

AN INVESTIGATION OF THE PURIFICATION
OF SYNTHETIC BRINE WITH REVERSE OSMOSIS

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J. LANNY TUCKER

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ABSTRACT

AN INVESTIGATION OF THE PURIFICATION OF SYNTHETIC BRINE WITH REVERSE OSMOSIS

By

J. Lanny Tucker

A study was made of the use of reverse osmosis to remove inorganic ions from tap water and a synthetic brine solution. The equipment used included a pretreatment filter, an in-line mixing tank, an acid feed pump, and a high pressure pump. The system had appropriate pH, temperature, pressure, and flow rate instrumentation and controls. Water purification proceeded with a hollow fine fiber RO module manufactured by Dow Chemical Company. The module fibers were made of cellulose acetate and have an outside diameter of 50 microns.

The ion rejection of SO_4^{-2} , Ca^{++} , and Na^+ were determined over a period of time. Water recovery and water flux were calculated. A unique feature of the system was the ability to recycle waste water back into the feed. The equipment was first tested with tap water. Later experimentation was designed to find the ion rejection of Na^+ and SO_4^{-2} in a synthetic brine that had a concentration of over 8700 ppm of inorganics.

Analysis was made by injecting radioisotopes of the ion studied into the feed stream. This injection occurred with the hydrochloric acid used to control the pH between the limits of 5.5 and 6.0. Mixing of the tracers in the feed was assured in a 7 gallon mixing tank. Radioactivity was detected with liquid scintillation techniques.

Data were obtained by taking samples of feed, permeate, and concentrate streams. The resulting net counts were used to calculate ion rejection.

In the tap water experiments, rejection of all three ions was found to reach near 95% at steady state. A lower

water recovery (percentage of feed recovered as permeate) increased the ion rejection, while an increase in the amount of waste recycled lowered the product water quality. These results agree with those found in the literature for brackish waters (14). In addition, the divalent ions, SO_4^{-2} and Ca^{++} were rejected more easily than the monovalent Na^+ .

Experimentation with the synthetic brine produced consistent results with Na^+ . Rejection was near 90% at steady state with a recovery of 70%. Product water quality declined when water recovery was increased. Results from experiments with the sulfate ion were not consistent enough to draw conclusions. The reverse osmosis system behaved as if the module contained some carbonates and sulfates which lowered product quality.

The use of reverse osmosis in the Lansing area to purify brackish water appears to be feasible from the standpoint of the technique. Further studies using Marshall formation brine should be performed to investigate the economic feasibility.

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By

J.^{AMES} Lanny Tucker

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To Jesus Christ

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INTRODUCTION

Tremendous interest has been generated during the past fifteen years for reverse osmosis as a promising method for economic recovery of water from saline solutions. Using this technique, desalination is achieved by forcing a salt solution under pressure past a semi-permeable membrane which passes water more readily than organic material or inorganic ions. A flowsheet of a typical process system is shown in Figure 1. The method differs from electrodialysis in that the driving force is pressure instead of electrical potential.

Reverse osmosis has several distinct advantages. The method is simple in concept; operation is at ambient temperature; and membranes are being continually developed which give successively better rejections and higher fluxes at lower pressures. In fact, the technology has moved so fast that current desalting plant operations are feasible and available for municipal and industrial use in plants with capacities up to 10 million gallons per day(M GPD). Desalting in large quantities of 50M GPD or more can be practically considered for operation in the late 1970's or early 1980's(20).

It appears that the first proposal that salt rejection by membranes might be useful in desalination was made by C.E. Reid at the University of Florida to the Office of Saline Water in 1953(16). Research was begun by Loeb and Sourirajan at UCLA to develop a cellulose acetate membrane with a high flux. This work was continued by General Dynamics and Aerojet General up to the present day. Today, research in reverse osmosis is carried out by many universities and corporations. Much of this work is sponsored by the Office of Saline Water

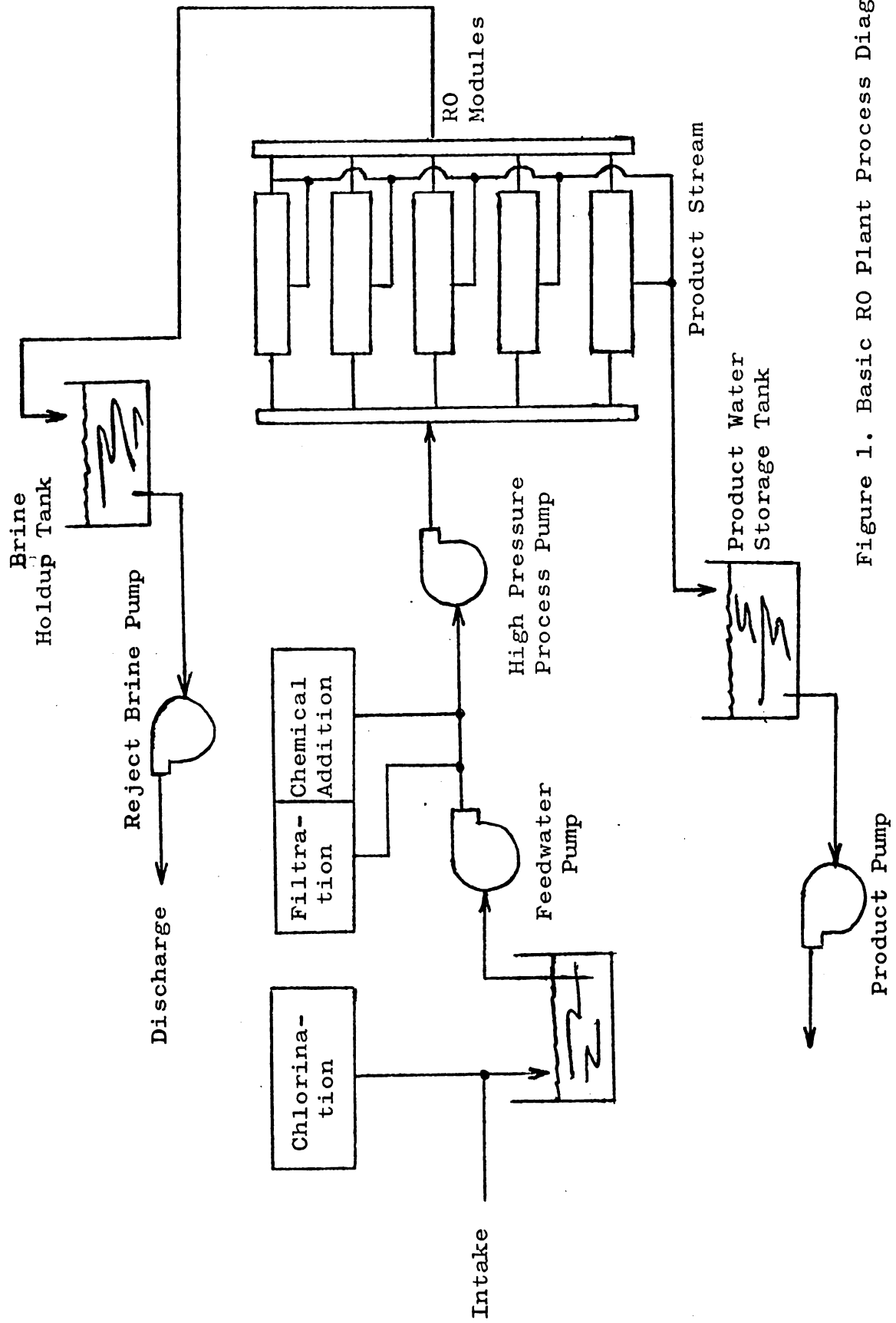


Figure 1. Basic RO Plant Process Diagram

in the U.S. Department of the Interior. It is carried out in all parts of the world, and is subject to comparison with other desalination techniques such as freezing, flash distillation, electrodialysis, exchange diffusion, and piezodialysis.

Much attention has been paid by researchers in reverse osmosis to obtaining fresh water from the sea. But of more interest to inland experimenters is the economic feasibility of using the method to purify brackish waters, industrial wastes, and municipal drain-off and sewage. Power requirements and other economic factors point out that reverse osmosis is advantageous over other processes such as distillation and electrodialysis in purifying brackish waters. Reverse osmosis removes the organics or ions from the fresh water while the other methods remove the water from the contaminants and require the same energy for every feed stream(14). The Federal government has sponsored development of a 250,000 GPD test bed for brackish water(20). Of primary emphasis to its users is development of membranes with capacities of 10 or 50 times the present cellulose acetate ones.

Recent research has accomplished the following(19):

1. Development of blend cellulose acetate membranes which give higher production rates for brackish water.
2. Development of the novel composite concept(ultra-thin film barrier on a microporous membrane backing or support).
3. Discovery of efficient membranes of cellulose acetate butyrate.
4. Development of highly specialized films, tubes, and hollow fibers for purification.
5. Preparation of cellulose acetate fibers by the unique thermal precipitation method.
6. Progress in development of technology for in plant removal and membrane replacement.

It has been known for many years that below the fresh water table in the central region of Michigan is a vast deposit of brackish water. This deposit of water is called the Marshall formation and can be found at a depth of about 600 feet(18). Late 19th Century drillers had hoped the salt content would be high enough so that commercial sale of the minerals would be profitable. A U.S. Geological Survey of 1900 showed the concentration to be about 8768 ppm(18). This includes calcium, sodium, chloride, sulfate, and bicarbonate as the principal ions. The synthetic brine described in Appendix B closely resembles the composition of the Marshall formation.

Today, thought is being given to this brackish source as potential municipal water. Reverse osmosis is looked upon as one of the best means of purifying the Marshall formation.

The purpose of the present study was to become acquainted with the reverse osmosis process and equipment, to determine particular ion rejection rates both from tap water and a synthetic brine solution, and to obtain data on the membrane fluxes of the equipment.

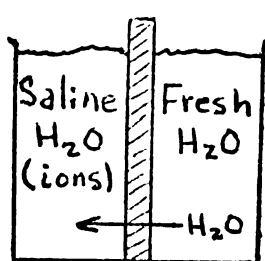
The equipment was provided by Dow Chemical Company with the understanding that they would be allowed any and all information derived from its use. Analysis was accomplished by using radioactive tracers injected into the feed stream. No report in the literature has been made as to use of this technique in reverse osmosis research. However, it is being currently used in experimentation sponsored by the Office of Saline Water of the U.S. Department of the Interior at Clarkson College.

THEORY

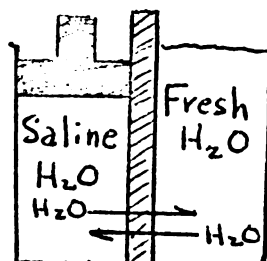
Reverse Osmosis Operation

Osmosis, as well as reverse osmosis, depends upon the existence of a membrane that is selective in the sense that some components of a solution can pass through but not the others (semi-permeability).

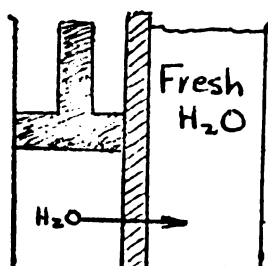
Both processes can be simply illustrated as in Figure 2.



Osmosis



Osmotic Equilibrium



Reverse Osmosis

Figure 2. Basic Principles of Osmosis and Reverse Osmosis

Under normal conditions, water will flow from the fresh container to the concentrated solution. The driving potential is called the osmotic pressure($\Delta\pi$). Actual flow of fluid is related to the chemical potential of the solution, which is a function of the solution pressure, temperature, and the number and types of molecules in solution.

When an external pressure(equal to the osmotic pressure) is applied to the concentrated salt solution, the flow of fluid is in equilibrium. As this external pressure is increased, water is forced from the concentrated

solution into the fresh water container, leaving the ions behind. This water flux can be described by:

$$J_1 = K_1(\Delta P - \Delta \pi) \quad (1)$$

or,

$$J_1 = K_1 P_{\text{eff}} \quad (2)$$

where,

P_{eff} = the effective membrane driving pressure

ΔP = pressure difference between the feed stream and the product stream

K_1 = membrane permeability constant(GPD/ft²-psi)

J_1 = product water flux(GPD/ft²).

The movement of ions across the membrane, though not desirable, cannot be entirely stopped. This flux can be approximated by:

$$J_2 = B(C_w - C_p) \quad (3)$$

where,

J_2 = salt transfer flux(lb/hr)

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 pressures associated with typical brackish water feeds are 30-150 psi, whereas sea water may exhibit pressures as high as 450-600 psi. Therefore, reasonable water flux through current high salt rejecting cellulose acetate membranes requires pressures of 600-800 psi for brackish water, and up to 1500 psi for sea water(14).

Membrane Failure

Ideally, reverse osmosis membranes would pass all of the water forced through the system. But this objective

is difficult to obtain in practice. A decrease in water flux occurs for the following reasons:

1. Membrane fouling by scale, contaminants, etc.
2. Membrane compaction and compression--related to the effects associated with the sustained high pressure fluid crushing the porous structure of the membrane.
3. Irreversible hydrolytic deterioration of the membrane material-- related to the hydrolysis of the cellulose acetate to cellulose.

Fouling is reduced by proper pretreatment, both filtering and chemical, to remove organics, large sediments, iron, and manganese. Organics and sediments of silica are best removed by a system of filters in front of the reverse osmosis system. Iron and manganese removal is not quite as simple. It requires passing the water through zeolite sands of KMnO_4 where Fe and Mn are oxidized so that insoluble oxides are formed. These are subsequently filtered out(25).

Compaction is the long term degradation of the membrane. In-situ methods proposed to counteract this effect and to restore membranes to their original performance have largely failed to date(14). It appears that compaction is best reduced through proper design and manufacture of the membranes.

Hydrolytic degradation of cellulose acetate to cellulose is reduced only by controlling the pH of the feed within certain limits.

The ability of the membranes to reject salts also decreases with time. The major factors appear to be(14):

1. Membrane compaction-- the effect of the pressurized fluid on the thin membrane pore size.
2. Coupling-- transport mechanics predict a small coupling effect between the flow of pure water and inorganic ions.
3. Hydrolytic degradation of cellulose acetate to cellulose.

The first and last factors have already been discussed above in connection with decrease of water flux through membranes. Current knowledge has not determined the importance of the second factor in salt rejection. Further research is needed to identify the magnitude of the coupling effect and how to overcome it.

Membrane Transport Mechanisms

The transport of both water and salt across a membrane has not been adequately described in a physical theory so that all scientists involved could reach agreement. Of the many theories proposed, two stand out as having satisfied most of the experimental evidence to date. These are the solution diffusion model and the pore flow model.

The solution diffusion model pictures a homogeneous gel phase in which water and salts are dissolved and transported by means of diffusion as described by Fick's Law(22).

The pore flow model is being more widely accepted today. It is described thusly:

"A typical membrane material can be viewed as a water swollen, rubber-like sheet of material with an active surface layer of 0.1 to 0.3 percent of the total thickness. The thin active layer contains water molecules bound to the polymer structure by hydrogen bond. Dissolved salts and organic materials are rejected at the active layer because bound water is no longer available to dissolve solute. The pure water that passes through the bound water portions of the membrane layer is transported by successive forming and breaking of hydrogen bonds between water molecules and the "active sites." Under pressure, a water molecule approaches a membrane site where a molecule is already bound. The approaching water molecule forms a new bond as the previous molecule is freed by that site. By site transfer, bound water "diffuses" into the body of the membrane. In the swollen, sublayer body, capillary action then moves the water molecules through relatively huge pores to a sink at atmospheric pressure. The dense surface layer appears to limit the flux and is responsible for the greatest pressure drop across the membrane."(14)

Using this model, Kesting(23) concludes that in an asymmetric cellulose, 1.5 acetate membrane, two water mole-

cules bound to one "active" group(an -OH group) can be regarded as primary bound water. The next 3-9 moles of water absorbed by the membrane per "active" group is secondary bound water, and all water absorbed in excess of these values is basically "free" water.

Research in the transport mechanism of reverse osmosis is being encouraged by both private and governmental sources. Knowledge in this field is important to design of membranes with higher fluxes and lifetimes.

Membrane Configuration

There are four different basic membrane configurations currently being evaluated for use with reverse osmosis units. They are:

1. Plate and frame(PF)
2. Tubular(T)
3. Spiral wound(SW)
4. Hollow fine fiber(HFF)

The plate and frame configuration was the first type explored in early reverse osmosis development by Aerojet General Corporation. Current studies show it has advantages of simplicity, ruggedness, and on-site replacement. But its disadvantages of high equipment cost, difficult brine flow patterns, and high labor membrane replacement costs dim its future development into municipal use. The concept is shown in Figure 3(14).

The tubular configuration is similar to a typical shell and tube heat exchanger, as shown in Figure 4(14). Cellulose acetate is cast on the inner supporting wall. Its obvious advantages are its well defined flow passages, small filtration requirements, and ease of cleaning. But it has a low packing density, with a large number of tubes required per unit surface area, and is moderately high in initial cost. Research is aimed at lowering costs by developing in-situ casting of membranes.

