} were purchased outside the university. About 20 μCi was used in each experiment (2-2 1/2-hour operation).

Na^{24} and K^{42} were activated in the MSU Reactor Laboratory. Because of their short half-life, about 45 μCi had to be used in each experiment (see Appendices D and F).

3.2 Experimental Equipment

The hollow fine fiber RO module used in this study was manufactured by Dow Chemical Company. The auxiliary system (model SO300S serial 1175) was designed and made by Polymetrics of San Carlos, California (22). Other supplement equipment was either fabricated by the MSU Division of Engineering Research Shop or purchased outside of the university.

The process diagram is shown in Figure 7. The front and rear of the equipment are shown in Figures 8 and 9 respectively.

Equipment used with the RO system included:

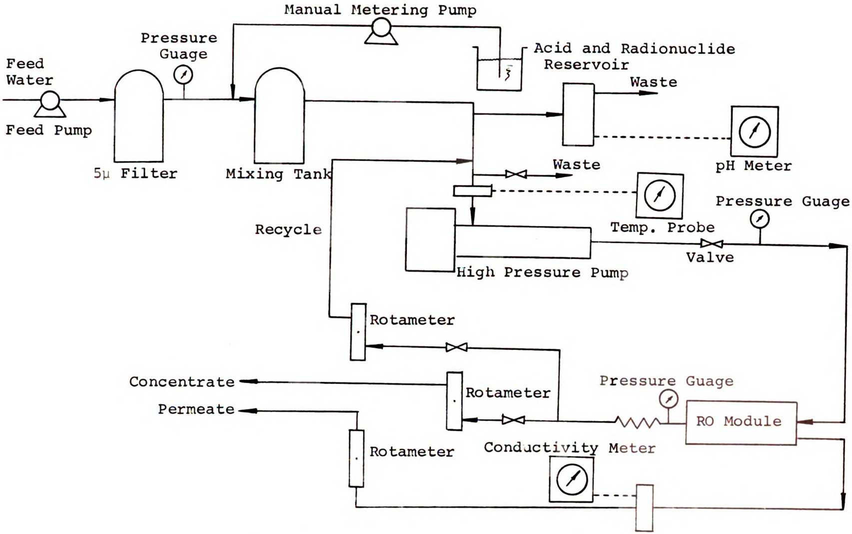
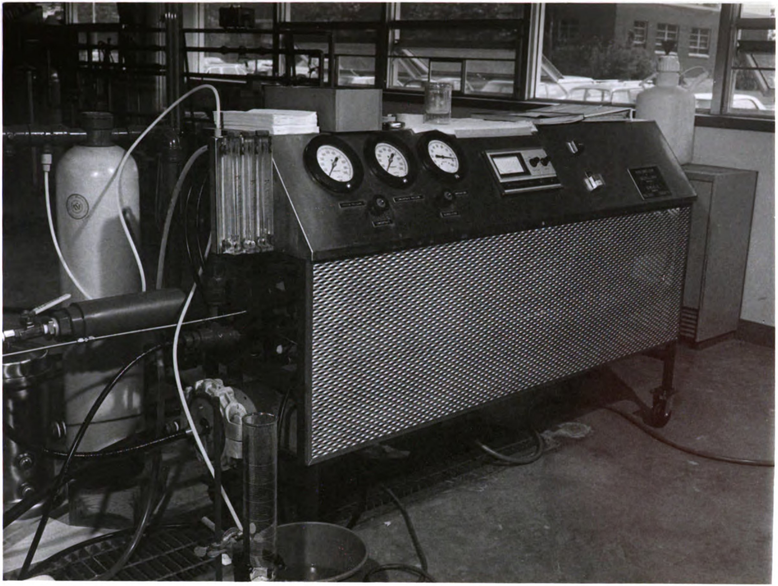


Figure 7. Flow Diagram of Reverse Osmosis System

Figure 8. Front View of Dow Reverse Osmosis Unit



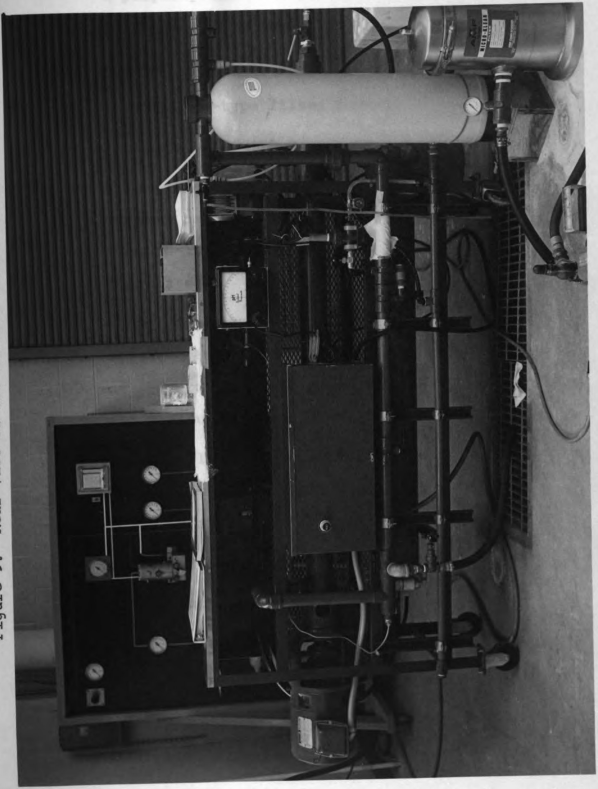


Figure 9. Rear View of Dow Reverse Osmosis Unit

-- 2 polyethylene tanks, each with a capacity of 55 gallons, for feed brine storage

-- 1 motor pump with 1 HP

-- 1 cartridge-type filter housing (5 μ)

-- 1 mixing tank with a capacity of 7 gallons

-- 1 manual controlled chemical feed pump with a maximum capacity of 3.4 gpd. and a dial setting from 30-100 to indicate percentage of maximum feed rate

-- 1 high pressure pump, Gould Multistage Centrifugal 15 HP, 450 volts, 3 phase with a capacity of 2-6 gpm., maximum working pressure of 800 psi., and maximum working temperature of 160°F

-- 2 Dow hollow fine fiber(CA) RO modules with specifications as described in Table 2 (only one used at a time)

The instruments included:

-- 1 feed water pH monitor

-- 1 feed water temperature guage

-- 1 product water conductivity monitor

-- pressure guages for the feed, system and concentrate

Table 2

Dow Hollow Fiber Module Specifications

Specifications	Model J-267	Model L6J2
Shell Dimensions	6.6" O.D. x 61" Long	
Shell Material	Epoxy Clad Sch. 40 Steel	
Channel Covers	Aluminum	
End Closure	Victaulic Couplings	
Max. Operating Pressure	600 psig	
Temperature Range	10 - 30°C	
pH Range	4.0 - 8.5	
Water Recovery Range	10 - 90%	
Chlorine Tolerance	1 ppm. Continuous	
Flow Mode of Single Cartridge	Radially Inward	Radially Outward
Active Area of Single Cartridge	1187 ft^2	1895 ft^2
Size of Fiber	50μ O.D.	35μ I.D. x 77μ O.D.

-- product water flow meter

-- concentrate brine flow meter

The start-up of the system is accomplished with an automatic "on" button. The system can turn itself off when the inlet pressure drops below the minimum required for high pressure pump operation (about 10 psig.).

4. EXPERIMENTAL METHODS

4.1 Preliminary Test

One of the main problems which occurred at the beginning of the experiment was a difficulty in dissolving all the chemicals to make up the synthetic brine. A test was done in laboratory scale to solve this problem. It was found that for every batch of 50 gallon brine, 650 ml. of concentrated HCl acid should be added to 30 gallons of tap water before the chemicals are added, beginning with $NaHCO_3$, then NaCl, $MgCl_2$, KCl, Na_2SO_4 and $CaCl_2$ respectively. Stirring was done after each chemical was added. Tap water was then added to make up 50 gallons of synthetic brine.

When this synthetic brine of pH about 5.6 was left at room conditions, the chemicals began to precipitate after 80% of the water was evaporated. From the chemical report (23) of the synthetic brine, $CaSO_4 \cdot 2H_2O$ will precipitate at water recovery of 83%. At this recovery, the solubility product of $CaSO_4$ in the brine solution is 0.0016949. If the HCO_3^- ions in the brine are reacted with H_2SO_4, $CaSO_4 \cdot 2H_2O$ will precipitate at a water recovery of 39%. This is the reason why HCl acid should be added in the brine instead of H_2SO_4 acid.

Another problem was the precipitation of hydrated iron oxide in the membrane module. This was due to the use of commercial grade $CaCl_2$ (92% $CaCl_2$) which contains some iron oxide. It has been found that iron hydroxide is one of the major constituent of fouling layers formed during brackish water disalination (24). In the present study, purified grade $CaCl_2$ was used instead. This resulted in less iron oxide precipitation.

4.2 Experimental Procedure

Synthetic brine was prepared as described in section 4.1. in the polyethylene tanks. It was desirable to have the room fully ventillated so that acid fumes could be dispersed quickly.

Prior to experimentation, calibration of the pH meter was necessary (22). The pH probe had to be checked to see that there was enough saturated KCl solution.

The procedure for start-up and experimentation was as follows:

Steps

1. The brine or concentrate valve was opened fully.

2. A check was made that an adequate supply of radionuclide solution was available, and that the pumplines were primed and leak free.
3. Tap water was allowed to flush the system to remove air. This is completed when no bubbles appear in the brine rotameter.
4. The brine flow was adjusted to about 2 gpm.
5. The high pressure pump was then turned on with the "auto" button.
6. Re-adjustment was made of the concentrate flow for the desired rate.
7. When the flow was steady (about 15-20 minutes), flow rates of both concentrate and permeate were measured by weighing the amount of water at definite times. This was done at least twice and an average value was taken.
8. Samples of feed, permeate and concentrate were taken to measure the background radioactivity level.
9. The radionuclide was then introduced into the system by turning on the chemical feed pump.
10. After the radionuclide had been introduced into the system for 15 minutes, the feed valve was switched from the tap water to the prepared

synthetic brine. The time was noted as the starting time (t = 0).

11. Samples of feed, permeate and concentrate were taken in small polyvials. Subsequent samples were taken at 60-minute intervals for 2-2 1/2 hours.
12. Periodic checks of the pressures, pH, temperature and conductivity were made during the experiment.
13. When all samples had been taken, the injection of nuclide was stopped.
14. The system was then flushed with tap water for at least 2 hours, usually at higher flow rates than were used during the run.
15. All power to system was turned off.

There were only two polyethylene feed tanks used in the experiment, so the feed valve had to be switched from one to the other after the brine was almost gone in the first tank. The brine had to be prepared and used at once.

It was very easy to lose the priming on the radionuclide feed pump. The best way to avoid this was to keep the suction end in solution at all times when not in use, to take it out of solution between pulses and to shake the bubbles out of the suction tube after placing it back into the solution.

4.3 Flushing of the System

The system had to be flushed at the end of each experiment to remove the radioactive ions and the precipitates from the brine. Tap water at 50 psig. with a flow rate 2-3 times that of the brine flow was usually used. From time to time, the system was flushed with radiacwash solution (chelating agent) using recycle flow for 2-3 hours. The radiacwash (1/2 gallon radiacwash in 50 gallon tap water) helps to solubilize radioactive ions and also other chemical ions.

4.4 Safety Precautions

The following precautions were followed during the experiment at all times:

-- A pocket film badge was worn when using radionuclides.

-- Plastic gloves were used when preparing the radioactive samples and taking samples during the experiment.

-- To reduce contamination from leakages or spills on the equipment and floor, absorbent paper was taped to parts of the RO unit as well as to the floor near the outlet streams.