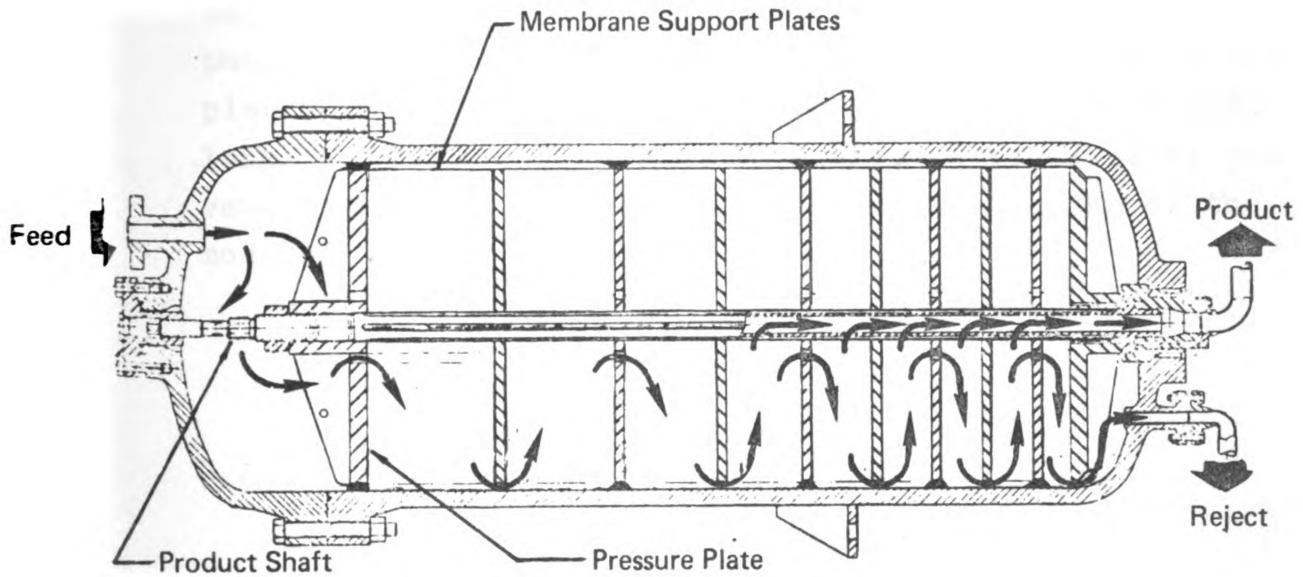


Figure 3. Plate and Frame Module Configuration

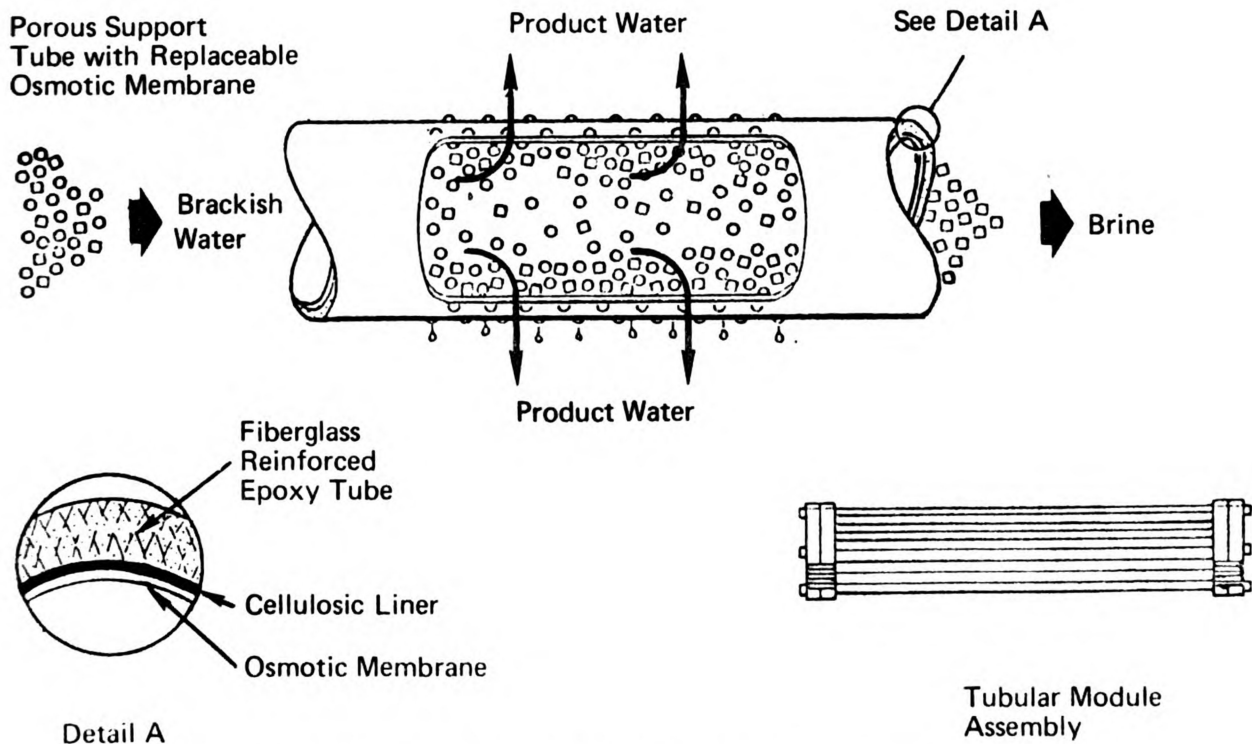


Figure 4. Tubular Module Configuration

Development of the spiral wound design has been the emphasis of Gulf General Atomic Company. High membranes packing density is possible, and it is adaptable to simple field replacement. However, the product flow path is long, and much feed water filtration is required to prevent plugging. Figure 5 shows a simple diagram of the module(14).

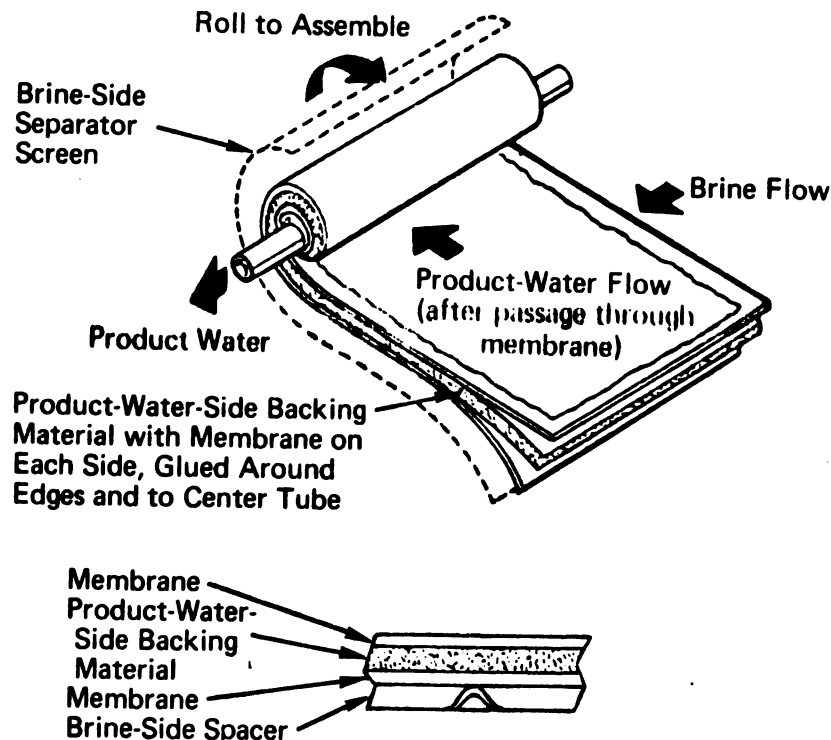


Figure 5. Spiral Wound Module Configuration

The hollow fine fiber concept has been developed by the Dow, Dupont, and Monsanto Companies. Figure 6 shows a typical module as manufactured by Dow Chemical. The configuration is similar to the tubular design with a large number of hollow fibers of very small diameter resting in a metal shell. The fibers are composed of unsupported membrane material, either cellulose acetate or nylon.

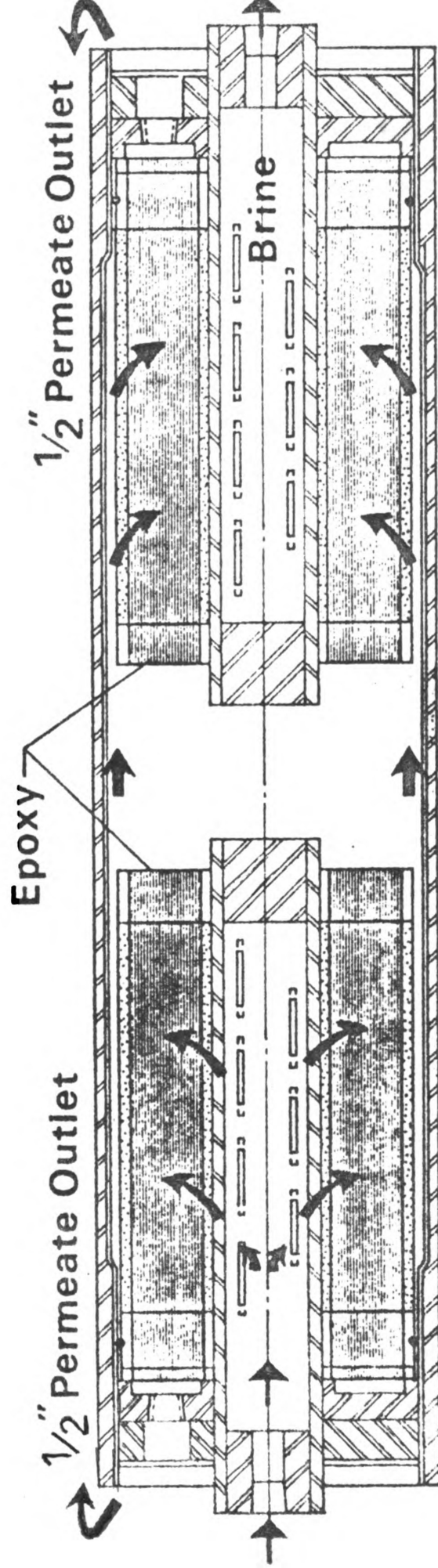


Figure 6. Dow Hollow Fine Fiber RO Module

Water flux for hollow fibers is expressed as a modified form of Equation 1(5):

$$J_1 = \frac{KA(\Delta P - \Delta \pi)}{t} \quad (4)$$

where,

K = permeability coefficient of the membrane for water

A = membrane area(ft²)

t = membrane thickness(in.).

This equation shows that the flux is directly proportional to K and A at a given temperature and inversely proportional to t. A major objective of water purification with membranes is to pack as much membrane area in as small a volume as possible. Hollow fibers allow a high packing density because no support material is needed for the membranes. With nylon fibers, as designed by Dupont, there is little membrane compaction. Lastly, hollow fiber reverse osmosis units can utilize polymers whose K would be far too low for use in the supported film type of modules. This will increase the probability of finding materials with high service life expectation.

Disadvantages of the HFF modules include need of considerable pretreatment of feedwater, factory replacement of modules, and lack of high efficiency membrane technology to date.

Reverse Osmosis System Parameters

A parameter of major importance in the reverse osmosis process is the recovery ratio. This is simply defined as the ratio of product water to feedwater flow rate. This parameter affects the system power requirements, plant costs, and chemical treatment cost.

The following mass flow equations hold true for any desalting process:

$$M_f = M_b + M_p \quad (5)$$

$$M_f C_f = M_b C_b + M_p C_p \quad (6)$$

where,

M = Flow rate

C = salinity

sub f = denotes feedwater

sub b = denotes reject brine

sub p = denotes product water.

The recovery ratio is defined as:

$$RR = M_p / M_f \quad (7)$$

Another quantity frequently important in reverse osmosis studies is the brine concentration ratio. This is defined by:

$$CR = C_b / C_f \quad (8)$$

It can be shown that the relationship between the recovery ratio and the concentration ratio is approximately:

$$RR \cong 1 - 1/CR = 1 - C_f / C_b \quad (9)$$

From Equation 9, it can be seen that a high recovery ratio corresponds to a highly concentrated reject brine.

Operating at high recovery ratio is advantageous for several reasons:

1. Reduced power requirements.
2. Reduced brine disposal requirements.
3. Reduced chemical treatment costs.

The factors limiting the maximum allowable recovery are scale formation and increased salt transport. It is necessary for a system to be optimized for maximum recovery with as little salt passage and scale formation as possible.

Two system hydraulics parameters of considerable importance in a RO module are concentration polarization and system fluid pressure losses.

Concentration polarization is said to occur when the salt concentration at the membrane is greater than that in the bulk feedwater stream(14). The adverse effects of this phenomenon are an increase in product water salinity,

an increase in membrane scaling, and an increase in the osmotic pressure to be overcome.

The most effective solution to this problem in a specific module configuration is the feedwater flow velocity. Turbulent flow greatly decreases the buildup of salinity at the membrane interface over laminar flow(1)(26). However, high water fluxes increase polarization effects. In practice, computer programs are used to evaluate local values of the polarization in particular modules. An optimum design must be found to include both parameters which decrease the effect, and those which increase it.

The concentration polarization factor can be defined as the ratio of the salt concentration measured at the wall of the membrane to the bulk salt concentration in the brine stream(C_w / C_b).

For both tubular and hollow fine fiber modules, polarization can be calculated by using the following equations (12) (14):

$$CPF = \frac{e^x}{\eta + (1-\eta)e^x} \quad (10)$$

$$x = (0.0044J_1 N_{SC}^{0.67} / f\bar{v}) \quad (11)$$

where,

CPF = concentration polarization factor

f = friction factor

\bar{v} = average feedwater stream velocity (ft/sec)

N_{SC} = Schmidt number

η = salt rejection factor

J_1 = product water flux (GPD/ft²)

The Schmidt number is a dimensionless quantity defined as ν/D_s , the kinematic viscosity of the stream divided by the salt diffusivity through the liquid. The salt rejection factor η is simply the fraction of salt rejected by the membrane. Computer programs have been designed to implement this equation for particular systems(12).

System pressure losses fall into two categories, brine side pressure drop(ΔP_b), and product water side pressure drop(ΔP_p). Therefore, the effective system driving pressure is defined by the following relationship:

$$P_{\text{eff}} = (P - \Delta P_{f_L} - \Delta P_p) - \Delta \pi \quad (12)$$

where,

P = high pressure pump outlet pressure

ΔP_{f_L} = pressure loss associated with concentration of feedwater stream

ΔP_p = product side pressure drop

$\Delta \pi$ = osmotic pressure gradient.

The brine side pressure drop is due to friction of the brine in the brine channel. Pressure losses are typically 5-15% of the total system pressure(14).

EXPERIMENTAL EQUIPMENT

The hollow fine fiber reverse osmosis module used in this study was manufactured by Dow Chemical Company. The auxiliary system was designed and made by Polymetrics of San Carlos, California. The supplemental equipment was either fabricated by the MSU Division of Engineering Research shop or purchased outside of the University. Figure 7 shows a basic diagram of the system. It must be noted that only one HFF module was used for experimentation instead of the two shown. Figures 8 and 9 show the front and rear of the equipment respectively.

Synthetic brine was stored in 55 gallon polyethylene drums. It was pumped into the system through a pressure release valve which bypassed excess water back to the feed tanks.

In order to minimize clogging of the fibers, a 5 micron cartridge filter was used to remove suspended matter. An in-line mixing tank of 7 gallon capacity follows the filter. It is here that hydrochloric acid and radioactive tracers are thoroughly distributed in the feedwater.

Feedwater was forced through the RO module by a Gould Model 3933 multistage, centrifugal pump of 15 HP. It is water lubricated and has a capacity of 2-6 GPM, but it can be operated at lower flows by bypassing liquid back to pump suction. The maximum working pressure is 800 psi; and the maximum working temperature is 160°F.

Desalination was accomplished with a single Dow CTA-A Hollow Fine Fiber RO Module. Its specifications are listed in Table 1.

Delivery of chemical treatment to the feed stream was made with a manual controlled feed pump manufactured by Precision Control Products Corporation of Waltham, Mass. It has a maximum capacity of 3.4 GPD with a dial setting from 30-100 to indicate percentage of maximum feed rate.