-- Contamination wipes were taken after each experiment to determine if the equipment was becoming too active for safety.

-- All sample polyvials and glasswares were thoroughly cleaned with radiacwash solution and hot water after each experiment.

-- All contaminated liquids were disposed of in the proper radioactive container.

-- The RO system was flushed with tap water for at least 2 hours after each experiment to reduce the amount of radioactivity in the system.

5. ANALYTICAL METHODS

The radioactivity in the samples was analyzed by using liquid scintillation spectrometry. The system used was a Packard Tri-Carb Liquid Scintillation Spectrometer System, Model 3003.

5.1 Sample Preparation

Ten millilitres of radioactive aqueous sample was mixed and shaken vigorously with 10 ml. of Packard Insta Gel Emulsifier in a polyethylene vial. If the solution was not clear, the vial with the solution was placed in ice water until it was clear.

For background counting, the aqueous solution sample collected before the injection of radionuclide was mixed with the Insta Gel.

5.2 Liquid Scintillation Spectrometer

Procedure:

1. The temperature in the counting chamber was adjusted to about 5°C.

2. The gain was set at maximum. This gain had been determined before for each nuclide (25).

3. The sample vial was then placed to count for 50 minutes or 100,000 counts depending on which was reached first. The sample no., time and counts in all three channels were printed out by a digital printer on paper tape.

This particular spectrometer has a sample changer with a capacity of 200 sample vials. Each successive sample is automatically counted one after another (25).

6. DATA

The experimental data using cartridge model J-267 are shown in Table 3 and cartridge model L6J2 in Tables 4-8.

The feed, system and concentrate pressures (see Appendix A) were kept within ranges of 12-16, 665-670 and 650-660 psig. respectively. The temperature of the feed brine was around 59-67°F, except in the first two experiments where hot tap water was used to dissolve the chemicals instead of cold water. The feed was adjusted within a pH range of 5.6-6.1 to avoid membrane deterioration and chemical precipitation.

The radioactivities of feed, permeate and concentrate streams (see Appendix A) were measured at particular times to determine the ion rejection of the membrane. Raw data are presented in Appendix E. At the same time, the conductivity of the permeate stream was also taken. Stream flow rates were measured to determine the water recovery and permeate flux (see Appendix A).

Appendix F includes methods of calculating permeate flux at operating temperature and at 25°C, and water recovery.

Table 3

Experimental Data Obtained for SO_4^{-2} Ion--Cartridge Model J-267

Expt. No.	Starting Time (hr.:min.)	Feed Pres. (psig.)	System Pres. (psig.)	Conc. Pres. (psig.)	Temp. (°F)	Conc. Flow Rate (gpm.)	Permeate Flow Rate (gpm.)	Permeate Flux at 25°C (gpd/ft^2)	Water Recovery (%)	Note
1	--	17-18	670	660	77-84	0.21	0.67	0.762	75.7	--
2	--	15	670	660	86-92	0.78	0.86	0.874	52.5	--
3	--	14	670	660	59-60	0.73	0.73	1.132	50.0	Tap water as feed

Expt. No.	pH Feed	Conductivity in Permeate Stream (micromho/cm. at 25°C)				
		Time (min.)				
		30	60	90	120	150
1	5.8	--	--	1.8K[a]	1.1K	1.0K
2	6.0	2.5K	4.1K	3.5K	3.4K	4.0K
3	5.7	0.24K	0.22K	0.22K	0.19K	0.19K

[a] K = multiplied by 10^3.

Table 4

Experimental Data Obtained for SO_4^{-2} Ion--Cartridge Model L6J2

Expt. No.	Starting Time (hr.:min.)	Feed Pres. (psig.)	System Pres. (psig.)	Conc. Pres. (psig.)	Temp. (°F)	Conc. Flow Rate (gpm.)	Permeate Flow Rate (gpm.)	Permeate Flux at 25°C (gpd/ft^2)	Water Recovery (%)
4	0	15	670	655	59-60	0.68	0.57	0.557	45.7
5	3:50	14	670	655	59-61	0.62	0.58	0.562	48.3
6	5:50	14	665	655	60-63	0.57	0.58	0.545	50.3
7	8:50	16	670	660	59-62	0.36	0.60	0.572	62.3
8	11:20	12	670	650	59-60	1.32	0.54	0.521	28.9
15	26:05	15	670	655	60-62	0.47	0.48	0.457	50.2
28	52:50	15	670	655	65-66	0.61	0.62	0.552	50.3

Expt. No.	pH			Conductivity in Permeate Stream (micromho/cm. at 25°C)						
	Feed	Permeate	Conc.	Time (min.)						
				30	60	90	120	150	180	240
4	5.7	--	--	0.4K[a]	0.25K	52	35	0.2K	--	--
5	5.5	5.8	7.1	56	70	0.42K	105	--	--	--
6	5.7	4.7	5.9	0.75K	0.25K	102	0.76K	--	--	--
7	5.7	4.7	6.0	180	0.62K	0.73K	0.2K	--	--	--
8	5.6	4.6	5.7	0.75K	0.2K	0.13K	0.42K	--	--	--
15	5.8	--	--	0.33K	1.12K	0.92K	0.96K	--	--	--
28	6.0	--	--	2.0K	2.4K	--	2.2K	--	2.0K	2.8K

[a] K = multiplied by 10^3.

Table 5

Experimental Data Obtained for Ca^{+2} Ion--Cartridge Model L6J2

Expt. No.	Starting Time (hr.:min.)	Feed Pres. (psig.)	System Pres. (psig.)	Conc. Pres. (psig.)	Temp. (°F)	Conc. Flow Rate (gpm.)	Permeate Flow Rate (gpm.)	Permeate Flux at 25°C (gpd/ft^2)	Water Recovery (%)
9	13:20	13-16	670	660	60-62	0.55	0.58	0.553	51.0
10	15:50	13-14	670	660	63	0.35	0.59	0.552	63.0
11	17:50	12	665	650	60-63	1.15	0.49	0.460	29.8
17	30:35	14	670	655	62-64	0.59	0.59	0.548	50.0

Expt. No.	pH			Conductivity in Permeate Stream (micromho/cm. at 25°C)			
				Time (min.)			
	Feed	Permeate	Conc.	30	60	90	120
9	5.7	4.9	6.0	0.91K[a]	0.38K	0.15K	0.11K
10	5.8	4.8	6.2	1.25K	0.18K	0.98K	0.14K
11	5.6	4.4	5.7	0.85K	0.09K	0.08K	0.09K
17	5.8	--	--	1.0K	0.19K	0.14K	0.30K

[a] K = multiplied by 10^3.

Table 6

Experimental Data Obtained for Na^+ Ion--Cartridge Model L6J2

Expt. No.	Starting Time (hr.:min.)	Feed Pres. (psig.)	System Pres. (psig.)	Conc. Pres. (psig.)	Temp. (°F)	Conc. Flow Rate (gpm.)	Permeate Flow Rate (gpm.)	Permeate Flux at 25°C (gpd/ft^2)	Water Recovery (%)
12	19:50	14	670	655	61-63	0.55	0.56	0.531	50.3
13	22:05	14-15	670	655	62-64	0.36	0.55	0.510	60.3
14	24:05	14-16	670	650	59-60	0.99	0.44	0.423	30.6
16	28:20	14-15	670	655	61-63	0.57	0.58	0.545	50.4

Expt. No.	pH			Conductivity in Permeate Stream (micromho/cm. at 25°C)			
				Time (min.)			
	Feed	Permeate	Conc.	30	60	90	120
12	5.8	4.9	6.05	170	97	0.96K[a]	0.2K
13	5.8	--	--	0.11K	0.38K	0.17K	0.62K
14	5.7	--	--	0.2K	0.16K	0.1K	0.25K
16	5.8	--	--	1.24K	0.34K	0.21K	0.13K

[a] K = multiplied by 10^3.

Table 7

Experimental Data Obtained for K^+ Ion--Cartridge Model L6J2

Expt. No.	Starting Time (hr.:min.)	Feed Pres. (psig.)	System Pres. (psig.)	Conc. Pres. (psig.)	Temp. (°F)	Conc. Flow Rate (gpm.)	Permeate Flow Rate (gpm.)	Permeate Flux at 25°C (gpd/ft^2)	Water Recovery (%)
18	32:50	14	665	655	62-63	0.57	0.58	0.544	50.5
19	34:50	14	670	655	62-64	0.39	0.61	0.572	61.2
20	36:50	14	665	650	60-61	1.14	0.50	0.474	30.3
21	38:50	14	670	655	63-65	0.41	0.64	0.588	61.3
22[a]	40:50	13-14	670	650	62-63	1.21	0.52	0.485	30.2

Expt. No.	pH Feed	Conductivity in Permeate Stream (micromho/cm. at 25°C) Time (min.) 30	60	90	120
18	5.7	0.94K[b]	1.25K	0.64K	0.25K
19	5.8	1.64K	0.28K	0.32K	1.5K
20	5.7	0.38K	0.20K	1.05K	0.15K
21	5.8	1.4K	0.14K	1.04K	1.45K
22	5.8	0.09K	0.09K	0.1K	0.12K

[a] Flushing with radiacwash for 1 hr. before the experiment.

[b] K = multiplied by 10^3.

Table 8

Experimental Data Obtained for K^+ Ion--Cartridge Model L6J2

Expt. No.	Starting Time (hr.:min.)	Feed Pres. (psig.)	System Pres. (psig.)	Conc. Pres. (psig.)	Temp. (°F)	Conc. Flow Rate (gpm.)	Permeate Flow Rate (gpm.)	Permeate Flux at 25°C (gpd/ft^2)	Water Recovery (%)
23	42:50	15	670	655	65-67	0.43	0.64	0.575	60.0
24[a]	44:50	14-16	670	655	64-66	0.45	0.62	0.563	52.2
25[b]	46:50	12-13	665	650	62-63	1.31	0.55	0.510	29.4
26	48:50	14	670	655	65-67	0.62	0.62	0.552	50.0
27	50:50	15-16	670	660	65-66	0.43	0.64	0.571	60.0

Expt. No.	pH Feed	Conductivity in Permeate Stream (micromho/cm. at 25°C)			
		Time (min.)			
		30	60	90	120
23	5.8	0.23K[c]	0.29K	0.23K	0.12K
24	6.0	3.0K	2.1K	2.7K	3.1K
25	6.1	2.4K	1.5K	2.2K	2.2K
26	5.9	2.7K	2.5K	2.4K	2.4K
27	5.9	3.0K	2.5K	3.2K	2.0K

[a] Leaking in feed line.

[b] Radionuclide injection pump cleaning before the experiment.

[c] K = multiplied by 10^3

7. RESULTS

Four different ions were measured to find the efficiency of the hollow fine fiber RO module: Ca^{+2}, Na^{+}, K^{+} and SO_4^{-2}. The raw radioactivity data in Appendix E were used to calculate the percentage of salt rejection of the RO module, by using the equation:

$$\text{\% Ion Rejection} = 100 \times \frac{(\text{Feed Activity} - \text{Permeate Activity})}{\text{Feed Activity}}$$

To determine whether the result was accurate, a parameter called the CA Ratio was designed. This ratio was defined as the ratio of projected concentrate activity rate to actual concentrate activity rate (see Appendices A and F).

Ideally, this ratio should equal 1.0. A value less than 1.0 indicates that more radioactivity is leaving the system than entering (theoretically impossible). This may be due to improper mixing in the RO system or error in scintillation counting or to dissolution of precipitate within the apparatus. A CA Ratio greater than 1.0 indicates that some of the nuclide is depositing in the system or there are errors in scintillation counting.

Appendix F includes methods of calculating ion rejection, water recovery and standard deviation.

7.1 Cartridge Model No. J-267

This cartridge was used by Tucker in his M.S. Thesis (5). It was plugged with precipitates which caused scattered results and low ion rejection. In the present study, the experiments were rejected using the same cartridge to determine % ion rejection of SO_4^{-2} in the synthetic brine.

The result is shown in Experiment 1 in Table 9. To remove the precipitates, the system was flushed with radiacwash for 3 hours. Then the experiment was repeated. The result using synthetic brine as feed is shown in Experiment 2 in Table 9 and Figure 10. Another experiment using tap water as feed is shown in Experiment 3 in Table 9 and Figure 11.

Improvement in % ion rejection is shown in Experiments 2 and 3. This might be caused by flux increasing which helps to reduce the concentration polarization or by flushing. The improvement of CA ratio (see Table 9) indicates that some precipitates were removed by flushing. However, % ion rejection of SO_4^{-2} in both experiments is still low (69-71%). The ion rejection in Experiment 3 is lower than that in Experiment 2. This may be due to the precipitation of chemicals during Experiment 2.

Table 9

Results Obtained for SO_4^{-2}, Ca^{+2} Ions

Ion	Expt. No.	Starting Time (hr.:min.)	Water Recovery (%)	% Ion Rejection					CA Ratio				
				Time (min.)					Time (min.)				
				30	60	90	120	150	30	60	90	120	150
SO_4^{-2}	1	--	75.7	--	--	24.1 ± 4.6	20.0 ± 5.8	40.0 ± 2.7	--	--	1.27	1.02	1.93
	2	--	52.5	70.3 ± 1.9	71.7 ± 1.8	71.3 ± 1.8	71.5 ± 1.8	72.2 ± 1.8	1.17	1.06	0.97	1.00	0.95
	3	--	50.0	75.1 ± 2.1	71.6 ± 2.2	67.0 ± 2.3	69.7 ± 2.2	69.6 ± 2.2	1.53	1.06	1.04	1.05	1.01
SO_4^{-2}	4	0	45.7	94.2 ± 3.1	98.0 ± 2.9	98.9 ± 1.6	99.4 ± 1.5	100 ± 1.5	--	--	1.28	1.18	1.15
	5	3:50	48.3	99.1 ± 1.3	97.7 ± 1.2	98.7 ± 1.1	98.3 ± 1.2	----	1.90	1.15	1.17	1.12	--
	6	5:50	50.3	98.9 ± 1.7	96.2 ± 1.7	97.1 ± 1.9	99.6 ± 1.9	----	1.92	1.18	0.88	0.81	--
	7	8:50	62.3	96.8 ± 1.4	95.1 ± 1.2	96.0 ± 1.2	97.2 ± 1.2	----	3.05	1.24	1.24	1.21	--
	8	11:20	28.9	100 ± 2.6	100 ± 2.7	100 ± 2.8	100 ± 2.9	----	1.25	1.09	1.15	1.03	--
	15	26:05	50.2	97.2 ± 1.6	98.8 ± 1.7	97.8 ± 1.7	98.2 ± 1.6	----	1.33	1.14	1.09	1.21	--
	28	52:50	50.3	86.0 ± 1.3	86.3 ± 1.3	88.6 ± 1.2 (120 min.)	88.6 ± 1.3 (180 min.)	89.8 ± 1.4 (240 min.)	1.24	1.12	1.09	1.02	1.08
Ca^{+2}	9	13:20	51.0	94.1 ± 1.8	91.0 ± 1.7	96.4 ± 1.6	94.0 ± 1.6	----	2.26	1.07	1.12	1.08	--
	10	15:50	63.0	90.0 ± 1.7	89.6 ± 1.6	88.6 ± 1.5	89.1 ± 1.5	----	1.27	1.15	1.12	1.12	--
	11	17:50	29.8	92.5 ± 2.3	95.7 ± 2.2	96.8 ± 2.2	98.5 ± 2.1	----	0.79	0.85	1.05	1.05	--
	17	30:35	50.0	84.6 ± 4.2	86.9 ± 1.5	87.6 ± 1.5	90.2 ± 1.5	----	0.47	1.11	1.09	1.13	--

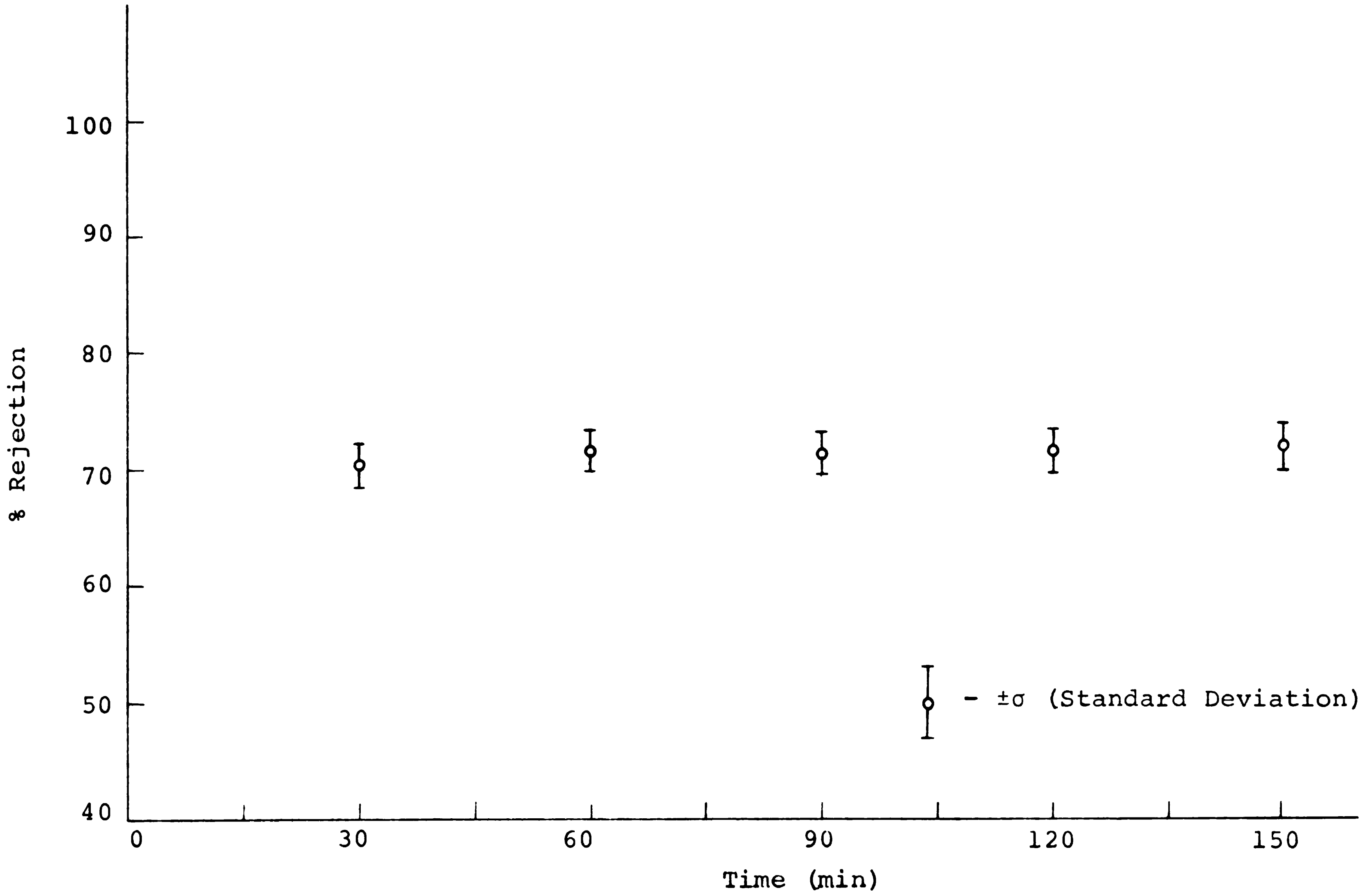


Figure 10. % Ion Rejection vs. Time for SO_4^{-2} Ion at 50% Water Recovery (Expt. 2)

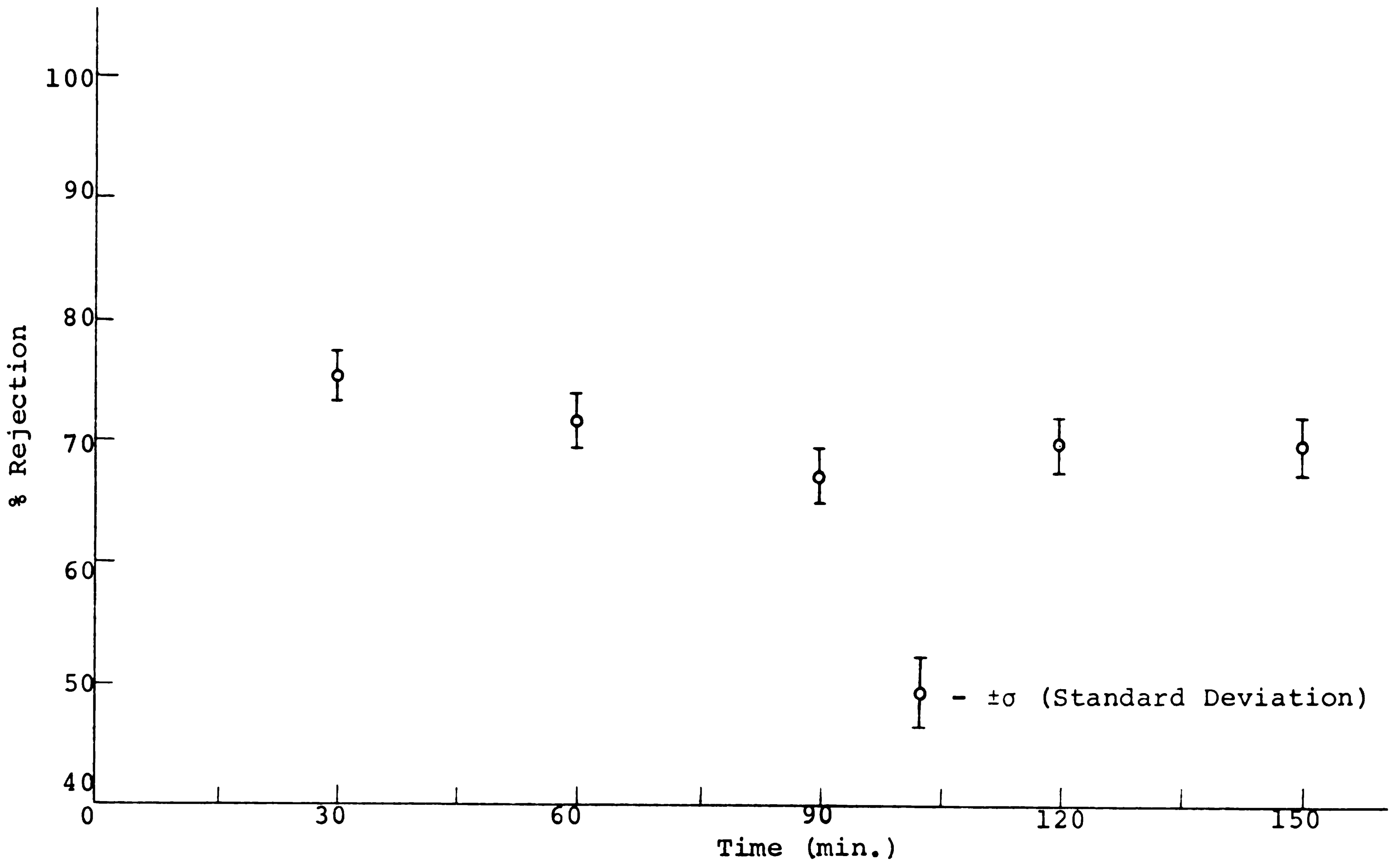


Figure 11. % Ion Rejection vs. Time for SO_4^{-2} Ion at 50% Water Recovery (Expt. 3)

After Experiment 3, it was decided that the cartridge model J-267 is inefficient and should be replaced by a new one.