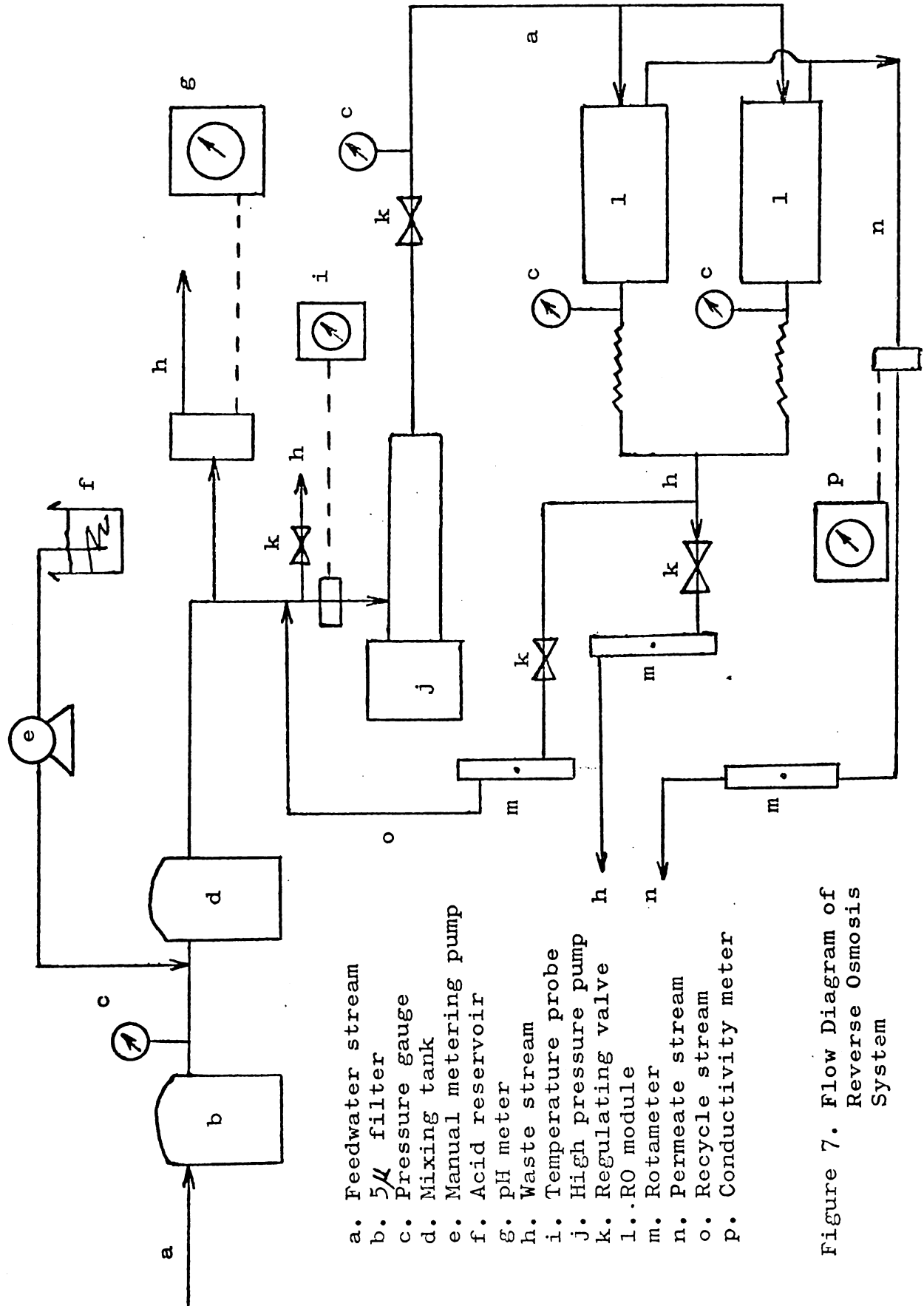


Figure 7. Flow Diagram of Reverse Osmosis System

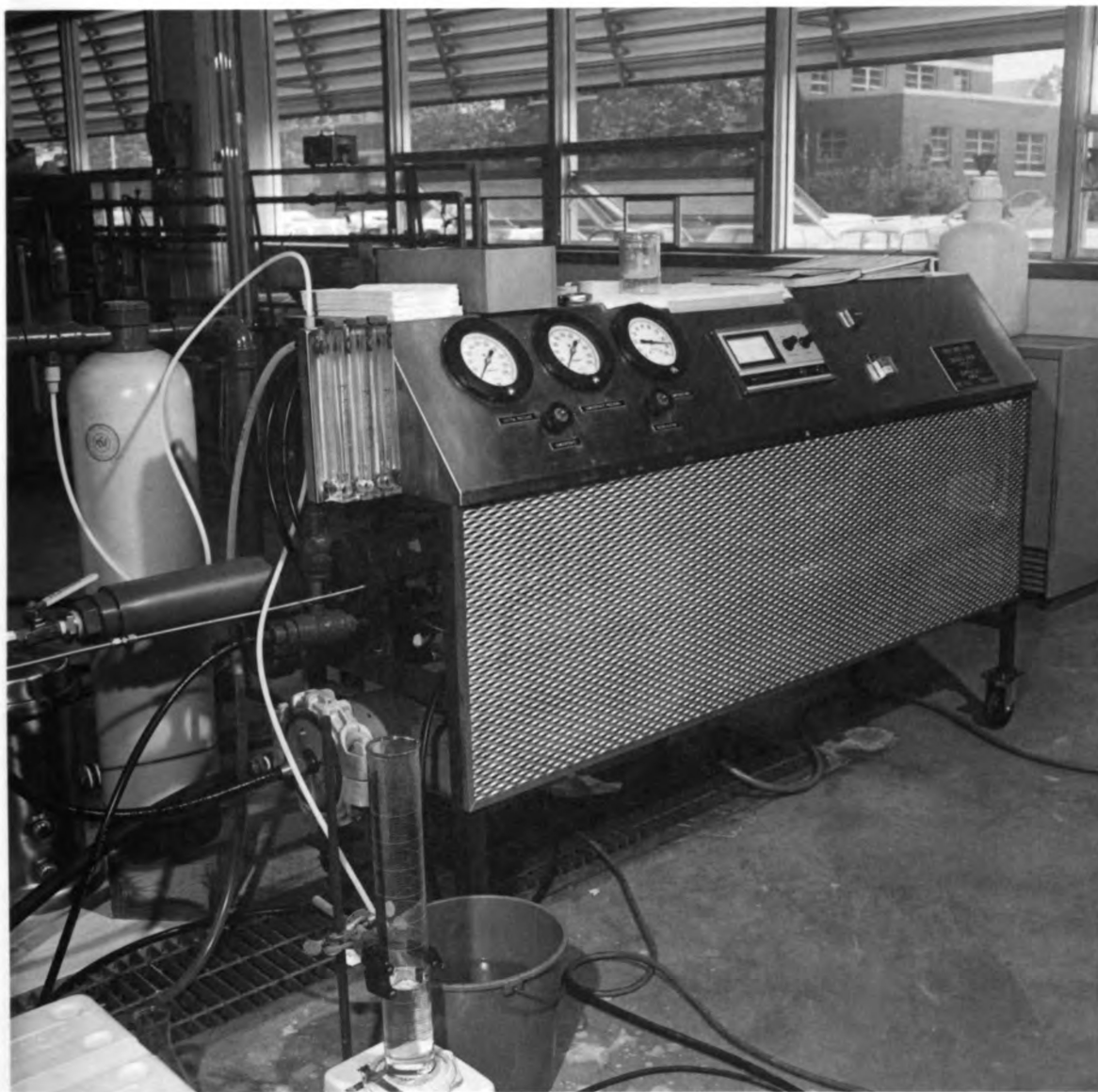


Figure 8. Front View of Dow Reverse Osmosis Unit

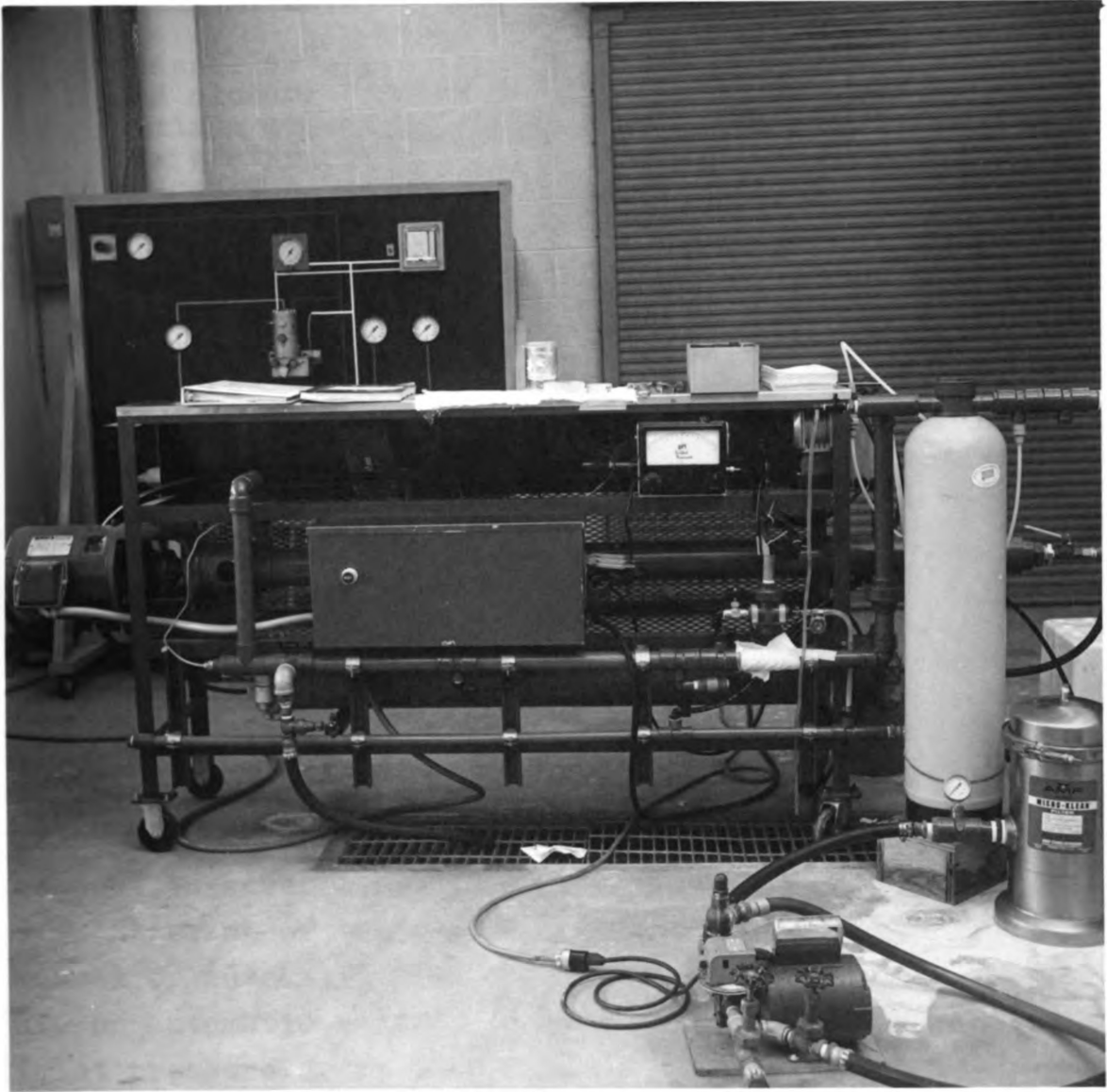


Figure 9. Rear View of Dow Reverse Osmosis Unit

Table 1: Dow Hollow Fiber Module Specifications

Shell dimensions	6.6"O.D. x 61" long
Shell material	Epoxy Clad sch. 40 steel
Channel covers	Aluminum
End closure	Victaulic couplings
Maximum operating pressure	600 psig
Temperature range	10° to 30°C
pH range	4.0 to 8.5
Water Recovery range	10 to 90%
Chlorine tolerance	1 ppm continuous
Flow mode of single cartridge	Radially inward
Active area of single cartridge	1187 sq. ft.

The system contains adequate instrumentation with a pH meter and temperature probe in the feed stream; pressure gauges after the filter, high pressure pump, and RO modules; conductivity probe in the product water stream; regulating valves in concentrate and recycle streams; and rotameters for all outlet streams.

The pH meter is an Analytical Big Scale meter, Model 707, produced by Analytical Measurements, Inc. It allows for calibration with a buffer solution before use in experimentation. Though not used in the present study, the Balsbaugh Laboratory conductivity meter is available for readout on several scales in the permeate stream.

Start-up of the system is accomplished with either manual or automatic "on" buttons. It is better to operate on automatic so the system can turn itself off when inlet pressure drops below the minimum required for pump operation (about 10 psig).

EXPERIMENTAL METHODS

Prior to experimentation, calibration of the pH meter and rotameters was necessary. The pH meter probe reservoir was filled with KCl solution before connecting the probe to the meter. When that was done, the probe was rinsed in distilled water and placed in some pH=7 buffer. The Asymmetry knob was rotated until the pointer read pH=7. The rotameters were calibrated by timing the flow of a quantity of water into a graduated flask. It was useful to perform this operation for every run because of the many bubbles of gas that appeared in later experiments.

The first half of experimentation was made with tap water as feed. Cold water was fed directly from an indoor spigot to the prefilter at about 50-60 psig. Later, when synthetic brine was mixed and used, the feedwater was pumped into the prefilter at about 20 psig. Before start-up, an acid solution was mixed for pH control and poured into the acid reservoir(a 1000 ml graduated cylinder held by a ringstand clamp).

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

1. The brine, or concentrate, valve was opened fully.
2. Check was made that an adequate supply of acid solution was available, and that the pump was primed and leak-free.
3. The main tap water valve was opened to the system.
4. Tap water was allowed to flush the system to remove air. This is completed when no bubbles appear in the brine rotameter.
5. The brine flow was adjusted to about 2 GPM.
6. If prior check had been made to see if motor rotation is correct, the high pressure pump was then turned on with the "auto" button.
7. Re-adjustment was made to the concentrate flow for

the desired rate; recirculation rate was adjusted if used.

8. The acid pump was adjusted until the proper pH of 5.5 to 6.0 was achieved. This sometimes required 30 to 40 minutes.

9. If the system was at equilibrium, flow rates were constant, and the pH was steady, the radionuclide was added to the acid supply vessel. Mixing was accomplished with a magnetic stirring rod.

10. Samples of feedwater, product, concentrate, and recycle(if necessary) streams were taken in small vials. Subsequent samples were taken at 30 minute intervals for perhaps $1\frac{1}{2}$ to 3 hours, depending upon how long feedwater solution or the acid solution lasted.

11. Periodic checks of the pH and temperature were made during the experimentation.

12. Flow rates were measured with a graduated flask at least twice during an experiment, and an average value taken.

13. When all samples had been taken, the injection of nuclide was stopped, and an uncontaminated acid solution was pumped into the feedwater.

14. The system was flushed for several hours after experimentation, usually at higher flow rates than were used during the run.

15. All power to the system was turned off, and the high pressure pump shut down.

16. Feedwater flow to the system was stopped.

It was very easy to lose the priming on the acid control 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 after replacing in solution.

Synthetic brine was mixed in the polyethylene drums according to the proportions listed in Appendix B. The best method of mixing was to pour the chemicals into about

20 gallons of hot tap water and 200 ml of hydrochloric acid. After stirring a few minutes with a wooden paddle, cold tap water was added to the 50 gallon mark. It was desirable to have the room fully ventilated so that acid fumes could be dispersed quickly.

Safety Precautions

The use of radioactive tracers necessitated some precautions for safety to prevent gross contamination of people, equipment, and waste streams.

A pocket film badge was worn at all times when in both the Reactor Lab and the Chemical Engineering Lab. The equipment was always slightly contaminated after the first use of radioisotopes. Absorbent paper was taped to parts of the RO unit as well as to the floor near the outlet streams. This was discarded frequently to reduce contamination from leakages or spills on the equipment.

Plastic gloves were used when preparing the radioactive sample in the Reactor Lab. But if one was careful when taking samples during experimentation, no gloves were needed because hands and sample vials would remain uncontaminated.

Contamination wipes were taken during each experiment to determine if the equipment was becoming too active for safety. All of these samples were low in activity except when a drop or two of acid solution would leak from the acid pump. Appendix C shows the activity of each contamination sample.

All sample vials and glassware were thoroughly cleaned with soap and hot water after each experiment. Contaminated liquids were disposed of in the proper radioactive container.

Most of the radioisotope samples used had theoretical activities between 20 and 45 microCuries before mixing with the feedstream of the RO unit. Samples of S^{35} and Ca^{45} were usually 20 μ Ci in strength, while more of Na^{24} was used in

experimentation because of its much shorter half-life. The entire amount of the radioactivity was never used. The acid reservoir was a 1000 ml graduated cylinder into which the suction end of the acid pump was dropped. It required a minimum of about 100-150 ml of solution to function. Therefore, out of a 1000 ml of acid solution, perhaps 10% of that solution (and radioisotope) was not used.

The radioactive sample used in the system which was not retained in the system or taken out with samples, was released to the sewer. This did not constitute any health problems because of the amount of water released with it. During experimentation with tap water, the system used about 100 gallons of water per hour, diluting about 1/3 of the original amount of activity (6 to 15 μCi). This is based on operation of the system for 2 hours for experimentation and at least an additional hour for flushing.

With the synthetic brine operations, the feed rate was reduced to about 75 gallons per hour because of the lower feedstream pressure. Dilution was slightly less because an experiment was run in $1\frac{1}{2}$ hours. But, more time was spent flushing the system than with the tap water feed.

ANALYTICAL METHODS

Liquid scintillation spectrometry was used to measure the radioactivity of experimental water samples. This method afforded a fairly efficient, consistent, and time saving analysis of the beta-emitting nuclides studied during this research.

The system used was a Packard Tri-Carb Liquid Scintillation Spectrometer System, Model 3003. The details about scintillation theory and about a typical scintillation system can be found in Appendix A. Preliminary adjustments had to be made in the system before it could be used. First of all, the temperature control of the counting chamber was adjusted until the chamber temperature stabilized at about 5°C. Secondly, a high activity sample of the nuclide to be studied (S^{35} , Ca^{45} , Na^{24}) was used to determine the maximum gain for each nuclide in one or all channels. This was done by counting the sample for a minute at different gain settings and plotting counts per minute (cpm) vs. % gain setting. Appendix D contains the results of these plots, as well as calculations for the detector efficiency.

The particular spectrometer used is convenient for sample analysis because it has a sample changer with a capacity of 200 sample vials. A sample is counted for a preset number of minutes or counts. Each successive sample is automatically counted by the detector after one, or both, of the limits is reached. The sample number, time elapsed, and counts in all three channels are printed out by a digital printer on paper tape.

In this study, radioactive samples of S^{35} and Ca^{45} were detected by mixing 9 ml (± 1 ml) of the aqueous sample with 9 ml of Packard Insta-gel Emulsifier in a polyethylene vial. This was placed in the sample chamber (after vigorous shaking) to be counted for 50 minutes, or 100,000.

counts, whichever limit was reached first. An empty vial was counted for background. It was convenient to let the samples count overnight. Therefore, samples from each experiment were counted at least twice.

The high-energy beta emissions of Na^{24} were detected with the same spectrometer, but using a different technique-- Cerenkov radiation. This method requires no scintillation liquid. Eighteen milliliters of the aqueous samples were poured into polyethylene vials and placed in the counting chamber. The vials held 20 ml when full, and measurement of 18 ml into several vials provided experience for pouring the rest of the samples. This method introduced some error into the activity readings of the samples. The quantity of liquid in the vials may have differed from 18 ml by ± 1 ml. The same time and count settings were used, but the optimum gain settings were changed.

Samples were discarded in the contaminated waste receptacles after counting.

DATA

All experimentation was carried out within a pH range of 5.7 to 6.1. Within these limits, membrane deterioration was kept to a minimum and the high concentration of calcium, sulfate, and chloride ions did not cause large amounts of precipitation. The performance of the system was studied by measuring the relative activities of feed, permeate, and concentrate streams. This data led to rejection rates over a period of time for particular ions such as SO_4^{-2} , Ca^{++} , and Na^+ . Stream flow rates were also measured. Raw data is presented in Appendix C.

Temperature and pressure data were gathered for each experiment. The system pressure changed very little during experimentation (staying near 700 psig for tap water, and about 670 psig for the synthetic brine). By increasing the concentrate or recycle flow rates, the concentrate pressure was lowered to as low as 510 psig. The feedwater temperature (which is near to the operating temperature) was recorded so that fluxes could be corrected to 25°C (77°F). This was done by using a chart provided by Dow Chemical Company listing correcting ratios to 25°C for temperatures from 10°C to 30°C (Figure 25, Appendix D).

Appendix D includes methods of calculating rejection, recovery, water flux, and standard deviations.

Experimentation was divided into two segments. The first part utilized tap water as a feed stream. It was intended to be a period of learning proper techniques and of determining some of the variables of the system. The more important portion of the experimentation was use of a synthetic brine of roughly 8700 ppm as a feed stream. For this stream, rejection was measured for SO_4^{-2} and Na^+ , water flux was calculated, and overall behavior of the RO unit was observed over a period of time.

The experimental data derived from the experiments is

Table 2: Experimental Data Obtained for SO_4^{-2} Ion and Ca^{++} Ion Using Tap Water as Feed Stream.

Exp. No.	System Press. (psig)	Concen. Press. (psig)	pH	Temp. (°F)	Conc. Rate (GPM)	Permeate Flow Rate (GPM)	Flux 25°C $\frac{\text{GPD}}{\text{ft}^2}$	Recov-ery (%)	% Ion Rejection			
									60	90	120	150
SO ₄ ⁻² ion												
Recovery = 70-75%												
1	705	695	5.9	59	0.45	1.15	1.90	71.8	83.9			
2	705	700	5.8	58	0.40	1.05	1.77	72.4	65.0	76.5	76.0	
3	705	695	5.9	59	0.40	1.10	1.73	73.3	80.4	81.7	81.3	
5	705	700	5.9	60	0.40	1.15	1.79	74.2	83.0	80.2	77.8	
9	710	700	5.9	57	0.40	1.10	1.77	73.3	95.3	95.4	96.1	97.1
10	705	695	5.9	64	0.40	1.13	1.66	73.8	94.9	95.6	95.2	
Recovery = 50%												
11	705	695	6.0	57	1.00	1.05	1.69	51.2	96.2	95.6	96.7	
12	705	695	5.9	59	1.00	1.05	1.66	51.2	96.8	96.5	99.1	
Ca ⁺⁺ ion												
No recycle flow												
13	710	700	5.8	59	0.40	1.15	1.82	74.2	93.8	88.0	94.6	
14	710	700	5.8	59	0.40	1.14	1.81	74.0	94.0	94.2	94.7	
15	710	700	5.9	59	0.40	1.14	1.79	74.0	68.3	93.3		
0.60 GPM recycle flow												
16	705	695	5.8	64	0.40	1.12	1.61	73.6	85.5	93.9		
17	705	695	5.8	58	0.40	1.13	1.82	73.8	84.4	92.3	91.5	

Note: Experiments 4,6,7, and 8 were system flushings to determine the residual activity in the system(See Tables 6 and 7).

Table 3: Experimental Data Obtained for Na⁺ Ion Using Tap Water as Feed Stream.

Exp. No.	System Press. (psig)	Concen. Press. (psig)	pH	Temp. (°F)	Conc. Flow Rate (GPM)	Permeate Flow Rate (GPM)	Flux 25°C GPD ft ²	Recovery (%)	% Ion Rejection				
									Time (min.)				
										60	120	150	
<hr/>													
No recycle flow													
19	705	695	6.0	59	0.40	1.10	1.77	73.3				98.2	
20	705	695	5.9	60	0.40	1.12	1.75	73.6	93.1	93.5	92.3		
21	705	695	5.9	60	0.40	1.12	1.75	73.6	88.2	91.9	95.2		
22	705	695	5.7	58	0.40	1.13	1.82	73.8	85.2	93.4	92.7		
<hr/>													
0.60 GPM recycle flow													
23	705	695	5.9	59	0.40	1.12	1.77	73.9	95.7	95.7	95.8		
24	705	695	6.0	64	0.40	1.12	1.68	73.6	96.6	95.5	96.9		

Note: Experiment 18 was attempted, but there was not enough radioactivity in the samples (less than 4000c/50 min.).

Table 4: Experimental Data Obtained for Na⁺ Ion Using Synthetic Brine as Feed Stream.