7.2 Cartridge Model No. L6J2

The ion rejection of 4 different ions (SO_4^{-2}, Ca^{+2}, Na^+, K^+) were determined, each at 3 different water recoveries (30, 50 and 60%). Synthetic brine was used as feed in every experiment.

The results of SO_4^{-2} ion rejection are shown in Experiments 4-8, 15 and 28 in Table 9 and Figure 12.

The ion rejection results are quite high, especially at water recovery of 30%. This is due to the new cartridge used. There was no effect due to precipitation and membrane compaction yet.

The results of Ca^{+2} ion rejection are shown in Experiments 9-11 and 17 in Table 9 and Figure 14.

The results of Na^+ ion rejection are shown in Experiments 12-14 and 16 in Table 10 and Figure 15.

The results of K^+ ion rejection are shown in Experiments 18-27 in Table 10 and Figure 16. Experiments 19-21 showed a fluctuation of results. This was caused by precipitation of ions. The system was then flushed with radiacwash for 1 hour. Experiment 22 gave better results but during Experiment 23, there was a leakage in the feed line. The system had to be opened

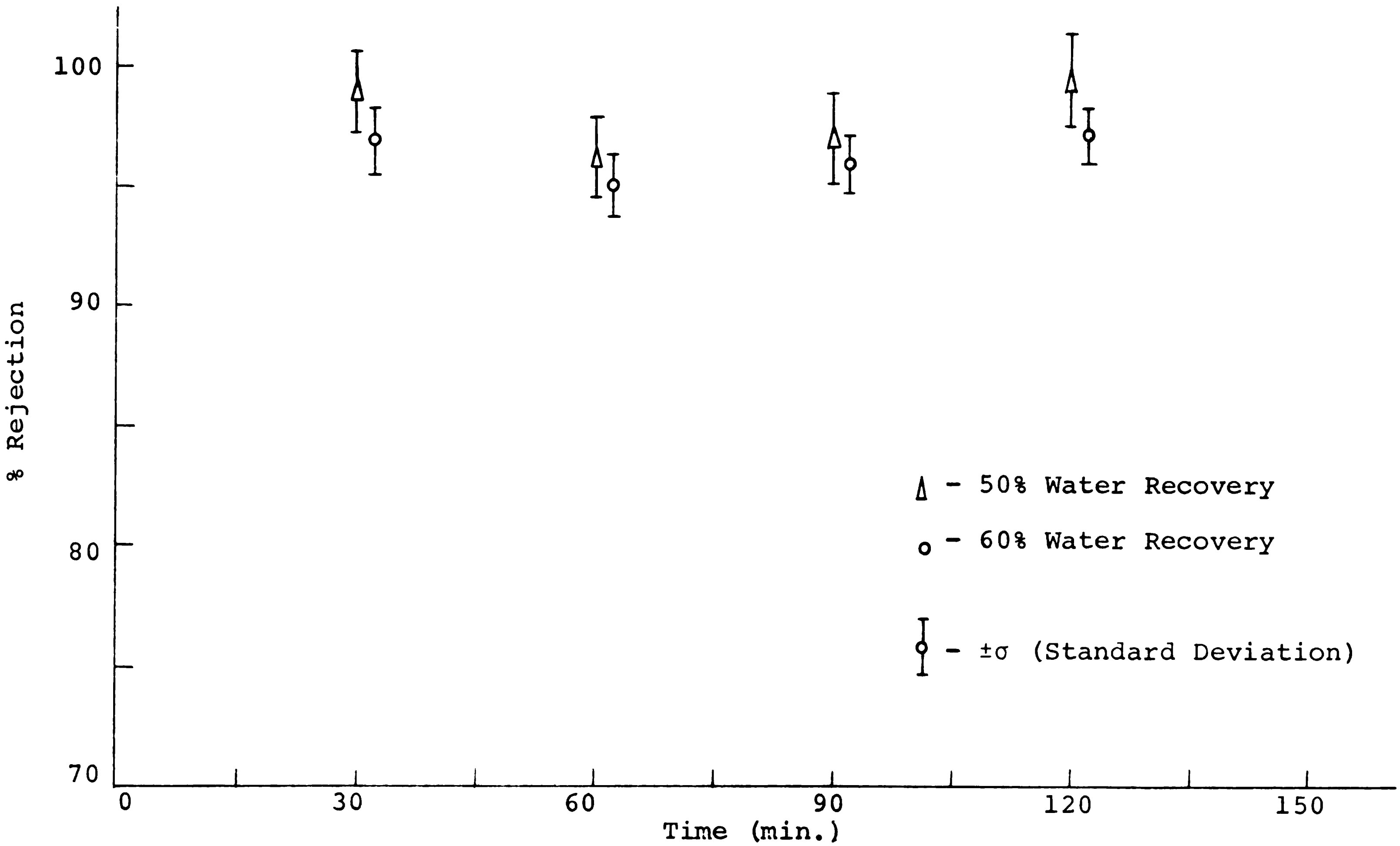


Figure 12. % Ion Rejection vs. Time for SO_4^{-2} Ion (Expts. 6-7)

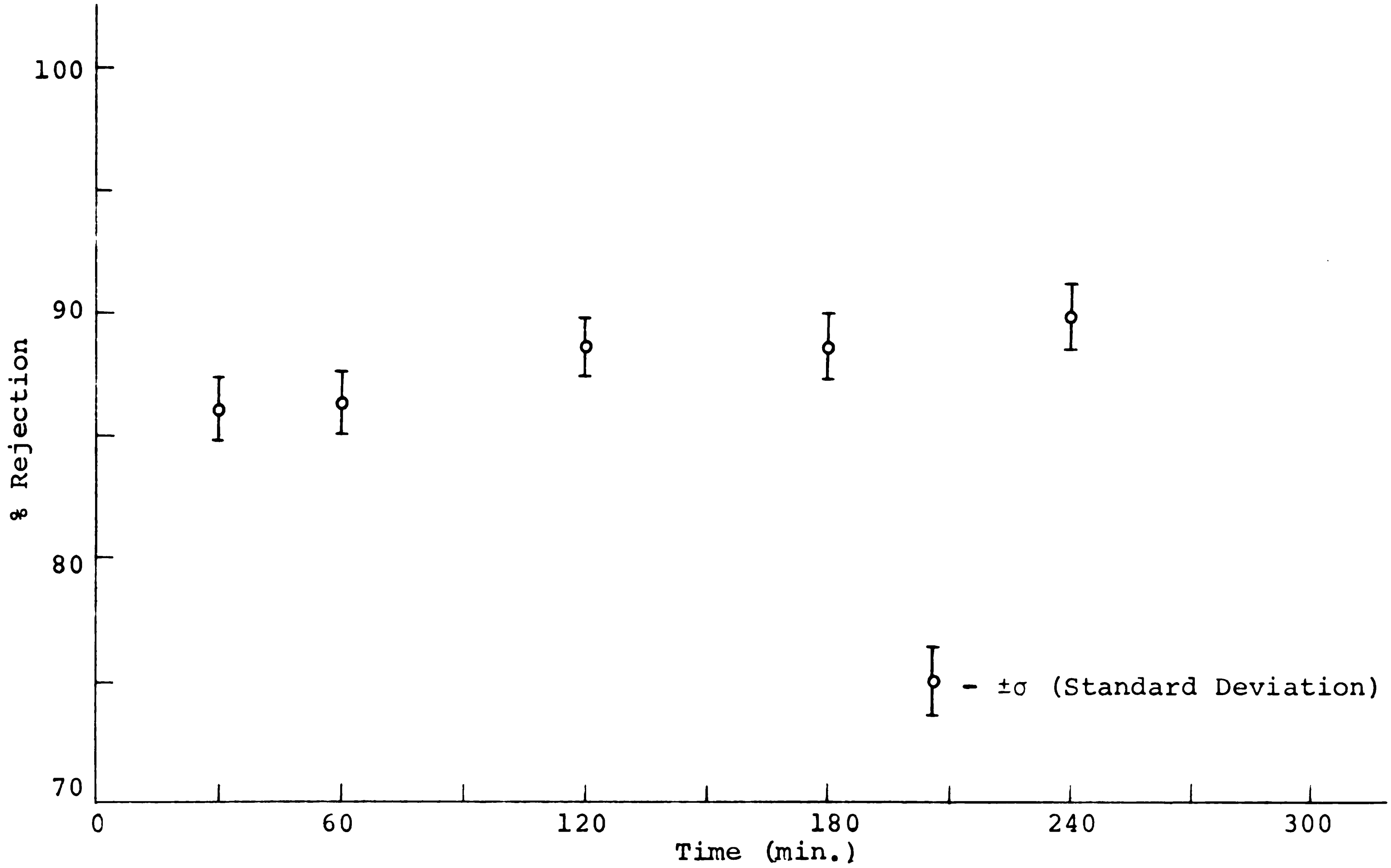


Figure 13. % Ion Rejection vs. Time for SO_4^{-2} Ion at 50% Water Recovery (Expt. 28)

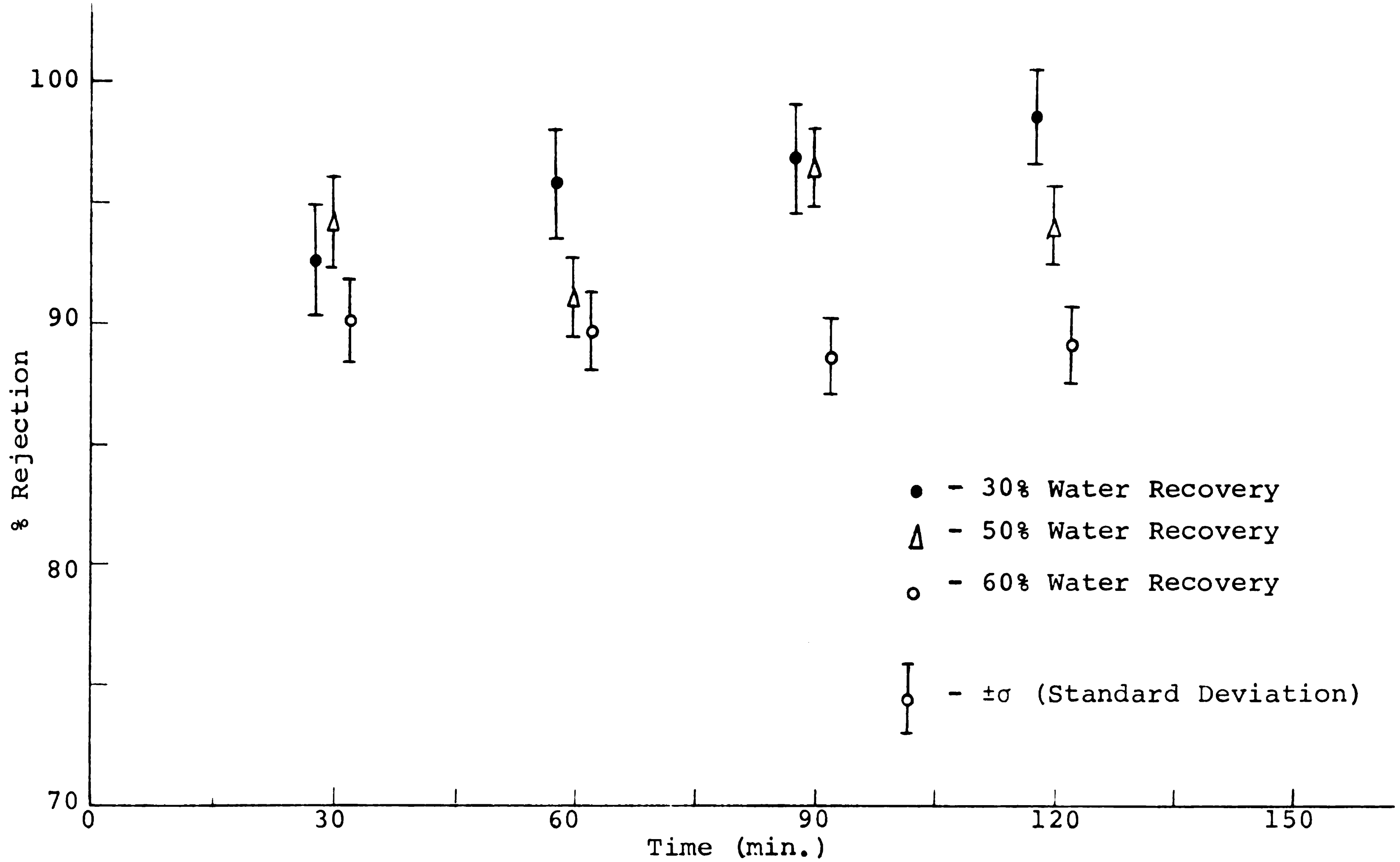


Figure 14. % Ion Rejection vs. Time for Ca^{+2} Ion (Expts. 9-11)