Exp. No.	System Press. (psig)	Concen. Press. (psig)	pH	Temp. (°F)	Conc. Flow Rate (GPM)	Permeate Flow Rate (GPM)	Flux 25°C $\frac{\text{GPD}}{\text{ft}^2}$	Recovery (%)	% Ion Rejection	Time (min.)
										30 60 90
No recycle flow										
25	675	665	6.0	90	0.19	1.10	1.13	85.1	81.9	85.9
26	675	665	6.0	80	0.41	0.92	1.13	69.1	82.9	87.5
27	675	665	5.9	85	0.42	0.75	0.75	64.0	88.7	92.3
28	675	665	6.2	85	0.42	0.97	1.05	69.7	81.7	92.9
29	670	660	6.0	90	0.40	1.03	1.06	72.2	87.5	89.2
30	670	660	6.0	90	0.38	0.99	1.02	72.3	93.9	82.1
31	670	660	5.9	80	0.44	0.96	1.12	68.4	88.5	88.9
32	675	665	6.0	88	0.21	0.93	0.96	81.7	87.5	83.2
With recycle flow										
33	670	640	6.0	90	0.32	0.99	1.02	75.5	90.2	88.3
34	670	635	6.0	95	0.28	1.00	1.01	78.2	89.4	91.1
Exp. No.	Recycle Rate (GPM)	CA Ratio	Time (min.)							
			30 60 90							
25	0.00	0.91	1.31							
26	0.00	0.59	0.73							
27	0.00	0.66	0.83							
28	0.00	0.70	1.06	1.06						
29	0.00	0.73	1.09	1.12						
30	0.00	6.40	0.52	1.07						
31	0.00	1.00	0.90	0.99						
32	0.00	0.66	0.98	0.91						
33	1.75	0.97	0.99	0.90						
34	2.60	0.54	0.89	0.94						

Exp. No.	System Press. (psig)	Concen. Press. (psig)	pH	Temp. (°F)	Conc. Flow Rate (GPM)	Permeate Flow Rate (GPM)	Flux 25°C $\frac{\text{CPD}}{\text{ft}^2}$	Recovery (%)	% Ion Rejection		
									Time (min.)		
									30	60	90
No recycle flow											
35	670	660	6.0	93	0.27	0.98	1.00	78.5	84.6	85.8	88.8
36	670	660	6.0	87	0.29	1.00	1.03	77.5	77.3	73.8	
37	670	660	6.1	85	0.28	0.92	0.98	76.7	51.1	54.1	
38	670	660	5.9	90	0.29	0.91	0.94	76.1	35.7	55.2	
39	670	660	5.9	85	0.29	0.90	0.96	75.5	37.0	30.9	
With recycle flow											
40	670	610	5.9	80	0.25	1.03	1.20	80.6	87.3	86.0	
41	665	510	5.9	90	0.25	1.02	1.05	80.1	86.8	90.0	
Exp. No.	Recycle Rate (GPM)	CA Ratio									
		Time (min.)									
		30	60	90							
35	0.00	0.94	0.92	0.97							
36	0.00		1.03	1.09							
37	0.00		1.09	0.90							
38	0.00		1.91	0.82							
39	0.00		0.89	1.18							
40	2.00		12.7	1.11							
41	2.75		0.66	0.73							

tabulated in Tables 2-5. The tabulations include experimental conditions such as temperature, pH, and flow rates, as well as the system parameters such as ion rejection, water flux, and water recovery. Table 2 contains data obtained from the tap water experimentation for the SO_4^{-2} and Ca^{++} ions. In Table 3 is the same type of data for Na^+ ion in tap water. Tables 4 and 5 list experimental data for the SO_4^{-2} and Na^{++} ions in the synthetic brine solution.

Certain experimental data was not tabulated either in the raw data of Appendix C or in the data tables of this section. It was noted in early experiments with sulfate ion that some radioactivity remained in the module after the radioisotope was no longer being pumped into the system. In Experiments 4,6,7, and 8, attempts were made to determine how much activity resided in the module.

Experiments 4 and 6 produced sample activities far above the concentrations of radioisotopes used up to that time. It was concluded that either the samples had been contaminated while being prepared for counting, or the scintillation spectrometer was working improperly. Experiment 7 was a flushing of the mixing tank by forcing tap water through the tank and draining it before it reached the high pressure pump. The activities are shown in Table 6.

Table 6: Activities of 9 ml Samples of Mixing Tank Flush.

Time(min)	Net Counts/50 min. (corrected for background)
00	1754
60	1918
90	1739
150	1693
210	3223
270	1668

Experiment 8 was a flushing of the RO system to see when the residual activity would reach a steady value. The activities, corrected for background, are listed in Table 7.

Table 7: Data Obtained from System Flushing to Determine Residual Activity.

Permeate Rate = 1.10 GPM Temperature = 59°F
 Concen. " = 0.87 " pH = 6.0
 Recycle " = 0.00 " System Pressure = 705 psig

Time (min.)	Feed Activity (c/50min)	Permeate Activity (c/50min)	Concen. Activity (c/50min)
15	3801	1423	8764
60	2571	1474	5414
120	2795	1183	1170
180	1174	1093	1190
240	1229	1226	1215

The activities in all three streams seemed to reach a steady value after 4 hours. Because of this substantial residue in the module for SO_4^{-2} ion, the experimental data had to be corrected by subtraction of stream activities taken at steady state after flushing. This is essentially a background correction. The problem of a residue for Na^+ was small due to its short half-life. A couple of hours flushing after an experiment seemed to remove almost all radioactive Na^+ ions.

RESULTS

The raw data contained in Appendix C was used to calculate the percentage of salt rejection by the RO module. This was done by using the equation:

$$\% \text{ Ion Rejection} = \frac{100(\text{Feed Activity}-\text{Permeate Act.})}{\text{Feed Activity}} \quad (13)$$

Rejection was determined at different time intervals in hopes of showing an approach to steady-state for each particular ion.

Consistency in the rejection results is fairly easy to see with the use of tap water. Inconsistent results can be discarded on the basis of experimental conditions and the raw activities. However, it was not as easy to find consistent results with the synthetic brine.

Therefore, a parameter was designed to test the accuracy of results. This is arbitrarily called the CA Ratio. Its rigorous definition and a sample calculation are given in Appendix D. In brief, this ratio compares two products: the product of the concentrate flow rate and its activity as determined by material balance (Equation 6) to the same product as determined by using the experimental flow rate and activity for the concentrate stream. Ideally, this ratio should be equal to 1.0. A value less than one indicates that more radioactivity is leaving the system than entering (theoretically impossible). A better explanation is inaccurate feed activity data from improper mixing in the RO system or errors in scintillation counting. A CA Ratio greater than one indicates some of the nuclide is staying in the system, perhaps as precipitates, or that the scintillation counting of the concentrate stream is in error. The standard deviation of the ratio is about 0.05 (based on typical activities of 10,000 c/50 min).

Water recovery was an important system parameter to calculate. The percentage of water recovered by the RO

system is simply the fraction given by:

$$\% \text{ Recovery} = \frac{100(\text{Permeate Rate})}{\text{Permeate Rate} + \text{Concen. Rate}} \quad (14)$$

The denominator is actually the feed rate. For the system under study with one HFF module, the nominal design feed rate is 1.62 GPM(2332 GPD)(21).

Water flux is the permeate rate in GPD divided by the active membrane area of the RO module. For the Dow HFF module, this area is equal to 1187 ft²(21). Example calculations of both water recovery and water flux are included in Appendix D.

Results With Tap Water

The first half of experimentation utilized tap water as a feed stream. This was convenient because indoor spigots in the Chemical Engineering Lab delivered water to the system at a high inlet pressure of 50-60 psig. System operation gives the best results if the inlet stream is pressurized to at least 50 psig. Analyses of the tap water indicated it contained 350-370 ppm of inorganic materials.

Three different ions were studied in the tap water, SO₄⁻², Ca⁺⁺, and Na⁺. The ion rejection approach to steady state was studied for each ion. Differences in recovery were investigated with the sulfate ion, while the use of the recycle stream was studied with calcium and sodium.

Figures 10 and 11 show the approach of SO₄⁻² ion rejection to steady state for 70% and 50% water recovery respectively. These plots are obtained with data points from Experiments 9-12 primarily. Previous experimentation did not appear to give consistent results due to several reasons. These were inexperience with sample preparation for scintillation counting, improper scintillation counting conditions(% gain, temp., etc.), and lack of reaching steady radioisotope injection into the RO system. The point at 150 minutes in Figure 11 is inaccurate and should not

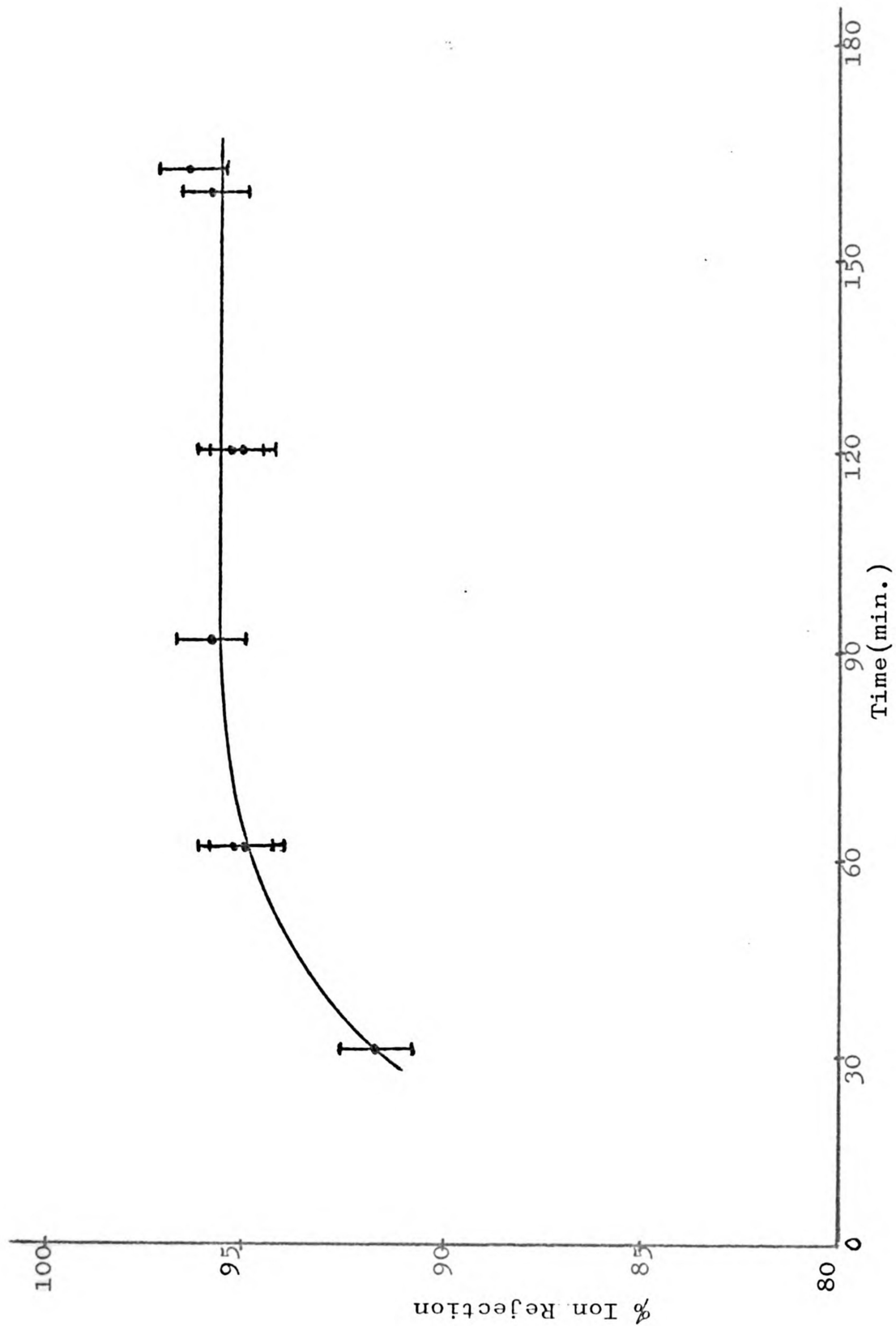


Figure 10. Plot of % Ion Rejection vs. Time for SO_4^{-2} Ion at 70% Water Recovery Using Tap Water as Feed Stream

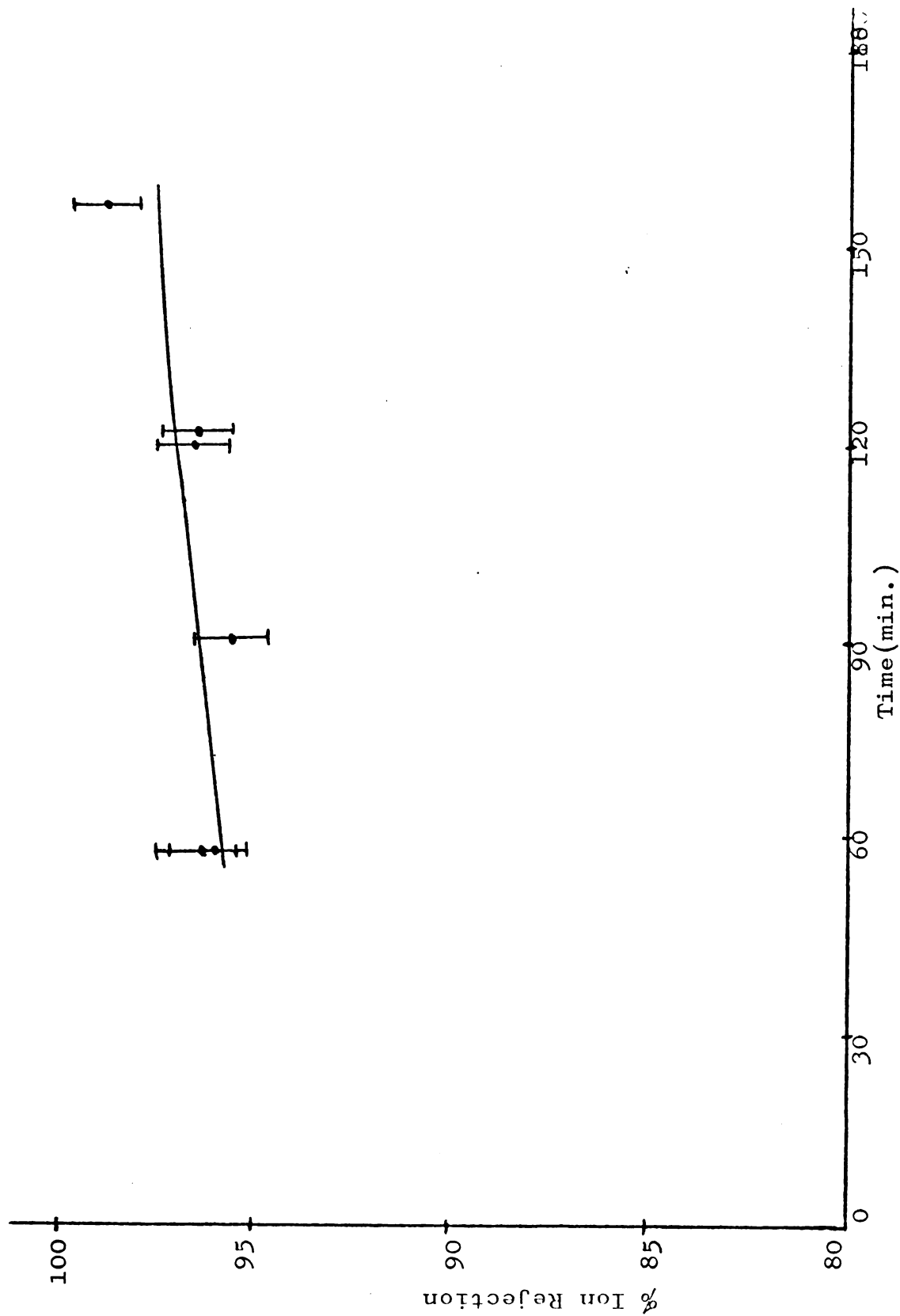


Figure 11. Plot of % Ion Rejection vs. Time for SO_4^{2-} Ion at 50% Water Recovery Using Tap Water as Feed Stream

give the appearance of an increase in the curve. The CA Ratio of this point is about 1.25. The experimental data indicates that the permeate activity is low. This may be due to error in sample preparation.

Figure 12 shows the results of the effect of water recovery on % ion rejection for SO_4^{-2} ion. As the amount of water recovered as permeate increases, the amount of ions rejected by the membrane decreases.

Figures 13 and 14 show the change in % ion rejection with time for Ca^{++} ion at 60% recycle and no recycle respectively. Two data points were found to be inconsistent and were not plotted in Figure 14. These were the 88% rejection of Experiment 13 and the 68% rejection of Experiment 15, as listed in Table 2. They were not included on the plot because their CA ratios were very far from 1.00.

The results of experimentation with Na^+ ion in tap water are presented in graphical form in Figures 15 and 16. The first of these plots shows the approach of ion rejection to steady state with a 60% recycle stream used. All of the data points from Table 3 are plotted because of their close agreement.

Figure 16 contains a graph of ion rejection vs. time also. But the experiments involved used no recycle stream. Experiments 21 and 22 contain the most consistent data. Experiment 19 was rejected because the low sample activities contain large statistical errors. Data from Experiment 20 seems good after 60 minutes having passed. The position of the curve at 60 minutes is debatable because the data lists 3 points within a spread of 8%.

Results With Synthetic Brine

The experimental results obtained from the synthetic brine are not as easily analyzed as those from tap water. It was more difficult to find consistent data with % rejection vs. time. There were definite trends, however, that deserve the discussion given in the next section.

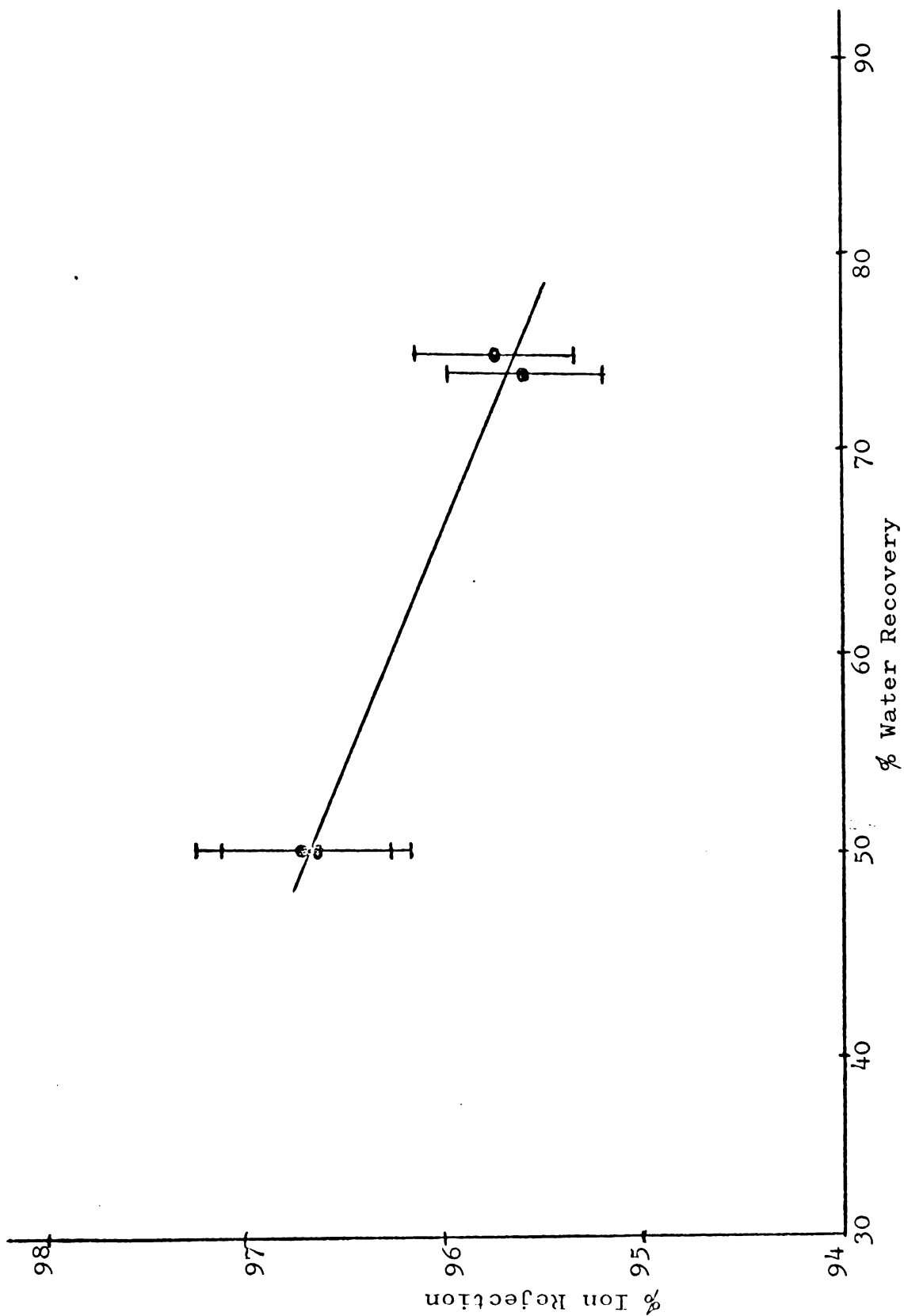


Figure 12. Plot of % Ion Rejection vs. % Water Recovery for SO_4^{2-} Ion After 120 Min. Using Tap Water as Feed Stream