Table 10

Result Obtained for Na^+, K^+ Ions

Ion	Expt. No.	Starting Time (hr.:min.)	Water Recovery (%)	% Ion Rejection				CA Ratio			
				Time (min.)				Time (min.)			
				30	60	90	120	30	60	90	120
Na^+	12	19:50	50.3	82.1 ± 4.0	79.2 ± 4.2	81.0 ± 4.0	85.9 ± 4.2	1.15	0.97	1.21	1.06
	13	22:05	60.3	82.4 ± 0.8	89.3 ± 0.7	84.5 ± 0.8	83.8 ± 0.8	1.26	1.54	1.19	1.16
	14	24:05	30.6	87.3 ± 1.1	86.6 ± 1.2	87.0 ± 1.2	87.2 ± 1.2	1.03	1.00	1.02	1.03
	16	28:20	50.4	82.0 ± 2.1	79.0 ± 2.2	80.5 ± 2.3	80.8 ± 2.4	1.10	1.00	1.01	1.00
K^+	18	32:50	50.5	81.3 ± 0.9	80.9 ± 0.9	81.0 ± 1.0	81.2 ± 1.0	1.19	1.13	1.01	0.92
	19	34:50	61.2	80.0 ± 0.9	62.5 ± 1.7	92.3 ± 2.5	63.2 ± 2.0	1.71	0.60	1.29	0.42
	20	36:50	30.3	92.5 ± 1.9	73.7 ± 2.9	64.9 ± 2.2	84.3 ± 1.2	6.66	0.97	0.37	1.40
	21	38:50	61.3	82.4 ± 0.9	78.1 ± 1.4	50.2 ± 2.8	90.3 ± 0.8	1.99	0.82	0.28	2.92
	22	40:50	30.2	86.1 ± 1.3	83.6 ± 1.6	77.9 ± 1.8	86.2 ± 1.4	1.01	0.88	0.68	1.06
	23	42:50	59.9	78.0 ± 1.1	83.6 ± 1.1	86.1 ± 1.0	--	1.15	1.09	1.42	--
	24	44:50	58.2	68.8 ± 1.4	81.8 ± 1.2	64.5 ± 1.9	--	1.00	1.82	0.74	--
	25	46:50	29.4	79.8 ± 1.0	81.3 ± 1.0	82.4 ± 1.0	82.0 ± 1.0	1.03	1.05	1.03	1.05
	26	48:50	50.0	74.5 ± 0.9	76.2 ± 0.9	77.1 ± 0.9	75.2 ± 1.0	1.11	1.12	1.07	1.00
	27	50:50	60.0	72.7 ± 1.0	72.5 ± 1.0	73.3 ± 1.0	75.7 ± 1.1	1.33	1.24	1.52	1.25

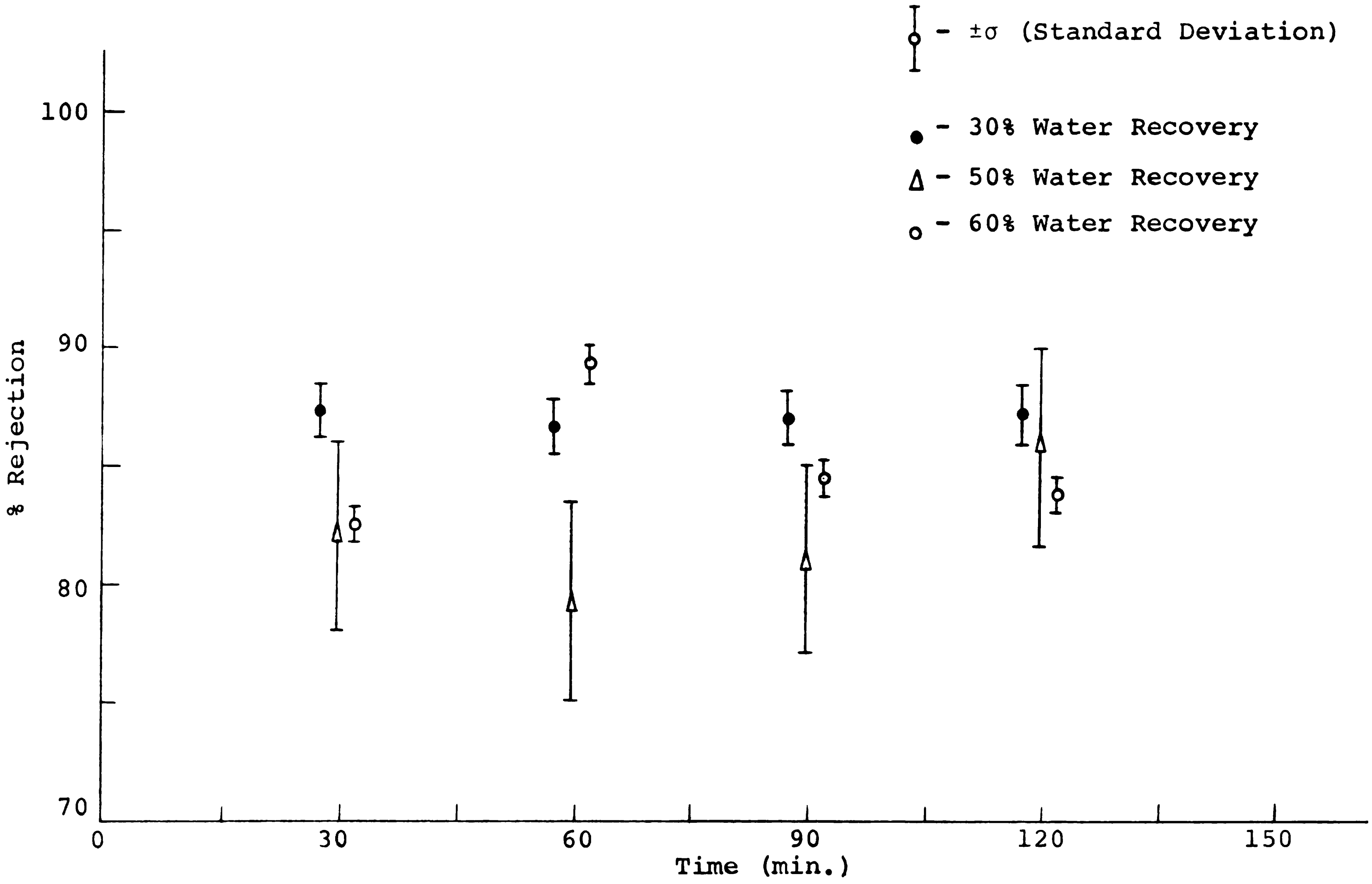


Figure 15. % Ion Rejection vs. Time for Na^+ Ion (Expts. 12-14)

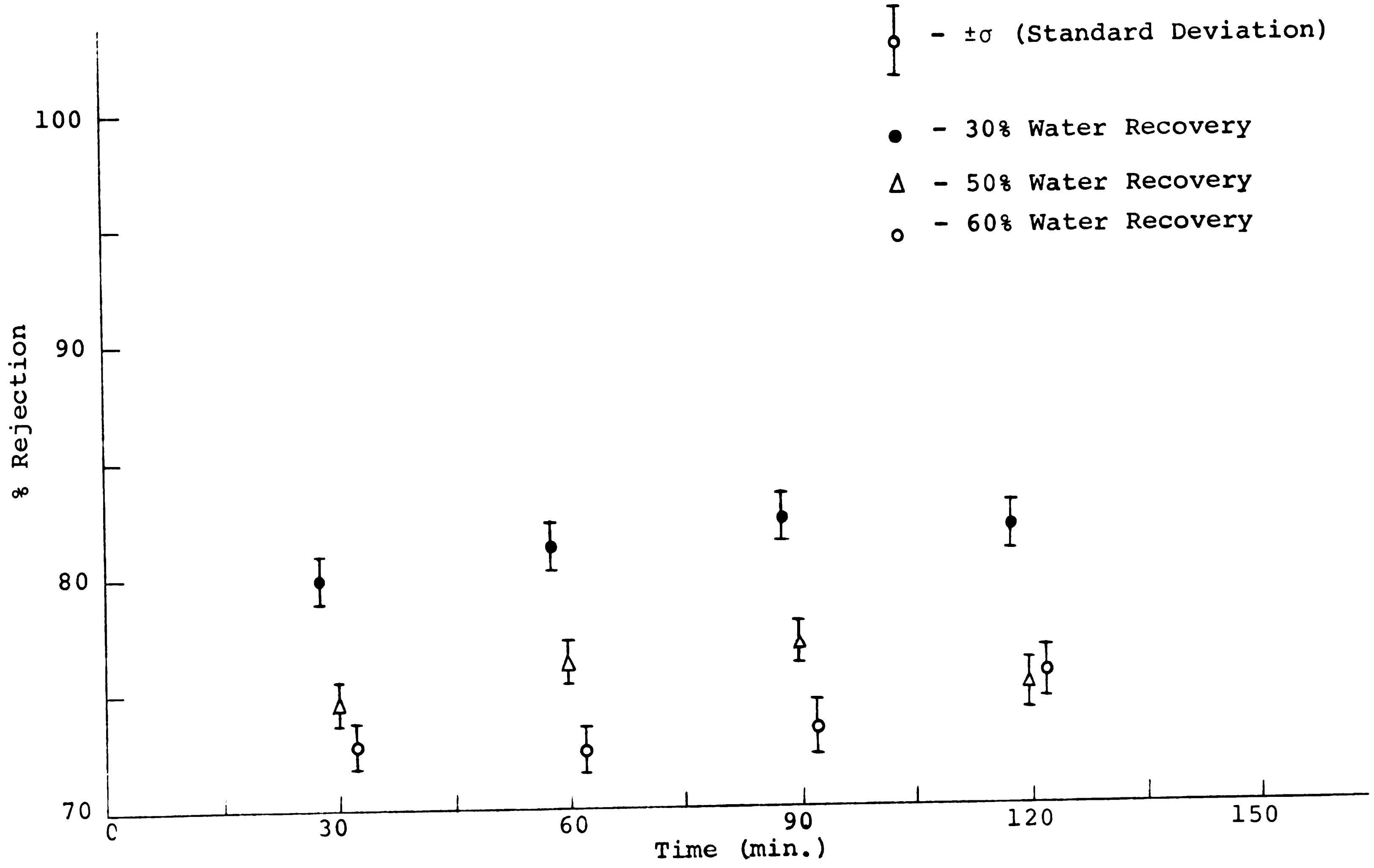


Figure 16. % Ion Rejection vs. Time for K^+ Ion (Expts. 25-27)

for repairs. There was a disorder in the suction end of the radionuclide injection pump during Experiment 24. The pump lines had to be cleaned. The results were improved in later experiments (Experiments 25-27).

7.2.1. Decrease of Ion Rejection

Experiments 15-17, 25 were also performed to determine the decrease of ion rejection after a longer period of time. This decrease in ion rejection can also be noticed from the conductivity data in Tables 3-8. The conductivity of the product stream was increased with no. of experiment or time especially from Experiments 23 to 24.

7.2.2. Steady State Flow

Most experiments showed consistent CA Ratio, except for the first 30 minutes. This was caused by the unsteady flow and mixing at the beginning. From the results, it is noticed that the steady state was approached in about 30 to 60 minutes.

8. DISCUSSIONS

8.1 Cartridge Model No. J-267

Experiment 1, which was repeated using the same condition as Tucker's Experiment 39 (5), showed the same scattering and low SO_4^{-2} rejection. This was due to the precipitation of ions in the membrane. For synthetic brine with 8700 ppm. concentration, $CaSO_4$ will precipitate if the water recovery is more than 83% (23). However, even when less than 83% recovery is used, precipitation can occur in the RO system because of the polarization effect as stated in 2.4.3. In Tucker's experiment, the water recovery used (70-85%) was too high. This high water recovery or low feed rate increased the concentration polarization effect. The ion concentration near the wall became more than the concentration in 83% water recovery, so the ions precipitated in or on the membrane.

Other causes might be the deterioration of the cellulose acetate with time or swelling of the membrane because of the high pressure used as discussed in 2.4.

Experiments 2 and 3 showed the result after the cartridge was flushed with radiacwash solution for 3 hours. The % ion rejection was improved with more consistent results. However, the % rejection of 70.0 is still too low to be practical. The cartridge was considered inefficient and was not used further.

When the cartridge was removed from the system, a lot of precipitates including iron oxide were found both in the solution and on the membrane wall (see Cartridge Model J-267 in Figure 17). The iron oxide came from the unpurified $CaCl_2$ used.

8.2 Cartridge Model No. L-6J2

8.2.1. % Ion Rejection

Of all the ions, SO_4^{-2} was shown to be the ion most rejected by the RO membrane as expected. The reasons are that the SO_4^{-2} ion has the largest charge and mass. The ion rejection usually increases with the change on the ion and its physical size (1). The next most rejected ion was Ca^{+2}. The next one should be K^+ because of its larger molecular size than Na^+. In this experiment, it was difficult to distinguish which one is more rejected, because of the precipitation of chemical ions and the resultant lowering of the ion rejection with time.

8.2.2. % Ion Rejection vs. Time

Figure 18 shows that the % ion rejection of SO_4^{-2} ion decreased with time. The time plotted is not

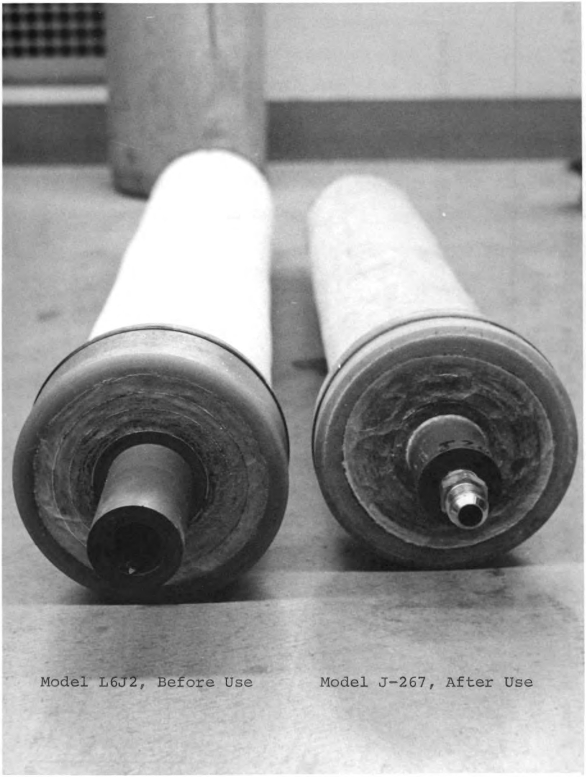


Figure 17. Dow Hollow Fiber Reverse Osmosis Cartridge

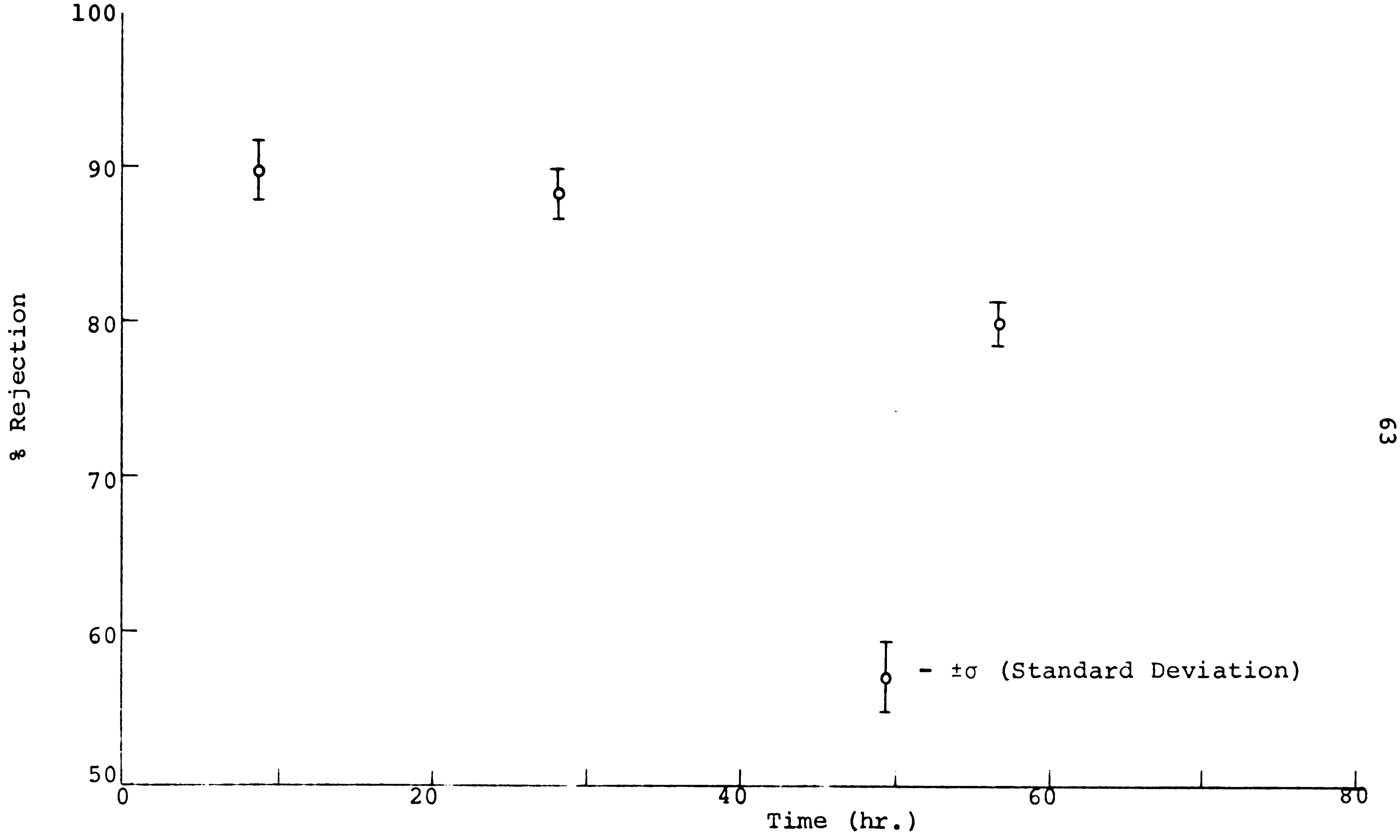


Figure 18. % Ion Rejection vs. Time for SO_4^{-2} Ion at 50% Water Recovery (Expts. 6, 15, 28)

continuous. It was accumulated from successive experimental times when synthetic brine was used as feed, not including flushing time at the beginning and end of each experiment.

It is noticed that the iron rejection dropped quite distinctly at a time close to 50 hours. At that time, the system was opened to repair leakage in the feed line. The membrane could have dried. This caused the deterioration of the CA membrane and thus decreased the rejection ability.

8.2.3. % Ion Rejection vs. % Water Recovery

The results of ion rejection vs. water recovery of 4 different ions are shown in Figure 19. From the results, the lower the water recovery, the higher is the ion rejection. This is due to the higher feed rate or turbulence when lower water recovery is used (the permeate rate remained almost constant for all experiments). This higher turbulence helped to reduce the concentration polarization effect and thus reduce the ion concentration near the wall. As discussed in 2.1, the salt flux depends on the feed concentration near the wall (C_w) as follows:

$$J_2 = KB\ (C_w - C_p)$$

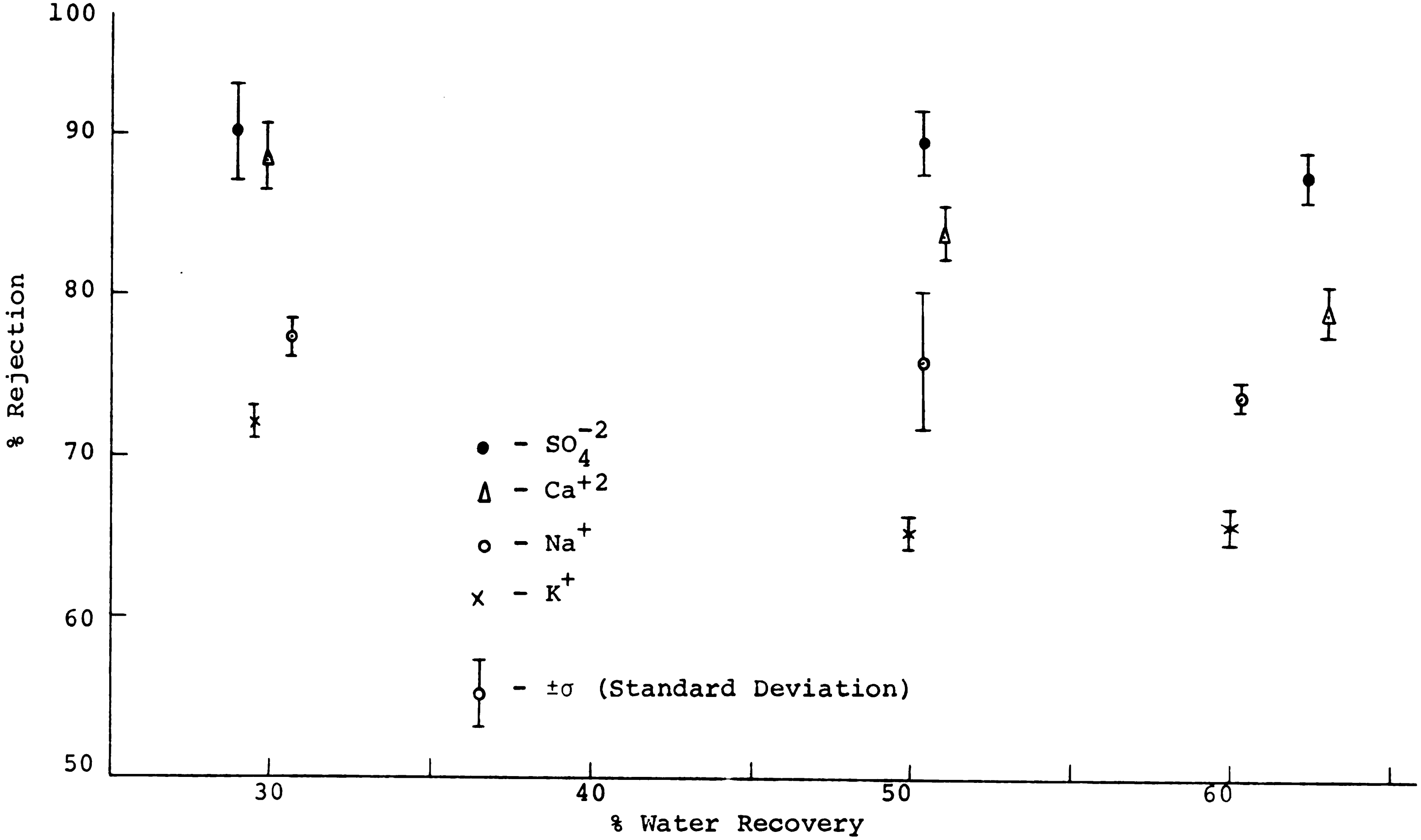


Figure 19. % Ion Rejection (at 120 min.) vs. % Water Recovery

For SO_4^{-2}, there is just a little decrease in ion rejection when water recovery is increased from 30 to 60%, about 3%.