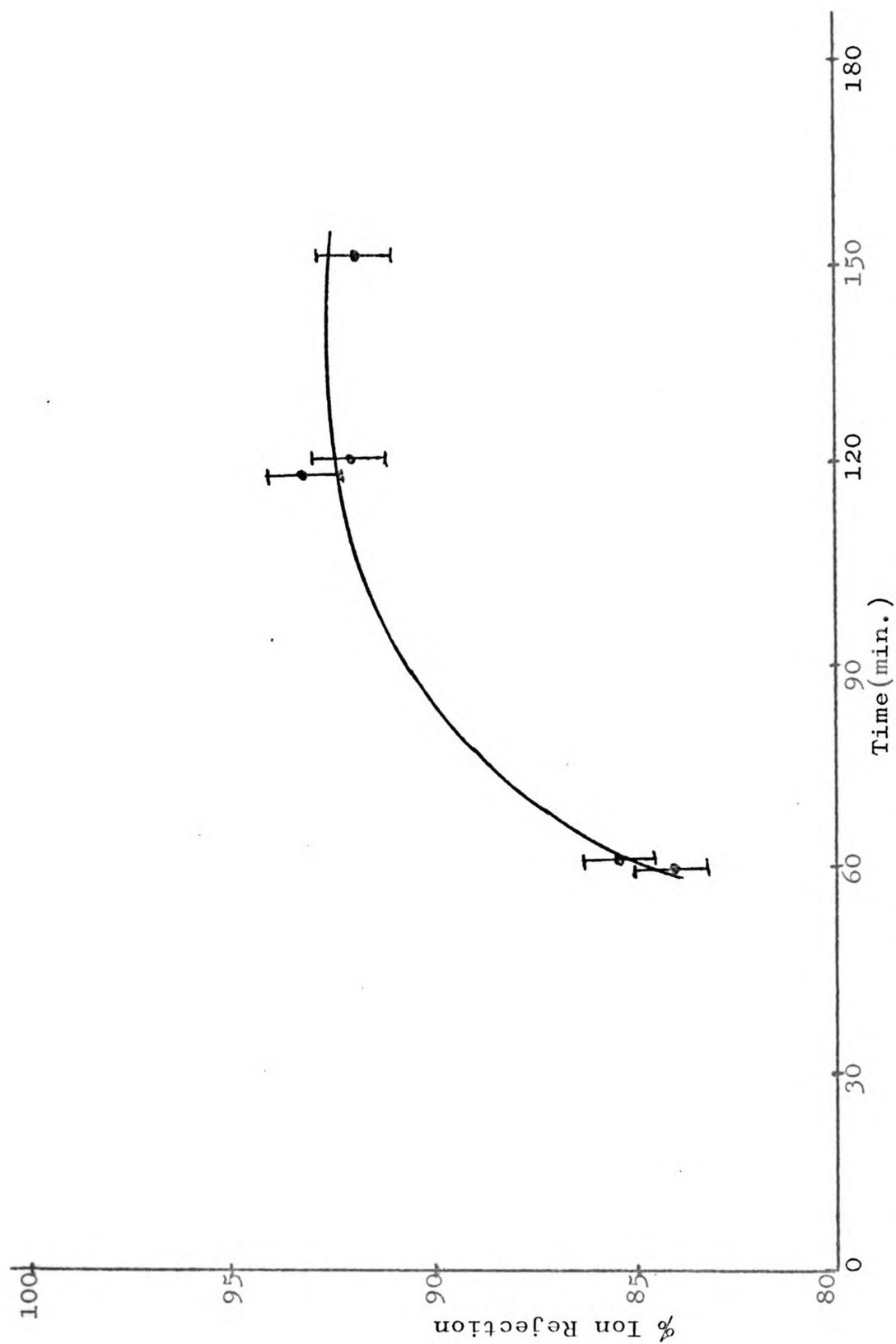


Figure 13. Plot of % Ion Rejection vs. Time for Ca^{++} Ion With 60% Recycle Using Tap Water as Feed Stream

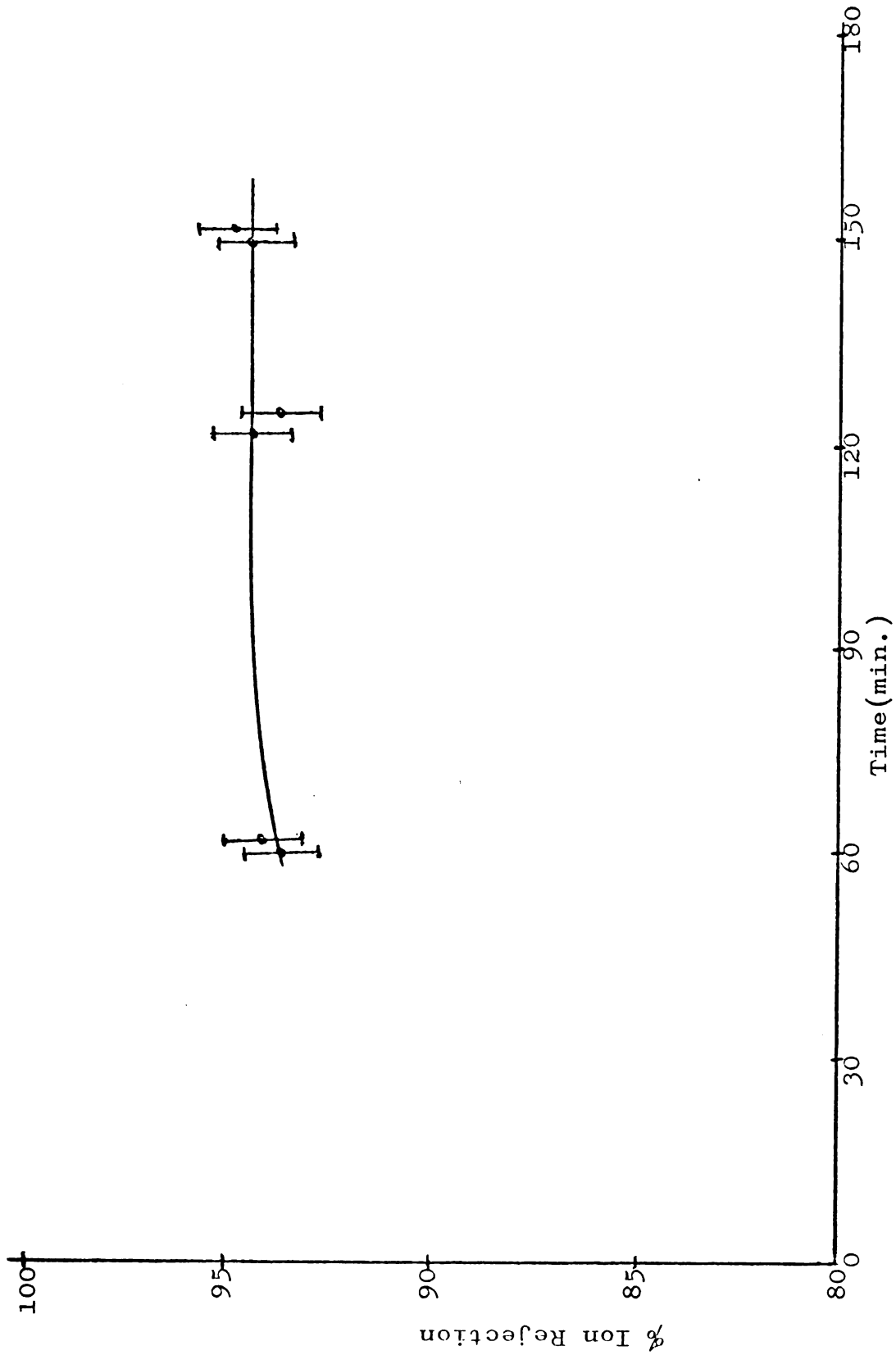


Figure 14. Plot of % Ion Rejection vs. Time for Ca^{++} Ion With No Recycle Using Tap Water as Feed Stream

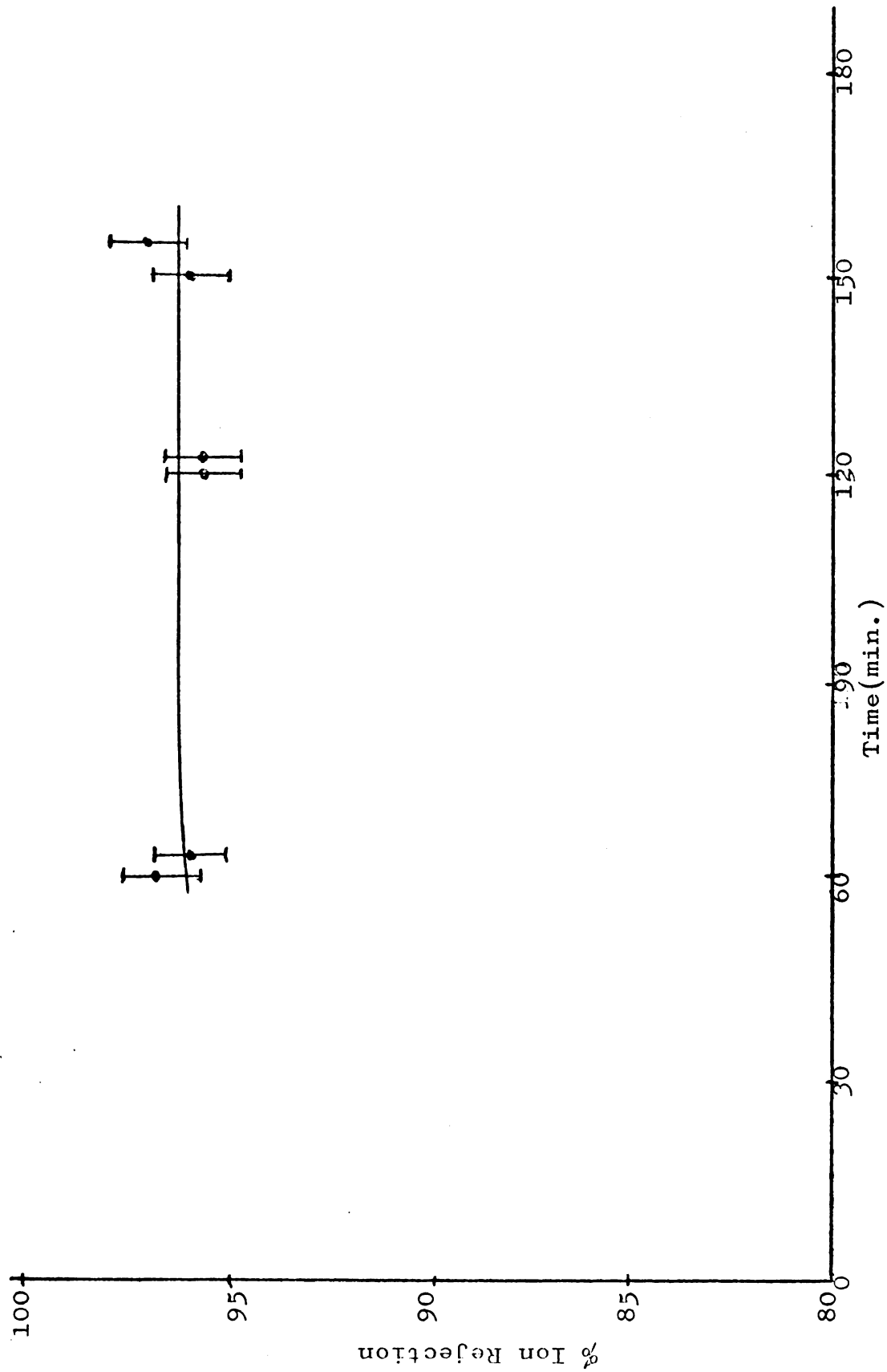


Figure 15. Plot of % Ion Rejection vs. Time for Na^+ Ion with 60% Recycle Using Tap Water as Feed Stream

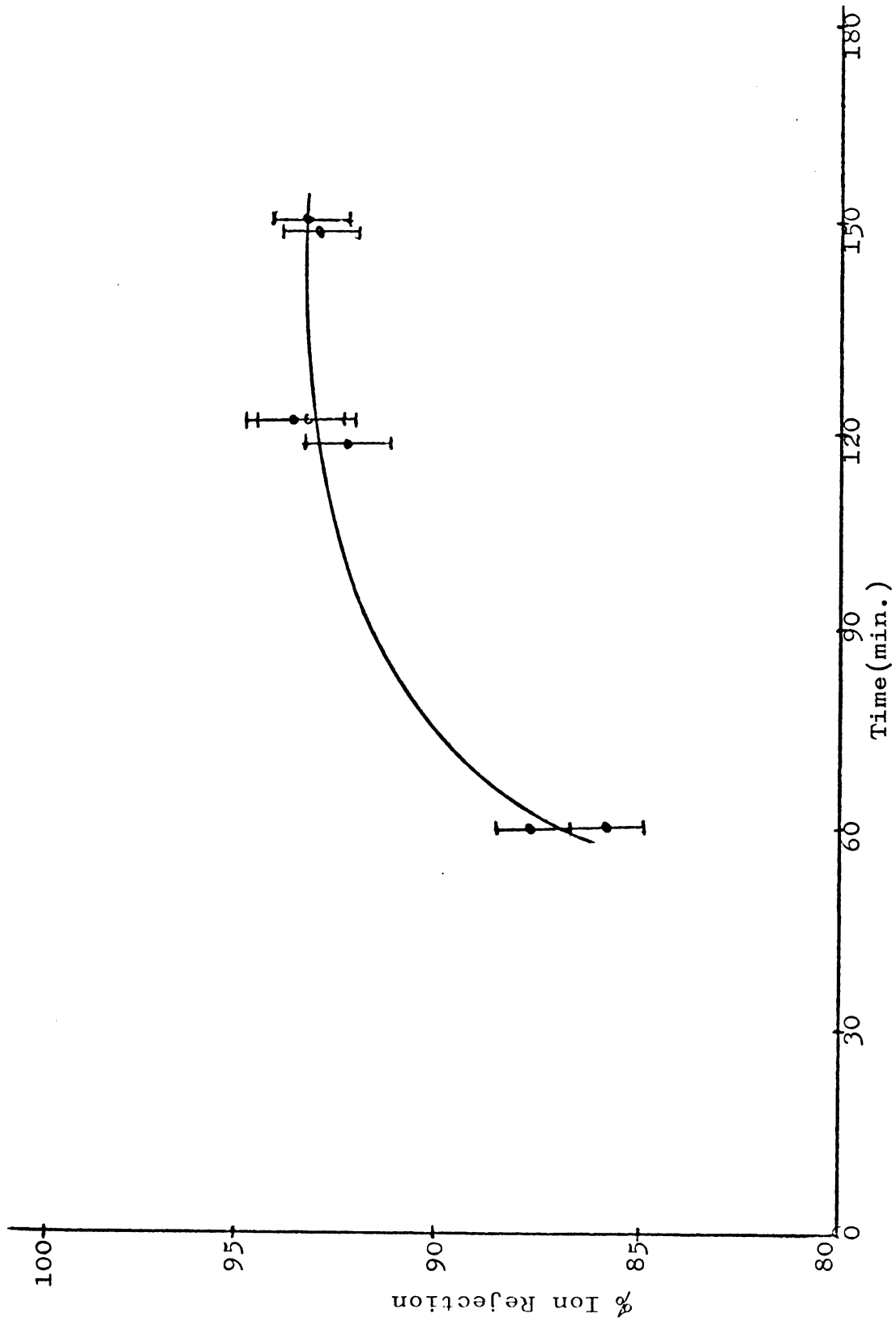


Figure 16. Plot of % Ion Rejection vs. Time for Na^+ With No Recycle Using Tap Water as Feed Stream

Figure 17 shows the change in Na^+ rejection with time where there is a high recycle rate of concentrated stream back to the feed. The data is quite consistent with CA ratios near 1.00 in most cases. The points at 60 minutes show the greatest deviation from the curve.

The rejection of Na^+ is shown to change with time in Figure 18 also. In this case, there is no recycle stream. Attention was given to the CA ratio of the data points listed in Table 4 to determine the most consistent data to plot. The deviation in this case is greater than with Na^+ in tap water, but the shape of the curve can still be discerned.

Experimentation with Na^+ was carried out at several values of water recovery. The relationship of water recovery to rejection at a steady state value is shown in Figure 19. The lone point at 85% recovery is neglected in drawing the curve because of its high CA ratio(1.31).

The most perplexing part of the research endeavor is shown in Figure 20. The rejection of SO_4^{-2} in synthetic brine over a period of time is unlike all other results. Much of the data collected for this ion was not accurate (if the CA ratio is a good basis for accuracy). Experiments 35-37 appear to give the best results, though certainly they are not consistent enough to draw conclusions about the SO_4^{-2} ion rejection in the brine.

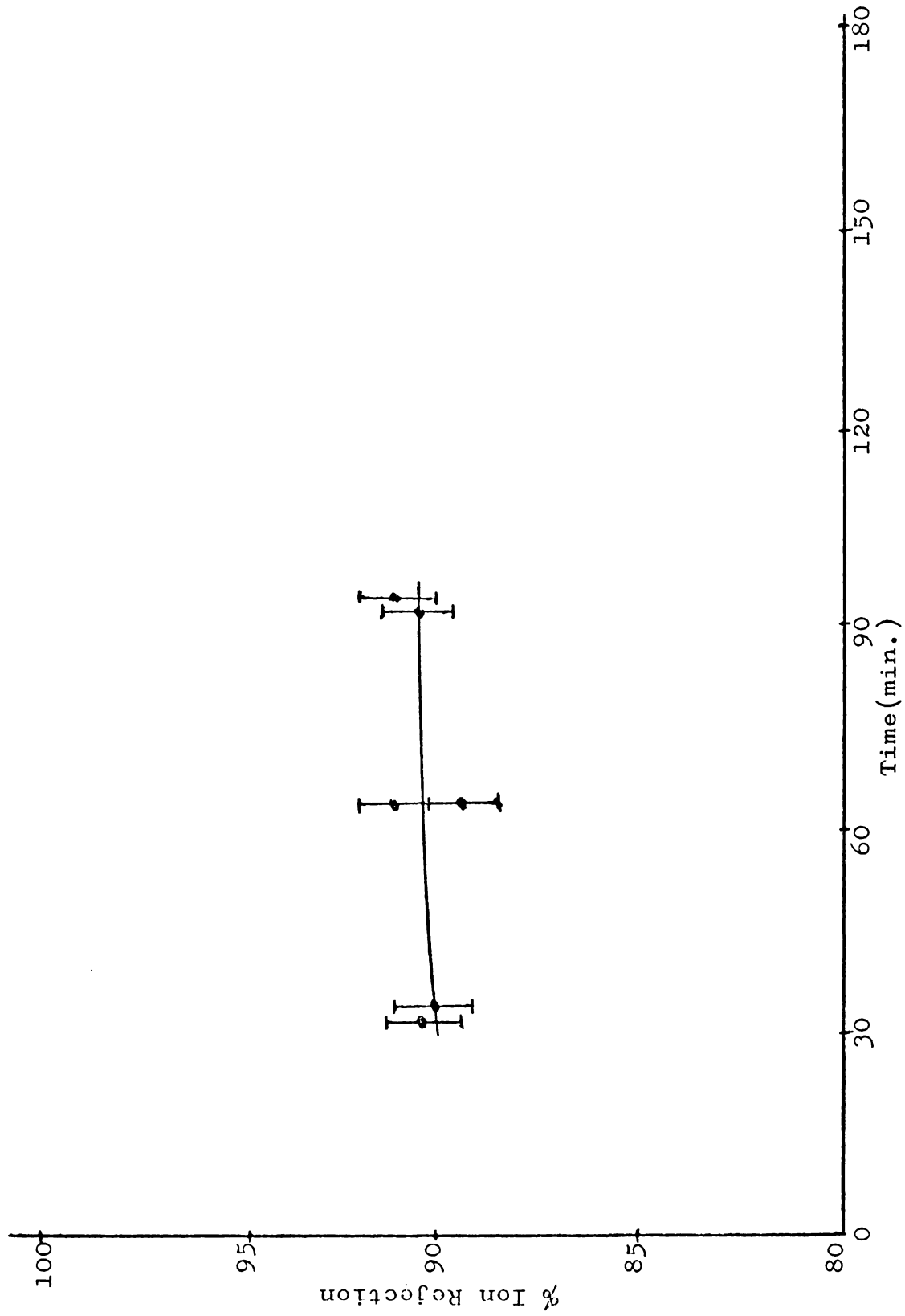


Figure 17. Plot of % Ion Rejection vs. Time for Na^+ Ion at 80% Recycle Using Synthetic Brine as Feed Stream

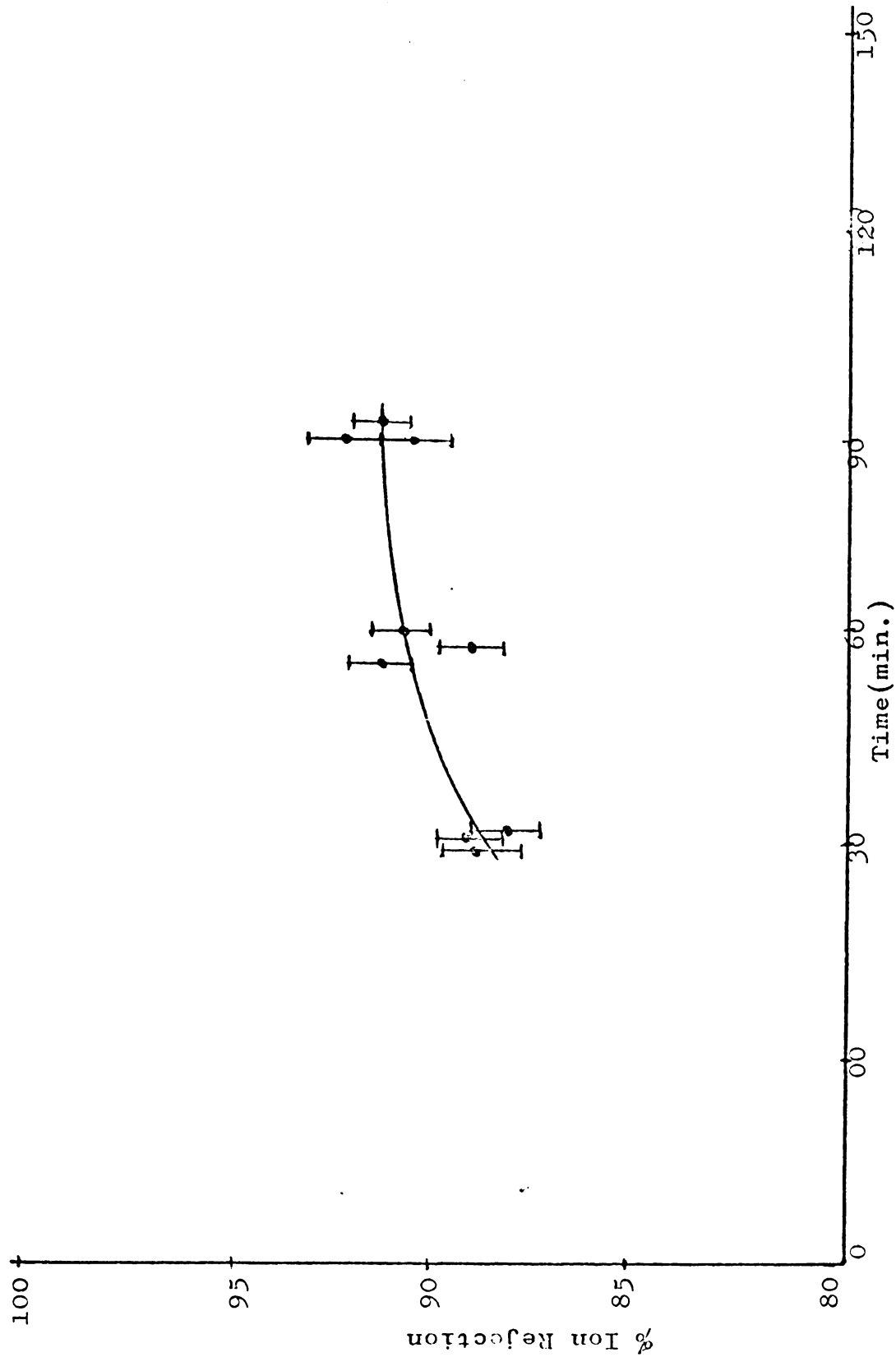


Figure 18. Plot of % Ion Rejection vs. Time for Na^+ With No Recycle at 70% Recovery in Synthetic Brine

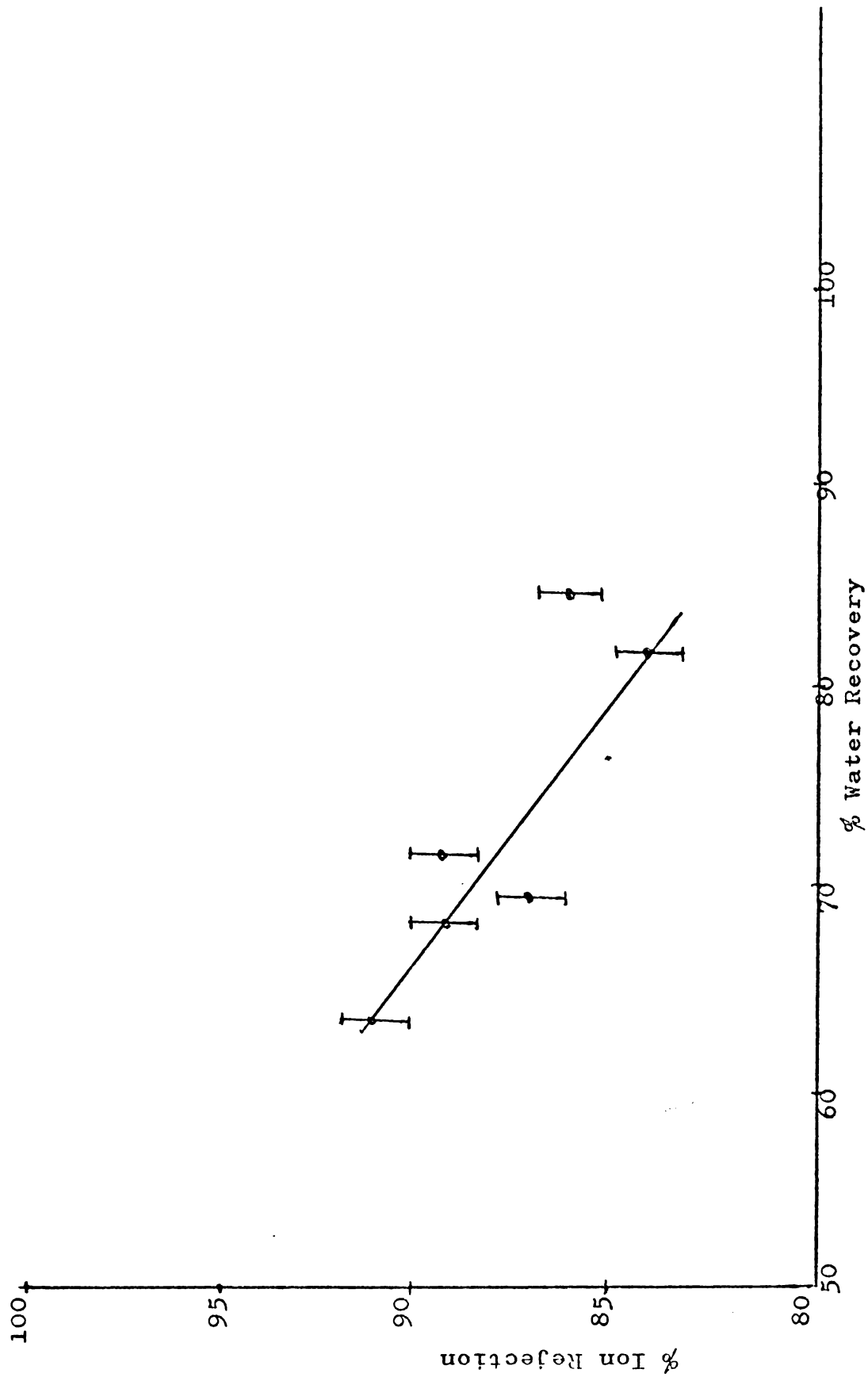


Figure 19. Plot of % Ion Rejection vs. % Water Recovery for Na^+ Ion After 60 Min. Using Synthetic Brine

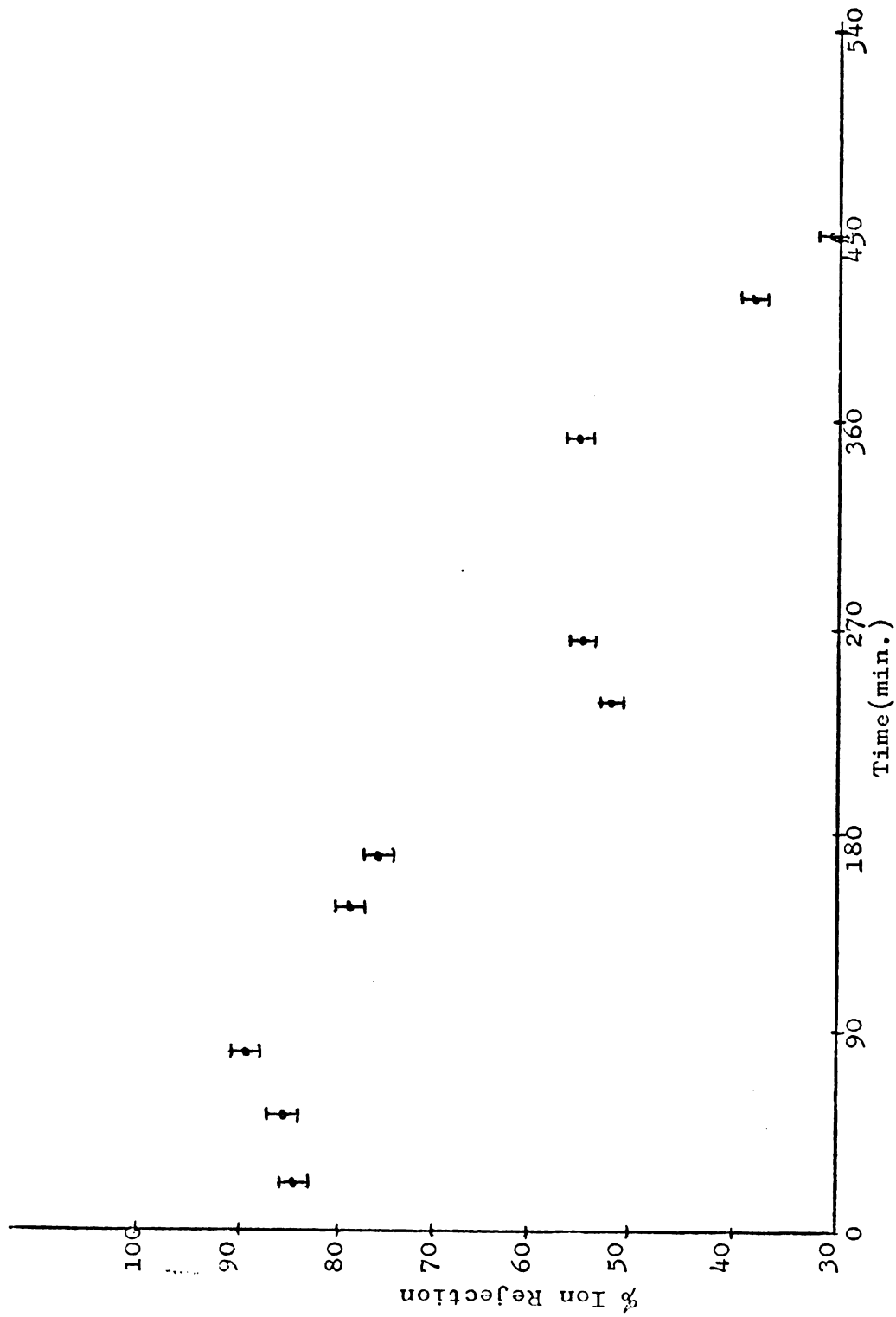


Figure 20. Plot of % Ion Rejection vs. Time (discontinuous) for SO_4^{2-} Ion Using Synthetic Brine as Feed Stream

ANALYSIS OF RESULTS

Tap Water

The results shown in Figure 10 indicate that steady state rejection of SO_4^{2-} ion is reached after about 90 minutes. The RO module removes 95-96% of the sulfate ions in the tap water (about 14 ppm). This rejection occurs when the system is operated near 70% water recovery.

If recovery is reduced to 50%, the steady state rejection increases, as Figure 11 shows. The increase is slight, say to 96-97%, but this increase would be significant if the feed stream contained a higher concentration of ions, and if a large amount of water is treated per day. Not only does the steady state rejection increase at lower recoveries, but steady state is reached at an earlier time after start-up. Steady state occurs near 60 minutes for 50% recovery, but not until 90 minutes for higher water recovery.

Figure 12 gives a better picture of the relationship between rejection and recovery than is obtained by examination of Figures 10 and 11. The result in this graph is what the literature predicts (12)(14). Lower water recovery indicates that more of the feed stream is being wasted. If the permeate rate remains constant, a lower recovery means a greater feed rate into the module. This increased velocity creates more turbulence for a reduction of concentration polarization (and salt transport through membrane). In some applications of reverse osmosis, however, the operation is designed to proceed at as high a recovery as possible to reduce operational and waste disposal costs. The slight loss in rejection can be tolerated in such cases.

When waste is not recycled into the feed, the rejection of Ca^{++} ions at steady state is about 93-94% (reduction from 80 to about 75 ppm for MSU tap water). Figure 14 indicates that steady state is reached near 90 minutes after start-up.

As the feed stream becomes more concentrated from recycling part of the waste, the rejection drops. For 60% recycle, Figure 13 indicates that it drops to 92-93% and does not reach steady state until 120-150 minutes. The increased salt flux is predicted by Equation (3)

$$J_2 = B(C_w - C_p)$$

The concentration of the feed stream at the wall C_w may be increased as much as 2-3 times what it was originally. It is interesting to note that though C_w may be increased considerably, the rejection of ions is reduced only a few percent once steady state is reached.

For the Na^+ ion, the use of recycle has an opposite effect upon ion rejection. Figure 15 shows steady state rejection of Na^+ to be 95-96% with 60% recycle. Rejection is shown to be only 93-94%, however, in Figure 16 when no recycle is used. The explanation for this phenomenon is difficult to come by from looking into the literature for similar results. The literature does indicate that under identical operating conditions, Na^+ ions are not rejected as easily as Ca^{++} ions. By comparing Figures 14 and 16, one can see those results(12).

Hypotheses might be forwarded to explain the Na^+ ion behavior, but none can be proven at this time. One is that the increase in Na^+ concentration with recycle increases the amount of Na_2SO_4 (which is more highly rejected than NaCl) (12). The same behavior would not arise with Ca^{++} ions because CaSO_4 is not rejected as easily as Na_2SO_4 . Another hypothesis is that the data taken was in error. But the apparent consistency of the results in this case has already been discussed and taken to be a fact.

The slight difference in values of water flux may be due mostly to error in taking flow rate measurements. The graduated flask allowed approximation of the flow rates to ± 0.05 GPM. Subsequent error of ± 0.05 was introduced into the values of water flux.

There was generally a slight decrease in water flux when water recovery was decreased. This is explained by the feed rate being above the nominal design rate of 1.62 GPM. With more water going into the module than it was designed to receive, less water is forced through the membranes. There was no appreciable change in water flux with use of the recycle stream.

Synthetic Brine

It was originally desired to determine the rejection of several ions in the synthetic brine. But time permitted the investigation of only two, Na^+ and SO_4^{2-} . Both were studied with and without the recycle stream. No attempt was made to look at the effect of low water recovery (50%). It is believed that the economics of municipal use of reverse osmosis will require operation at high recovery rates.

Rejection of Na^+ ion with high recycle rates is shown in Figure 17 to reach 90-91% at steady state. This point is reached quite early in the experimentation. However, when no recycle is used, steady state rejection is still near 90%, but it is not reached until after 90 minutes of operation. An explanation may be that the increased turbulence in the feed stream reduced concentration polarization to such an extent that high rejection is possible soon after start-up.

An ion rejection of 90% is quite good for a brackish solution of 8700 ppm concentration. But this amount of purification does not produce potable water. The product stream still contains about 870 ppm of inorganics. The Michigan Department of Public Health indicated to the author that drinking water should contain less than 300 ppm inorganics. When recycled concentrate is mixed with feed, the mixture concentration may reach 2-2½ times the original concentration. The product stream will contain more inorganics in it as a consequence.

There is a decline in ion rejection as the water re-

covery increases. This effect is shown over a range of about 20% recovery in Figure 19. With the water flux remaining nearly constant, the high water recovery allows concentration polarization to become a large influence upon rejection of ions at the membrane wall. Equations 10 and 11 show that the effect of concentration polarization is increased as the average feed velocity is decreased (as in high recovery).

Conclusions as to the rejection of SO_4^{-2} ion cannot be reached at this time. The data was either inconsistent or gave results that show a failure of the RO system to function properly. In Figure 20, rejection data is plotted as a function of time over several experiments.

The loss in rejection ability may be due to several reasons. First, after about 10 or 12 experiments with the synthetic brine, the module may need a thorough cleaning. Despite pH control near 6.0, the high concentration of inorganics may have caused some precipitation of sulfates, chlorides, and carbonates. The Dow Chemical Company should be able to give specifications as to how cleaning should be done.

Secondly, some of the cellulose acetate may have deteriorated to cellulose, leaving "holes" in some of the fibers. The large concentration of inorganics in the permeate stream supports this idea. However, when recycle is used, the rejection becomes much higher again.

Lastly, the concentration polarization affect may have become so great from the precipitates going back into solution that salt transport increased sharply. It was reduced with the added turbulence of recycled water.

CONCLUSIONS AND RECOMMENDATIONS

Basic Observations

The experimentation with reverse osmosis utilized two types of feed streams, tap water with 350-370 ppm inorganics and a synthetic brine with a concentration of 8700 ppm. Several parameters of the system were considered, including water flux, water recovery, and ion rejection. Of the many ions in both feeds, SO_4^{-2} , Ca^{++} , and Na^+ were studied in particular.