Water recovery plays an important role in Ca^{++} rejection, accounting for about 10% change when water recovery is varied from 30 to 60%. In this case, the Ca^{+2} ions can be precipitated as $CaCO_3$ or $CaSO_4$. $CaSO_4$ precipitates when its solubility product in the solution reaches 0.0016949 (23). At high water recovery, Ca^{++} may precipitate and thus the ion rejection is lower than usual.

For Na^+, the ion rejection decreased about 4% when water recovery was increased from 30 to 60%, whereas about an 8% ion rejection decrease was observed for K^+ at the same water recovery increase.

8.2.4. Permeate Flux

Figure 20 shows that the permeate flux remains almost constant with time (accumulated time from successive experiment), except at one point. This may be due to the error in measuring the flow rates at that point.

The permeate flux of the membrane model L6J2 is quite low because of the large active area of the membrane (1895 ft^2) and the low feed rate used. To increase the permeate flux, the low pressure applied

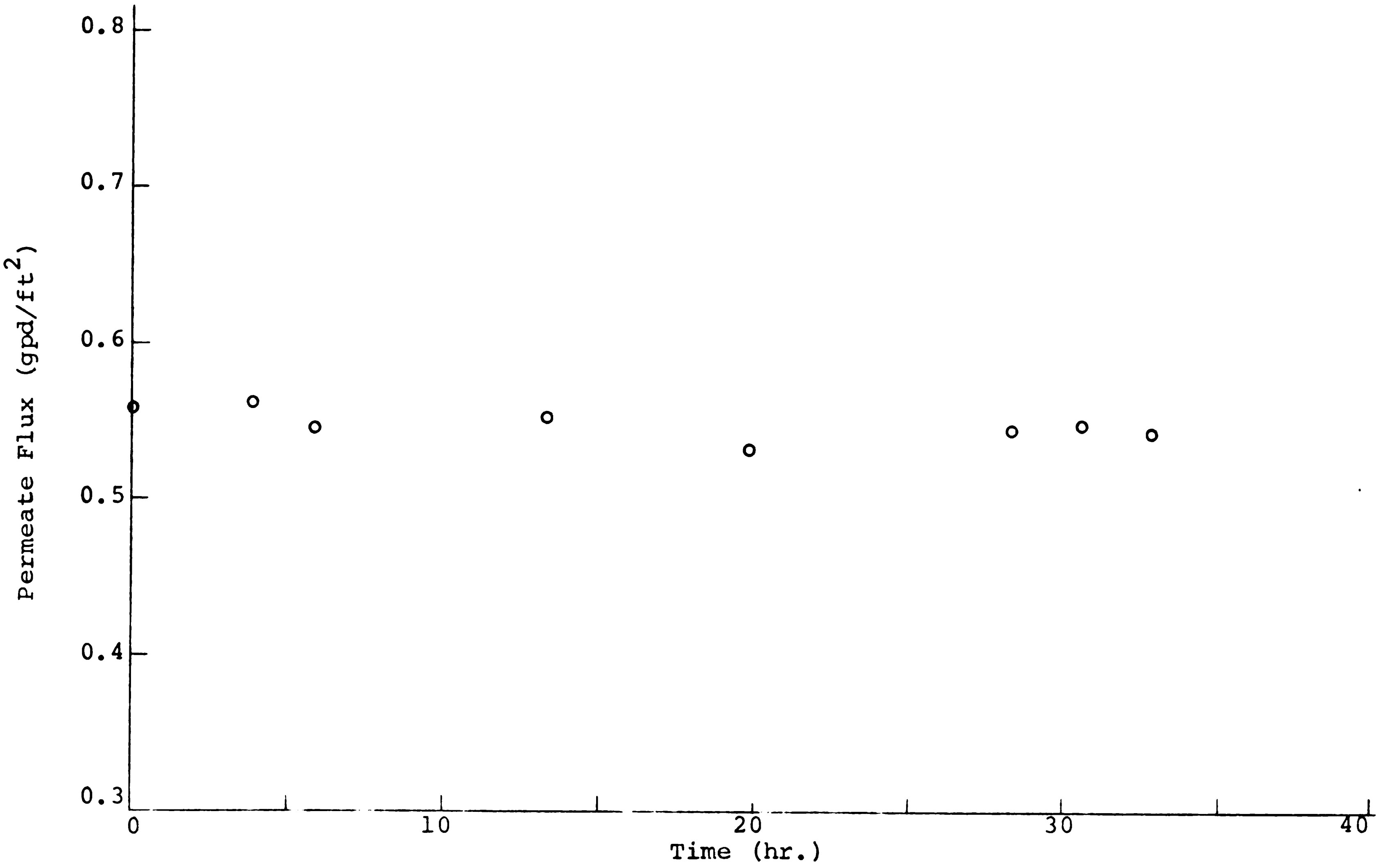


Figure 20. Permeate Flux at 25°C (50% Water Recovery) vs. Time

to pump the feed stream in should be increased. However, larger feed storage tanks should be used too. The increase in feed flow rate will help to reduce the concentration polarization effect, and improve the product quality.

8.2.5. CA Ratio

Most of the CA ratio at 30 and 50% water recovery are close to 1.0 (see Tables 9 and 10). This shows that there was no precipitation occurring during the experiments. At 60% recovery, CA ratios are much more than 1.0; however, they are consistent. The high CA ratio shows that the ions might be precipitating in the membrane. At this point, it can be concluded that there was precipitation occurring at 60% water recovery using synthetic brine as feed.

8.2.6. Conductivity

In some experiments, the conductivity was not constant as it should be. This may be due to insufficient mixing of feed solution, or precipitation in the membrane.

The increase of conductivity of the permeate stream with no. of experiments indicates that there was precipitation occurring during the experiments. The conductivity increased sharply in Experiment 24. This may be due to the dryness of the membrane as stated in 8.2.2.

8.2.7. pH

The pH of the feed brine was controlled between 5.5-6.0 to avoid deterioration of the membrane. The average pH is about 4.7 for the product stream and 6.0 for the concentrate stream. The lower pH in the product stream is due to the lower salt and higher CO_2 concentration. A lot of CO_2 was produced when HCl acid reacted with $NaHCO_3$ in the feed brine. Most CO_2 can permeate through the membrane (26) and thus lower the pH of the product stream.

The pH of the product water increased after letting the product water stand so the CO_2 could escape.

9. CONCLUSIONS AND RECOMMENDATIONS

Using synthetic brine as feed in Dow RO systems, ion rejections of the hollow fine fiber membrane were studied for SO_4^{-2}, Ca^{+2}, Na^+, K^+ ions. Ions with larger charge and mass, such as SO_4^{-2}, are more rejected by the membrane. Ion rejection is also quite high at low water recovery because of the high turbulence near the membrane walls.

The results also show that there are chemicals precipitated at 60% water recovery. Using 50-60% water recovery, the system has to be flushed with radiacwash solution or other cleansing agents every 20-hour operation. To avoid the chemical precipitation, low water recovery at 30% should be used. The system can then be flushed after longer periods of operation.

The average total ion rejection of the membrane is about 90% at 50% water recovery and system pressure of 670 psi. If higher system pressure (> 700 psi.) is applied at lower water recovery (30%), the ion rejection may be increased to 96%. The product water can then be used as potable water. Another alternate process consists of 2 RO systems in series using lower pressure to purify the brackish water to potable level.

Table 11

Summary of Results (Cartridge Model L6J2)

Ions	% Water Recovery	Flux at 25°C (gpd/ft^2)	% Ion[a] Rejection
Na^+	30.6	0.423	87.2
	50.3	0.531	85.9
	60.3	0.510	83.8
K^+	29.4	0.510	82.0
	50.0	0.552	75.2
	60.0	0.571	75.7
Ca^{+2}	29.8	0.460	98.5
	51.0	0.553	94.0
	63.0	0.552	89.1
SO_4^{-2}	28.9	0.521	≃100
	50.3	0.545	99.6
	62.3	0.572	97.2

[a] % Ion Rejection was measured at operating time of 120 min.

9.1 Recommendations

I. More conc. HCl can be added to the synthetic brine to lower the pH to 5.5. This may decrease the precipitation of chemicals.

II. The process using higher system pressure (700-800 psi) should be tried at 30% water recovery.

III. The process using lower pressure (300-400 psi) with 2 RO systems in series should be tried.

IV. The costs of both processes in II and III should be studied to determine the most suitable process for the brackish water.

APPENDICES

APPENDIX A

DEFINITION OF TERMS

APPENDIX A

DEFINITION OF TERMS

Definition of terms used in describing the operation of reverse osmosis process are as follows:

Feed stream.--An aqueous solution from which the water is to be removed.

Product or permeate stream.--The water which has permeated through the membrane.

Concentrate stream.--The aqueous solution which has had part of its water content removed.

Concentrate flow rate.--The rate of flow of concentrate stream expressed in term of gpm.

Permeate flow rate.--The rate of flow of product stream expressed in term of gpm.

Permeate flux.--The quantity of water permeating through a unit membrane surface during the time interval. This term is expressed as gal. of permeate water per sq. ft. of membrane surface per day.

Feed pressure.--The pressure applied to pump the feed stream into the filter (psi).

System pressure.--The pressure applied to the feed stream before going through the RO module (psi).

Concentrate pressure.--The pressure measured at the concentrate stream after passing through the RO module (psi).

% Water recovery.--The percentage of permeate water produced in a unit time period on the basis of the feed water used in the same unit time period.

$$\%\ \text{Water recovery} = \frac{\text{Permeate flow rate}}{\text{Permeate flow rate} + \text{Concentrate flow rate}}$$

% Ion rejection.--This term is used to measure process efficiency.

$$\%\ \text{Ion rejection} = \frac{(\text{Conc. of ions in feed} - \text{Conc. of ions in product}) \times 100}{\text{Conc. of ions in feed}}$$

CA ratio.--This term is used to measure the accuracy of the results.

$$\text{CA ratio} = \frac{(\text{Feed rate})\ (\text{Feed activity}) - (\text{Permeate rate})\ (\text{Permeate activity})}{(\text{Concentrate rate})\ (\text{Concentrate activity})}$$

APPENDIX B

ANALYSIS OF TAP WATER FROM MICHIGAN STATE UNIVERSITY

APPENDIX B

Table 12

Analysis of Tap Water from Michigan State University[a]

Constituent	Concentration (ppm.)
Ca as $CaCO_3$	310.
Mg^{+2}	27.
SO_4^{-2}	15.
Na^+	13.8
Cl^-	3.0
K^+	1.5
F^-	1.0
Fe^{+2}	0.0
Mn^{+2}	0.0
NO_3^-	0.0
Total dissolved solids	371.3
pH	7.6

[a] The analysis is from the State of Michigan Department of Public Health (30).