In both cases of tap water and synthetic brine, a steady state ion rejection was reached after at least 90 minutes. For the tap water, it was reached sometimes sooner than that. When a recycle stream was mixed with the feed, the ion rejection decreased slightly for all cases except Na^+ ions in tap water. As the water recovery was decreased by passing more water to the sewer, the rejection increased because of the increased turbulence near the membrane walls. However, the water flux decreased slightly in that case. The difference in ion rejection between the two feed stocks was only 5-6% at about the same recovery of 70-75%.

System performance remained constant with the tap water, primarily because of the low ion concentration. When the brine solution was used as feed, however, the performance dropped after a period of time. This fact is evident from the SO_4^{-2} rejection results in Figure 20. Water flux was noticeably less for the brine than for the tap water. This drop was caused by two factors: the smaller inlet feed pressure and the larger osmotic pressure of the brine solution.

Further testing will be necessary with the synthetic brine (or brackish water from the Marshall formation, if possible) to draw permanent conclusions as the use of reverse osmosis in Lansing. But this study shows the possibilities of 90% or higher ion rejection for brackish water at high

water recovery. At this rejection rate, drinking water could be obtained with two RO systems in series. The first system would handle the pretreated brine, and the second would purify the initial permeate to potable levels.

Operation of the Dow HFF system was quite simple once procedures were developed. The necessity of a module cleaning procedure was realized when later brine experiments showed poor ion rejection results. Flushing after experimentation removed most of the soluble ions, but other techniques are needed for removal of insoluble precipitates in the hollow fibers.

Suggested Research

There are several areas that should be investigated in the near future:

1. Using the synthetic brine, the SO_4^{-2} ion rejection should be measured again.
2. Operation should be tried at lower system pressures, say about 300-400 psig.
3. Tests should be performed on Marshall formation water for rejection and lifetime performance of the RO module.
4. A study should be done to optimize the Dow unit in regard to recovery vs. rejection in terms of power, pre-treatment, and waste disposal costs.

Suggested Experimental Improvements

The pressure relief valve on the synthetic brine delivery pump should be removed. It was initially thought that the pump would deliver too much feed to the system. But it appears that the system would operate better if more is delivered at pressures up to 50 psig.

Experimentation should be taken more often than in this study to show more accurate results.

The CA ratio used to test result consistency may not be entirely accurate. A better technique for determining consistency of results should be designed.

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APPENDIX A

Scintillation Spectrometry

Detection of radioactive ions in this study was accomplished by liquid scintillation techniques. When radiation interacts with certain substances known as fluors, small flashes of light(or scintillations) are produced. For most applications of scintillation counting, crystals are used as fluors: zinc sulfide is used to detect alpha particles; crystals of anthracene or naphthalene(with small amounts of anthracene) detect high energy beta particles; sodium iodide with thallium traces(NaI(Tl)) or germanium lithium(GeLi) crystals are used to detect gamma particles.

The basic scintillation system consists of a scintillation detector(crystal and photomultiplier), a high voltage supply, a preamplifier, and a scaler. This system is illustrated in Figure 21. Sometimes the inclusion of a linear amplifier and a discriminator is useful.

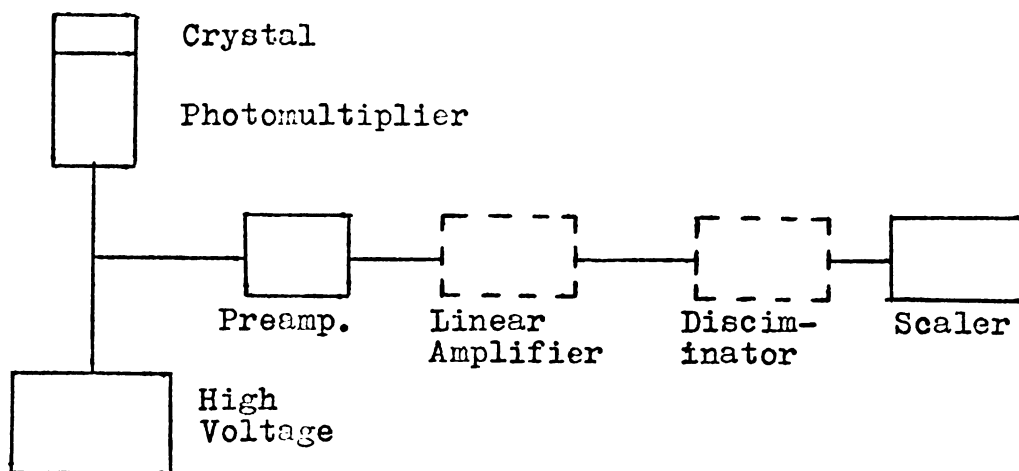


Figure 21. Block Diagram of a Basic Scintillation Counting System

The photomultiplier, or photocell, detects the small scintillations; and for each electron ejected from the cathode by a photon, nearly a million electrons reach the plate of the tube. This multiplication is accomplished by a system of electrodes called dynodes. A high voltage supply capable of up to 1200 volts makes the photomultiplier operable.

As the electrical impulses leave the photomultiplier, they are weak (high impedance) and must be changed into strong signals (low impedance) by a preamplifier. The pulses can then be conducted by cable to another amplifier, or to the scaler for counting.

When scintillation techniques are used, the sample activity as indicated by the scaler count depends on several variables, including the following:

1. Number of scintillations occurring in the fluor.
 - a. Source intensity, including background.
 - b. Geometry.
2. Distribution of intensities or scintillations
 - a. Source type
 - b. Crystal or fluor size and efficiency.
3. Phototube and optical system.
 - a. Efficiency of light transmission to cathodes of phototubes.
 - b. Amplification of phototube-- type of tube, and potential applied.
4. Associated electrical circuits.
 - a. Preamplifier between phototube and scaler
 - b. Discriminator setting on scaler input.

For a particular detector and scaler combination, most of these variables can be kept constant under normal conditions. Knowledge of the system being used and its variables will help to insure consistent detection of samples.

Detection of particles with low penetrating power, such as weak beta particles, cannot be accomplished with

crystal scintillators. Radiation of low penetrating power is absorbed either by self-absorption or by the surroundings before it has an opportunity to interact with the scintillator.

In 1950, Reynolds and Kallman independently announced that solutions of fluorescent substances in aromatic solvents were useful as beta detectors(3). These solutions, or liquid scintillators, are utilized in what is called liquid scintillation counting. The radioactive sample (perhaps in an aqueous medium) is dissolved in the liquid scintillator. A photomultiplier tube is used to detect the small flashes of light produced by collisions of beta particles with the fluorescent material in the scintillator solution. Sometimes two tubes are used to reduce thermal noise by means of a coincidence counting system.

The basic liquid scintillation system is shown in Figure 22. Pulses from both photomultiplier tubes are fed into the coincidence circuit where only simultaneously received pulses are accepted. Noise, or random pulses, are rejected. Noise is further reduced by operating the system at lower temperatures, say between -8 and 10°C , the exact temperature depending upon the solvent and solute being used. Some systems allow for separation of two or more radioactive nuclides by having more than one channel and scaler.

The velocity of light in a vacuum is about 3.0×10^{10} cm/sec; but the velocity of light c' in a medium of index of refraction η is

$$c' = c/\eta. \quad (15)$$

For water, which has a η equal to 1.33, the velocity of light c' is 2.26×10^{10} cm/sec(4). When a beta particle is emitted from decaying nuclides, and travels at speeds greater than c' , a bluish-white light is emitted. This emission known as Cerenkov radiation, is in the wavelength band between 3000 and 7000 angstroms(10).

It has been found that use of Cerenkov radiation can

be made to detect hard beta emitters with scintillation counters. The lower energy limit of electrons for stimulation of this emission is 260 keV(10). But for beta emitters the maximum energy has to exceed this value substantially because of the broad energy distribution.

The advantages of detecting Cerenkov radiation over conventional liquid scintillation counting are the facts that practically no sample preparation is necessary, and the technique is not subject to the problem of self-absorption.

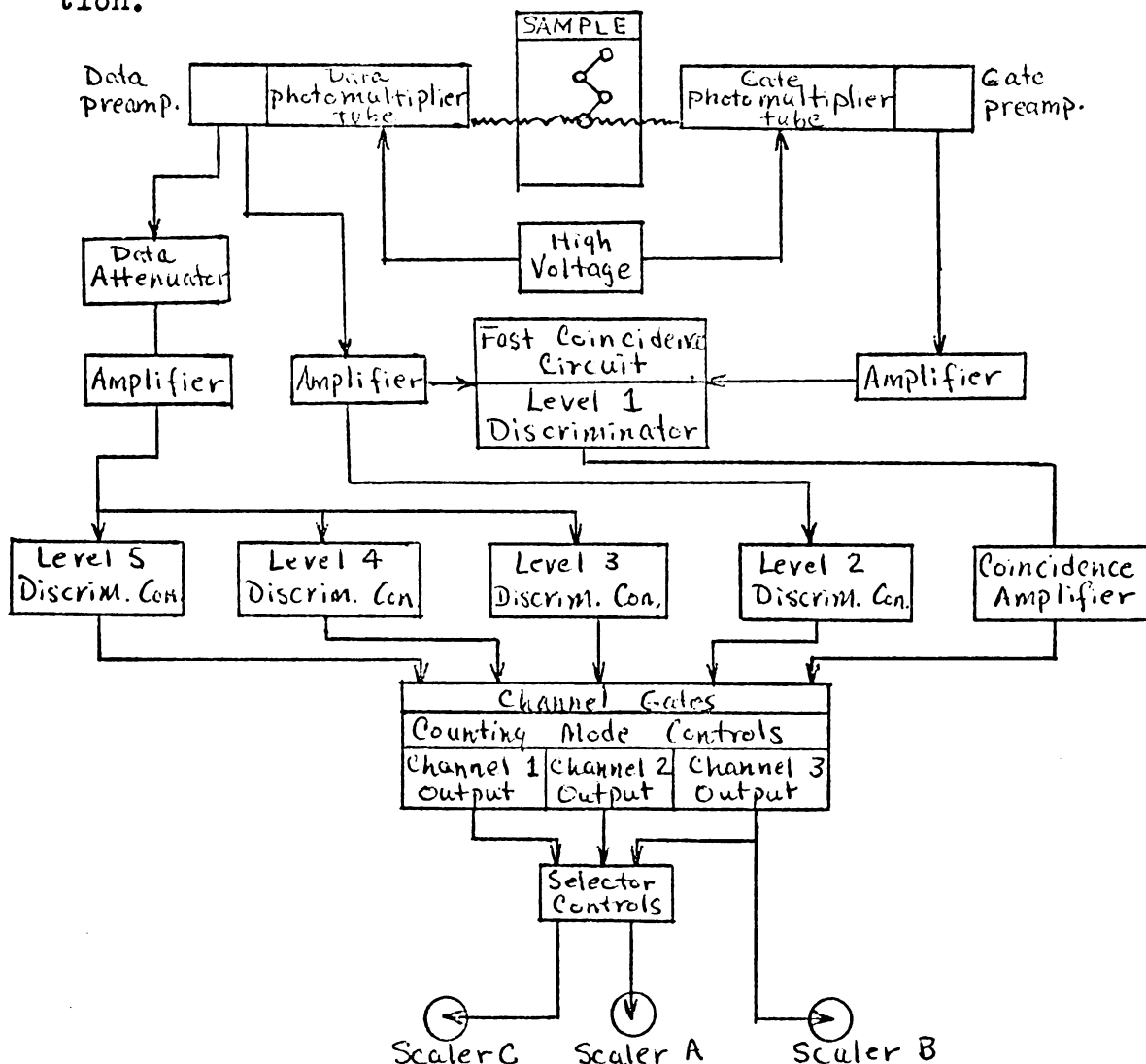


Figure 22. Packard Instrument Co. Scheme of Liquid Scintillation System

Conditions of measurement are well defined, handling of samples is easy, and samples can be reused for later investigation. Because of very high counting efficiency for relatively hard beta emitters, this method may also be used for samples with very low activity. Counting efficiency does not seem to vary much with a change in sample volume, as long as polyethylene counting vials are used instead of glass vials.

Neutron Activation and Radioactive Decay

During neutron activation, nuclei are excited by neutron capture and emit characteristic gamma rays. The activity produced in a specific nuclear species in an irradiation time t is given by(3):

$$A = N\phi\sigma(1 - e^{-0.693t/t_{1/2}}) \text{ disint./sec.} \quad (16)$$

where,

N = the number 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)

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

In most cases, activation of the sample occurs by a (n, γ) reaction. Therefore, the atomic number of the element does not change, but the atomic mass increases by one unit.

If the nuclide produced by activation is stable, the amount present will increase as irradiation continues. But because it is usually radioactive, it accumulates at a decreasing rate until an equilibrium amount is reached. This is the saturation level, and further irradiation is unneeded.

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. This is shown by the basic equation of radioactive decay:

$$-dN/dt = \lambda N \quad (17)$$

where,

dN/dt = disintegration rate of the radioactive atoms

λ = decay constant

N = number of radioactive atoms at time t .

Integration of equation 14 gives

$$\ln(N_0/N) = \lambda t \quad (18)$$

where,

N_0 = original number of atoms present

t = difference in time from t_0 .

The time required for the decay of one-half of the atoms in a radioactive sample is called the half-life. Using Equation 15, a relationship is found to relate it to the decay constant.

$$t_{\frac{1}{2}} = 0.693/\lambda \quad (19)$$

Experimental evidence shows that the beta particle (one of several emitted by radioactive decay) is identical to the electron. Its rest mass is 9.1×10^{-28} grams, and it has a charge Q of 1.6×10^{-19} coulombs. The beta particle is distinguished from an electron in that it is ejected from a nucleus. The product of beta decay is an element of atomic number one higher than the original element.



APPENDIX B

The following list contains two analyses of tap water from Michigan State University. The first analysis is from the State of Michigan Department of Public Health, while the second, in parentheses, was made by the Department of Natural Resources of Michigan State.

Table 8: Tap Water Analyses

<u>Constituent</u>	<u>Concentration, ppm(mg/l)</u>	
Fe ⁺⁺	0.0	(0.6)
Mn ⁺⁺	0.0	(0.01)
Ca ⁺⁺	80.	(100.)
Mg ⁺⁺	27.	(14.)
Na ⁺	13.8	(16.0)
K ⁺	1.5	(2.0)
NO ₃ ⁻	0.0	(0.04)
Cl ⁻	3.0	(3.0)
SO ₄ ⁻²	15.0	(30.0)
HCO ₃ ⁻	310.	(300.)
F ⁻	1.0	-----
PO ₄ ⁻³	-----	(0.02)
Total dissolved solids	371.3	(351.67)
pH	7.6	(7.6)

Table 9 contains an analysis of the synthetic brine used in the last part of this study(18).

Table 9: Synthetic Brine Analysis

<u>Constituent</u>	<u>Concentration, ppm(mg/l)</u>
Ca ⁺⁺	379.0
Fe ⁺⁺	8.5
Mg ⁺⁺	54.1
K ⁺	61.6
Na ⁺	2378.0

(Table 9 cont'd.)

SO_4^{-2}	443.4
SiO_2	57.0
Cl^-	2775.0
HCO_3^-	2611.4

This analysis corresponds to the following amounts of chemicals for every "batch" of 49 gallons of water.

Table 10: Chemical Makeup of Synthetic Brine

<u>Chemical Compound</u>	<u>Amount</u>
NaHCO_3	681.0 grams
CaCl_2	199.0 "
MgCl_2	40.1 "
KCl	22.3 "
Na_2SO_4	124.0 "
NaCl	565.0 "

APPENDIX C

Presented here is a complete listing of the activity vs. time data for all streams from all the experiments performed. All activities are net counts per 50 minutes, corrected for background and radioactive decay.

1. Nuclide = S³⁵

Experiment 1

Contamination(Module Wipe) = 2611 counts/50 minutes
Background = 468 counts/50 minutes

Time(min)	Feed	Permeate	Concentrate
30	15565	3003	51418
60	16516	2666	56780
75	15654	2214	57888

Experiment 2

Contamination(pH Meter Wipe) = 2251
Background = 487

00			2821
30	9876	2413	15697
60	10905	3813	33358
90	11142	2617	33021
120	9270	2229	27267

Experiment 3

Contamination(Acid Pump Wipe) = 2543
Background = 520

00			1717
30	10433	2209	43222
60	12559	2462	55616
90	12840	2355	57025
120	12806	2397	49999

Experiment 5

Contamination(Acid Pump Wipe) = 2457
Background = 561

30	9044	1543	38824
60	9303	1579	38779
120	8240	1634	35353
180	5885	1308	11232
220	7967	1539	35571

Experiment 9

Contamination(Module Wipe) = 2569

Background = 507

00	1132	1263	1104
60	8581	1613	32603
90	8777	1617	36087
120	8996	1570	32000
150	8994	1488	30821

Experiment 10

Contamination(Floor Wipe) = 2395

Background = 570

00	727	536	530
60	9389	976	37440
120	10687	1102	38395
150	9328	1041	37166
165	10060	989	36505

Experiment 11

Contamination(Acid Pump Wipe) = 24571

Background = 609

00	654	591	743
60	8810	902	19560
90	9892	994	18579
120	8776	862	18282

Experiment 12

Contamination(Acid Pump Wipe) = 51537

Background = 618

00	635	658	1014
60	10404	975	18805
120	10167	989	20621
150	10334	741	16139

Experiment 35

Contamination(Acid Pump Wipe) = 2896

Background = 409

30	20766	3203	80193
60	26273	3721	100094
90	23365	2623	96105

Experiment 36

Contamination = None Taken
Background = 412

00	5107	525	547
60	13539	3077	51126
90	13880	3637	53460

Experiment 37

Contamination(pH Meter Wipe) = 633
Background = 398

00	753	579	577
60	11866	6014	34110
90	14348	6823	35028

Experiment 38

Contamination(Acid Pump Wipe) = 1640
Background = 404

00	573	627	552
60	12255	7883	50093
90	23041	10335	52071

Experiment 39

Contamination(Floor Wipe) = 2873
Background = 404

00	789	578	799
60	21534	13563	40493
90	18766	12971	43516

Experiment 40

Contamination(Acid Pump Wipe) = 20724
Background = 415

Time(min)	Feed	Recycle	Permeate	Concentrate
00	563	790	438	582
60	5853	47322	6383	46400
90	18657	55464	8162	69081

Experiment 41

Contamination(Acid Pump Wipe) = 3773
Background = 411

00	723	807	550	531
60	17067	31996	4666	44080
90	20625	50983	5546	58840

II. Nuclide = Ca⁴⁵

Experiment 13

Contamination(Module Wipe) = 2537

Background = 582

00	457	479	492
60	9130	1017	38173
120	8799	1483	40555
150	9600	975	36577

Experiment 14

Contamination(Floor Wipe) = 1711

Background = 553

00	766	649	1165
60	10870	1260	39589
120	11562	1280	42114
150	12433	1263	42020

Experiment 15

Contamination(Acid Pump Wipe) = 1023

Background = 593

00	1059	563	792
60	3108	1213	46837
150	10566	1204	43311

Experiment 16

Contamination(Acid Pump Wipe) = 3296

Background = 593

00	1050	384	529
60	4107	828	33539
120	9331	894	31284

Experiment 17

Contamination = None Taken

Background = 593

00	1045	497	3444
60	4980	1112	42718
120	11017	1270	43233
150	11516	1390	40483

III. Nuclide = Na²⁴

Experiment 19

Contamination(Acid Pump Wipe) = 3924
 Background = 649

00	1834	1367
60	3550	1144
150	5643	1437

Experiment 20

Contamination(Acid Solution Spill) = 49647
 Background = 353

00	182	173
60	11205	937
120	11169	892
150	9338	881

Experiment 21

Contamination(pH Meter Wipe) = 599
 Background = 346

00	223	197
60	9238	1258
120	14366	1348
150	13465	832

Experiment 22

Contamination(Acid Pump Wipe) = 226
 Background = 343

00	664	178
60	8197	1293
120	14620	1099
150	13296	746

Experiment 23

Contamination(Module Wipe) = 13708
 Background = 387

00	84	149
60	25452	1229
120	24803	1224
150	23183	1149

Experiment 24

Contamination = None Taken

Background = 406

00	2028	420
60	27029	1283
120	26176	1496
150	24117	1138

Experiment 25

Contamination(Acid Pump Wipe) = 105

Background = 281

00	179	119	108
30	8328	1597	51195
60	14310	2108	53721

Experiment 26

Contamination(pH Meter Wipe) = 17

Background = 326

00	1370	214	1100
30	10995	1859	53092
60	13253	1703	53676

Experiment 27

Contamination(Module Wipe) = 49

Background = 339

00	770	163	1183
30	18179	2129	71111
60	24809	2064	75720

Experiment 28

Contamination = None Taken

Background = 283

00	2525	523	3706
30	15626	1999	66784
60	23557	2009	68719
100	21314	1841	62499

Experiment 29

Contamination(Acid Pump Wipe) = 35

Background = 331

00	3470	3381	9628
30	5154	645	23255

(Experiment 29 cont'd.)