APPENDIX C

ANALYSES OF THE MARSHALL FORMATION UNDERGROUND WATER

APPENDIX C

Table 13

Analyses of the Marshall Formation Underground Water

Constituent	Concentration (ppm.)
$Ca(HCO_3)_2$	1537[a]
$Fe(HCO_3)_2$	27
$Mg(HCO_3)_2$	329
K_2SO_4	213
SiO_2	57
NaCl	4575
$NaHCO_3$	1601
Na_2SO_4	429
Total solids	8768

[a] The analysis was found in the U.S. Geological Survey water supply paper No. 31, pages 38, 58 and 60 (1900) (4).

The above analysis corresponds to the synthetic brine analysis used in the experiment (excluding SiO_2).

APPENDIX D

NEUTRON ACTIVATION AND RADIOACTIVE DECAY

APPENDIX D

Neutron Activation

The Na and K radionuclides used in the experiment were activated by MSU Triga Reactor at Michigan State University. The activity produced in an irradiation time t is given by (29):

$$A = N\phi\sigma \ (1-e^{-\lambda t}) \qquad \text{. . . . . (6)}$$

$$\lambda = \frac{0.693}{t_{1/2}} \qquad \text{. . . . . (7)}$$

where:

A = activity produced (disintegration/sec. or dps)

N = the no. of atoms of the target nuclide in the sample, capable of forming the radioisotope in question

ϕ = the neutron flux (n/cm.^{2}-sec)

σ = the isotopic thermal neutron capture cross section (cm.^{2})

t = irradiation time

λ = decay constant = $0.693/t_{1/2}$

$t_{1/2}$ = the half life of the nuclear species produced, in the same units as t.

Radioactive Decay

The decay of radioactive nuclides is a first-order reaction in which the rate of change is proportional to the number of radioactive atoms present. The number of radioactive atoms present at any time t can be calculated by the following equation (28):

$$A = A_o e^{-\lambda t} \qquad \ldots\ldots\ldots \quad (8)$$

where:

A = no. of radioactive atoms remaining at time t

A_o = original no. of radioactive atoms present

λ = decay constant = $0.693/t_{1/2}$

$t_{1/2}$ = half life of the radioactive nuclide

APPENDIX E

RADIOACTIVITY DATA

APPENDIX E

Radioactivity Data

Data of radiactivity counted by the Scintillation Spectrophotometry for all streams (feed, permeate and concentrate) at different times. The activities are net counts per 50 minutes, corrected for background and radioactive decay.

1. Nuclide - S^{35}

Experiment 1

Time (min.)	Feed	Permeate	Concentrate
90	14699	11157	20238
120	13709	10979	21804
150	14647	8791	17004

Experiment 2

Time (min.)	Feed	Permeate	Concentrate
30	10459	3111	15870
60	11062	3133	18621
90	10922	3138	20210
120	11119	3170	20002
150	10947	3039	20803

Experiment 3

Time (min.)	Feed	Permeate	Concentrate
30	7231	1802	8303
60	7494	2130	12101
90	7426	2450	11958
120	7688	2328	12456
150	7443	2265	12450

Experiment 4

Time (min.)	Feed	Permeate	Concentrate
30	2250	130	---
60	2435	49	1341
90	7966	90	11435
120	8606	56	13352
150	9210	0	14778

Experiment 5

Time (min.)	Feed	Permeate	Concentrate
30	12906	122	13093
60	15259	357	25397
90	15773	201	25838
120	15223	259	26030
Experiment 6			
30	7153	82	7549
60	7740	296	13485
90	5964	171	13800
120	5358	24	13345
Experiment 7			
30	11461	371	9749
60	16111	794	33534
90	16035	637	33595
120	15734	446	33899
Experiment 8			
30	2613	0	2945
60	2437	0	3136
90	2323	0	2847
120	2358	0	3218
Experiment 15			
30	8325	235	12378
60	7319	91	12788
90	6949	150	12705
120	7705	137	12673
Experiment 28			
30	16005	2234	24220
60	16149	2211	27103
120	16896	1926	29371
180	15557	1771	29017
240	12530	1276	22166

2. Nuclide - Ca^{45}

Experiment 9

Time (min.)	Feed	Permeate	Concentrate
30	6831	406	5976
60	8129	733	14828
90	8431	303	15075
120	8316	503	15206

Experiment 10

30	8627	867	17138
60	9692	1007	21208
90	10440	1192	23298
120	10466	1137	23539

Experiment 11

30	4104	307	7221
60	4483	195	7455
90	4551	148	6112
120	4620	71	6229

Experiment 17

30	1467	226	5731
60	10924	1435	18482
90	10734	1331	18436
120	11121	1087	18792

3. Nuclide - Na^{24}

Experiment 12

30	1705	306	2719
60	1672	348	3092
90	1807	344	2723
120	1527	213	2704

Experiment 13

30	44411	7830	79702
60	47938	5129	73181
90	37043	5726	71371
120	37711	6093	73677

Experiment 14

Time (min.)	Feed	Permeate	Concentrate
30	21105	2689	28417
60	19052	2555	26415
90	17443	2271	23611
120	17566	2245	23532

Experiment 16

30	6362	1146	10617
60	5868	1231	10618
90	5302	1033	9538
120	5023	965	9276

4. Nuclide - K^{42}

Experiment 18

30	34036	6364	52206
60	34837	6639	56231
90	25902	4928	46785
120	30526	5733	60565

Experiment 19

30	33518	6719	44246
60	15660	5877	51492
90	3501	271	6648
120	10919	4023	51778

Experiment 20

30	6159	465	1296
60	4061	1070	5511
90	8852	3110	21225
120	18710	2935	18216

Experiment 21

30	36059	6346	41844
60	16059	3522	43731
90	8882	4421	57631
120	38051	3701	31598

Experiment 22

Time (min.)	Feed	Permeate	Concentrate
30	14223	1971	19238
60	11017	1809	17135
90	9170	2023	18097
120	13829	1904	17949
Experiment 23			
30	26659	5879	50147
60	20640	3389	42785
90	27575	3838	44380
120	--	2772	30838
Experiment 24			
30	20121	6282	39339
60	18973	3462	22355
90	11681	4147	29950
120	3354	--	3186
Experiment 25			
30	30054	6060	38904
60	31402	5883	40152
90	30361	5347	39730
120	31395	5652	40194
Experiment 26			
30	38088	9696	59824
60	40048	9526	63217
90	39944	9136	65857
120	34726	8620	60832
Experiment 27			
30	34348	9370	54112
60	35075	9650	59320
90	34751	9268	48050
120	28307	6894	48421

APPENDIX F

SAMPLES OF CALCULATION

APPENDIX F

Samples of Calculation

Samples of Calculation:

Experiment 14. - Na^+ at 30% water recovery

1. Amount of chemical to be irradiated for experimental use:

Approximate activity desired (A) = 45 μCi = $45 \times 3.7 \times 10^4$ dps.

Neutron flux (ϕ) = 2×10^{12} n/cm^2-sec

Isotopic thermol neutron capture cross section of Na^{24} (σ) = 5.3×10^{-25} cm.^{2}

Irradiation time (t) = 1/4 hr.

λ of Na^{24} = 4.62×10^{-2} /hr

From $A = N\phi\sigma\ (1-e^{-0.693t/t\ 1/2})$ . . . . (6)

$$\therefore \text{gms. pure Na needed} = \frac{(45 \times 3.7 \times 10^4)\ (23)}{(6.023 \times 10^{23})\ (2 \times 10^{12})\ (5.3 \times 10^{-25})\ \{1-e^{-(4.62 \times 10^{-2}/4)}\}}$$

$$= 5.216 \times 10^{-3}$$

$$\therefore \text{gms. NaOH needed} = (\frac{40}{23})\ (5.22 \times 10^{-3})$$

$$= 9.071 \times 10^{-3} \text{ gms.}$$

2. Radioactive decay after 600 min. or 10 hr.:

Activity after 10 hr. (A) = 11067 counts/50 mins.

t = 10 hr.

From $A_o = Ae^{\lambda t}$

$\therefore$ Initial activity = (11067) $(e^{4.62 \times 10^{-2} \times 10})$

= 17566 counts/50 mins.

3. % Ion rejection:

$$\% \text{ Ion rejection} = \frac{(\text{Feed Activity-Permeate Activity})}{\text{Feed Activity}} \times 100$$

$$= \frac{(17566 - 2245)}{17566} \times 100$$

$$= 87.2$$

4. Permeate flux:

$$\text{a) Permeate flux at T°C} = \frac{\text{Permeate flux rate}}{\text{Active membrane area of RO module}}$$

$$= \frac{(0.435 \text{ gpm})\ (60 \text{ min})\ (24 \text{ hr.})}{(1895 \text{ ft}^2)\ (1 \text{ hr.})\ (1 \text{ day})}$$

$$= 0.330 \text{ gpd/ft}^2$$

$$\text{b) Permeate flux at 25°C} = \frac{\text{Flux at temperature T°C}}{(1.0265)^{T-T_{25}}}$$

$$= \frac{0.330}{1.0265^{(-7.778)}}$$

$$= 0.423 \text{ gpd/ft.}^2$$

5. % Water Recovery:

$$= \frac{\text{Permeate flow rate}}{\text{Feed flow rate}} \times 100$$

$$= \frac{\text{Permeate flow rate} \times 100}{\text{Permeate flow rate + Concentrate flow rate}}$$

$$= \frac{0.44}{0.44 + 0.99} \times 100$$

$$= 30.6\%$$

6. CA ratio:

$$= \frac{(\text{Feed rate})\ (\text{Feed activity}) - (\text{Permeate rate})\ (\text{Permeate activity})}{(\text{Concentrate rate})\ (\text{Concentrate activity})}$$

$$= \frac{(1.43)\ (17566) - (0.44)\ (2245)}{(0.99)\ (23532)}$$

$$= 1.03$$

7. Standard deviation (σ):

The standard deviation of a net number of counts is the square root of the number of counts divided by the length of time the sample was counted.

$$\therefore\ \sigma_{\text{Feed}} = \left(\frac{17566}{50}\right)^{1/2} = 2.651 \text{ cpm.}$$

$$\sigma_{\text{Product}} = \left(\frac{2245}{50}\right)^{1/2} = 0.948 \text{ cpm.}$$

The standard deviation of the difference of two numbers is given as follows in counts per minute (cpm.):

$$(A \pm \sigma_F) - (B \pm \sigma_p) = (A-B) \pm (\sigma_F^2 + \sigma_p^2)^{1/2}$$

$$= (A-B) \pm \sigma_{DIF}$$

$$= \left(\frac{17566}{50} - \frac{2245}{50}\right) \pm \left(\frac{17566}{50^2} + \frac{2245}{50^2}\right)^{1/2}$$

$$= 306.420 \pm 2.815 \text{ cpm.}$$

The standard deviation of a quotient is given as follows in cpm:

$$\frac{(A-B \pm \sigma_{DIF})}{A \pm \sigma_F} = \left(\frac{A-B}{A}\right)\left[1 \pm \left\{\frac{\sigma^2_{DIF}}{(A-B)^2} + \frac{\sigma_F{}^2}{A^2}\right\}^{1/2}\right]$$

$$= \left(\frac{17566 - 2245}{17566}\right)\left[1 \pm \left\{\frac{2.815^2}{306.420^2} + \frac{2.651^2}{\left(\frac{17566}{50}\right)^2}\right\}^{1/2}\right]$$

$$= 0.872 \pm 0.012$$

$\therefore$ The standard deviation of this quotient is 1.2%.

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BIBLIOGRAPHY

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