60	6697	726	21417
90	6138	645	18272

Experiment 30

Contamination = None Taken
Background = 328

00	5150	577	16827
30	1060	65	572
60	3346	599	20136
90	5697	565	17898

Experiment 31

Contamination(Floor Wipe) = 47
Background =

30	6898	793	20024
60	6003	666	15752
90	5245	498	15301

Experiment 32

Contamination = None Taken
Background = 321

30	11200	1396	35888
60	10494	1697	48790
90	9187	1363	39778

Experiment 33

Contamination(Acid Pump Wipe) = 34
Background = 346

Time(min)	Feed	Recycle	Permeate	Concentrate
30	5485	12400	1225	18155
60	7608	15348	1892	25173
105	6709	13760	1371	20766

Experiment 34

Contamination(Acid Pump Wipe) = 55
Background = 298

30	10680	14289	1501	23306
60	10172	25970	2475	33773
90	9514	24666	2439	32580

APPENDIX D

The following are calculations used in the experimental methods of this study. This includes the analysis of activity vs. time data and in calibration of the scintillation spectrometer.

1. Amount of HCl needed for pH control with tap water as feedwater stream:

From a table containing strengths of HCl required for tap water alkalinity of 300 found in the Poly-metric operational manual, 1750 GPD requires 15% to full strength HCl for proper pH control(21).

$$\frac{(1.5 \text{ gal.})}{\text{day}} \frac{\text{day}}{(24 \text{ hr.})} \frac{(3.785 \text{ liters})}{\text{gallon}} \frac{(1000 \text{ ml})}{\text{liter}} = 236.6 \frac{\text{ml HCl}}{\text{hr.}}$$

2. Amount of Sodium Hypochlorite(bleach) needed for Cl_2 residual control of 1.0 ppm or less(21):

$$\frac{(1.21 \text{ gal. H}_2\text{O})}{\text{min.}} \frac{(7.57 \text{ ml bleach/min.})(60 \text{ min.})}{(100 \text{ gal. H}_2\text{O / min.}) \text{ hr.}} = 5.50 \frac{\text{ml}}{\text{hr}}$$

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

Assume: desired activity = $17.35 \mu\text{Ci}$, 15min. irradiation time, $\phi = 2 \times 10^{12} \text{ n/cm}^2\text{-sec}$, 1 hr between irradiation time and time of

$$\begin{aligned} A_0 &= A e^{\lambda t} \\ &= (17.35 \mu\text{Ci}) \exp((4.62 \times 10^{-2} / \text{hr}) 1 \text{ hr}) \\ &= 18.17 \mu\text{Ci} \end{aligned}$$

$$\text{grms pure Na needed} = \frac{(18.17 \mu\text{Ci})(37,000 \text{ cps}/\mu\text{Ci})}{(6.023 \times 10^{23} \text{ atoms/mole})}$$

3. (cont'd)

$$\frac{(23 \text{ gms/mole})}{(2 \times 10^{12} \text{ n/cm}^2\text{-sec})(5.3 \times 10^{-25} \text{ cm}^2)(1.15 \times 10^{-2})}$$

$$= 2.106 \times 10^{-3} \text{ gms}$$

$$\text{gms NaOH needed} = (2.106 \times 10^{-3} \text{ gms Na}) \frac{(40 \text{ gms NaOH})}{(23 \text{ gms Na})}$$

$$= 3.663 \times 10^{-3} \text{ gms}$$

$$\text{gms Na}_2\text{CO}_3 \text{ needed} = (2.106 \times 10^{-3} \text{ gms Na}) \frac{(106 \text{ g Na}_2\text{CO}_3)}{(46 \text{ g Na})}$$

$$= 4.853 \times 10^{-3} \text{ gms}$$

4. Scintillation spectrometer efficiency:

$$\frac{(17.35 \mu\text{Ci})}{(750 \text{ ml})} (10 \text{ ml sample}) \frac{(37,000 \text{ dps})}{\mu\text{Ci}} \frac{(60 \text{ sec})}{\text{min}} =$$

$$= 5.136 \times 10^5 \text{ dpm}$$

$$\text{Efficiency} = \frac{1.88 \times 10^5 \text{ cpm}}{5.136 \times 10^5 \text{ dpm}} (100) = 36.54\%$$

5. Salt Rejection:

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

$$= \frac{(12863 - 2910)100}{12863} = 77.38\%$$

6. Water Permeate Flux(not corrected to 25°C):

$$J_1 = \frac{\text{Permeate Rate(GPD)}}{\text{Active Membrane Area of RO Module}}$$

$$= \frac{(1.2 \text{ GPM})(60 \text{ min})(24 \text{ hr})}{(1187 \text{ ft}^2) (\text{hr}) (\text{day})} = 1.46 \text{ GPD/ft}^2$$

7. Recovery:

$$\% \text{ Recovery} = \frac{\text{Permeate Rate}}{\text{Permeate Rate} + \text{Brine Rate}} (100)$$

$$= \frac{0.750 \text{ GPD} (100)}{1.173 \text{ GPD}} = 63.94\%$$

8. Material Balance:

$$(\text{Feed Rate})(\text{Feed Activity}) = (\text{Permeate Rate})(\text{Permeate Activity}) + (\text{Concentrate Rate})(\text{Concentrate Activity})$$

9. CA Ratio:

The ratio is defined as the ratio of (Concentrate Rate)(Net Concentrate Activity) as determined by the material balance of No. 8 to the same quantity as determined from experimental values of the Concentrate Rate and its Activity.

Example:

$$(\text{Concentrate Rate})(\text{Concentrate Activity}) = 20,000$$

as determined from No. 8

$$(\text{Concentrate Rate})(\text{Concentrate Activity}) = 20,109$$

as from experimental data

$$\text{CA Ratio} = 20,000/20,109 = 0.996$$

10. Standard Deviation:

A 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.

Example:

$$\sigma_F = \frac{(16516)^{\frac{1}{2}}}{50 \text{ min.}} = 2.58 \text{ cpm}$$

$$\sigma_P = \frac{(2666)^{\frac{1}{2}}}{50 \text{ min.}} = 1.03 \text{ cpm}$$

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

$$\begin{aligned} (A \pm \sigma_F) - (B \pm \sigma_P) &= (A - B) \pm (\sigma_F^2 + \sigma_P^2)^{\frac{1}{2}} \\ &= 277 \pm \sigma_{\text{DIF}} = 277 \pm 2.78 \end{aligned}$$

(Standard Deviations cont'd.)

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

$$\begin{aligned} (A-B \pm \sigma_{DIF}) / (A \pm \sigma_F) &= (A/B) (1 \pm (\sigma_{DIF}^2 / (A-B)^2 + \sigma_F^2 / A^2)^{1/2}) \\ &= 0.838 \pm 0.0107 \end{aligned}$$

The standard deviation of the sum of operations is about 1.07%.

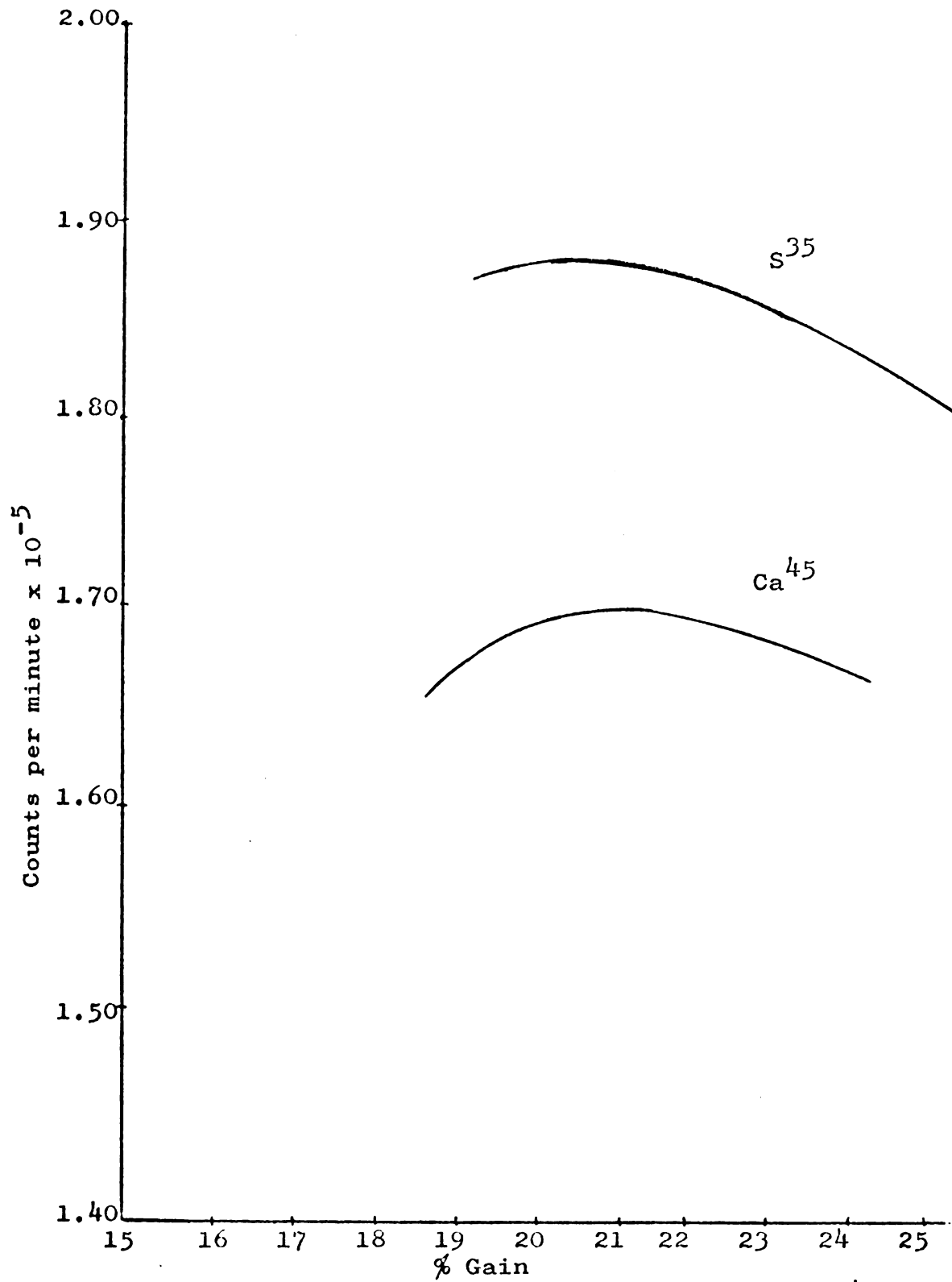


Figure 23. Activity vs. % Gain for S^{35} and Ca^{45}
Scintillation Detection

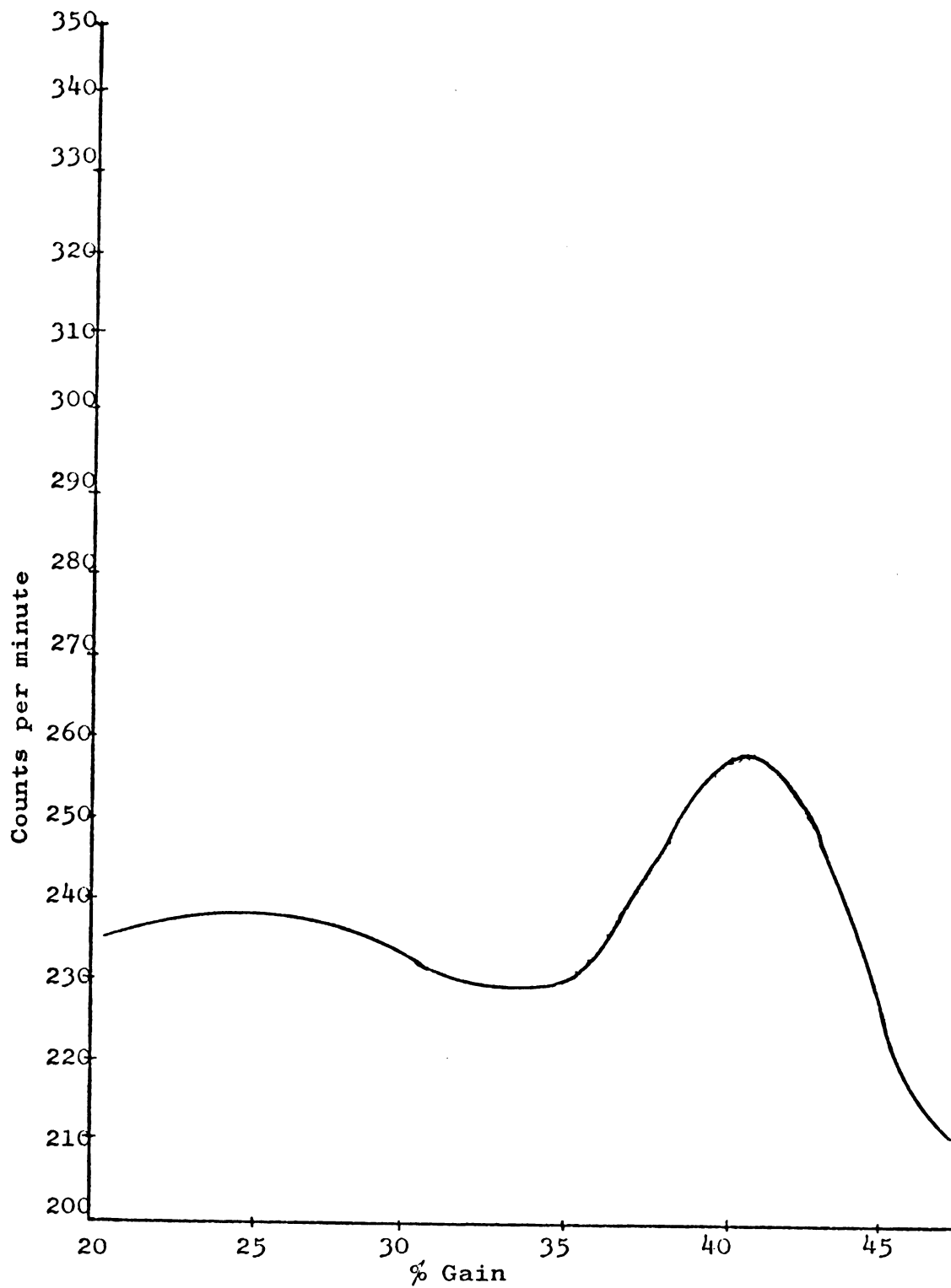


Figure 24. Activity vs. % Gain for Na²⁴ Scintillation Detection

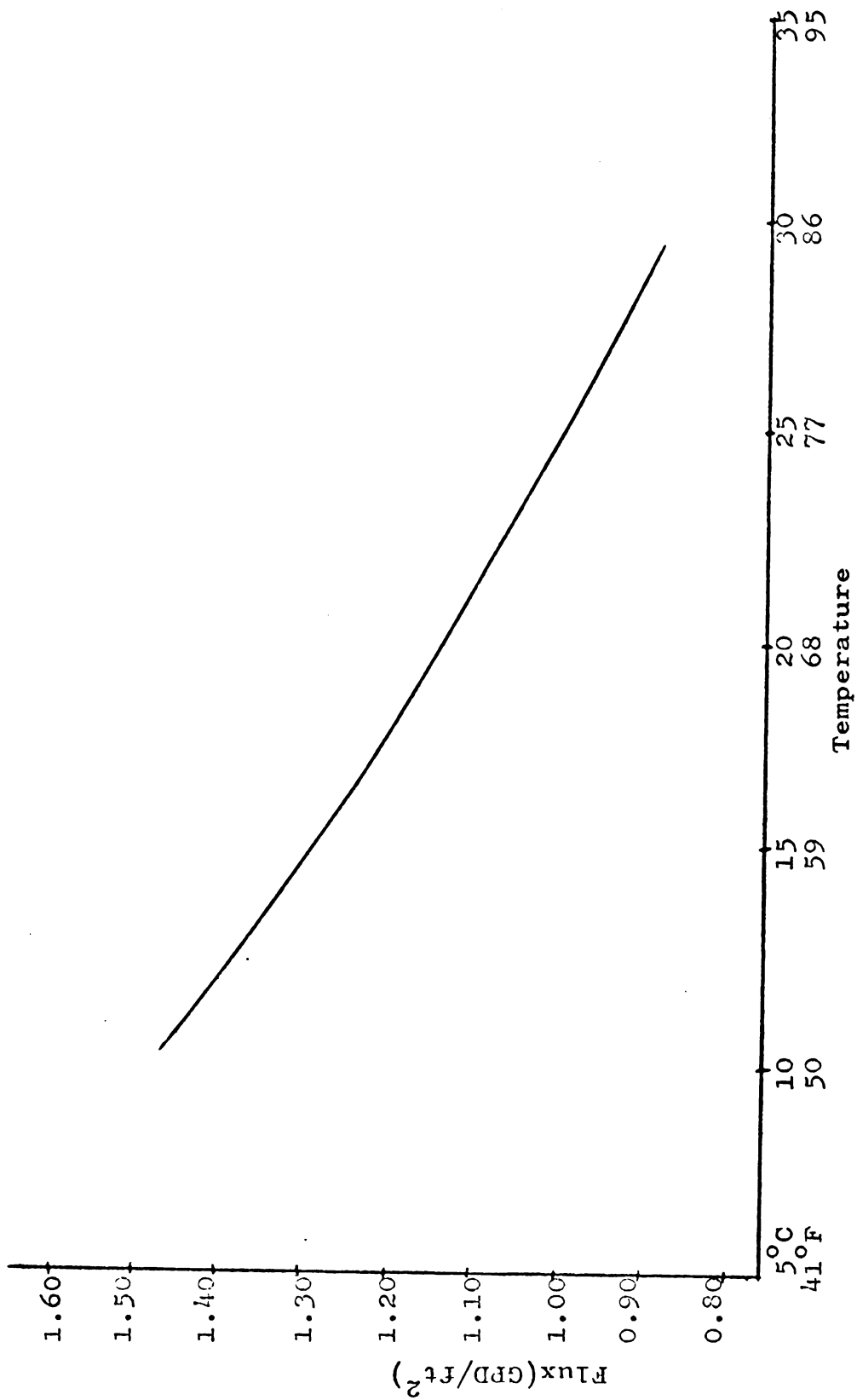


Figure 25. Plot of Permeate Flux(Relative to 25°C) vs. Operating Temperature for Dow Hollow Fine Fiber Module(21)

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