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**Environmental Protection Technology Series**

# **Applications of Reverse Osmosis To Acid Mine Drainage Treatment**



**National Environmental Research Center  
Office of Research and Development**

**U.S. Environmental Protection Agency  
Cincinnati, Ohio 45268**

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EPA-670/2-73-100  
December 1973

APPLICATIONS OF REVERSE OSMOSIS TO  
ACID MINE DRAINAGE TREATMENT

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## FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The studies in this report investigate techniques for pollution abatement from the acid waste of the coal mining industry and, at the same time, provide a means for recovery of a high-quality water which would be suitable for domestic or industrial use.

A. W. Breidenbach, Ph.D.  
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## ABSTRACT

Spiral-wound reverse osmosis systems were tested on acid mine drainage discharges at four different locations (Norton, West Virginia; Morgantown, West Virginia; Ebensburg, Pennsylvania; and Mocanaqua, Pennsylvania) whose water quality characteristics were quite varied. In addition, comparison studies were made of the hollow-fiber and tubular systems at Mocanaqua and of the spiral and hollow-fiber systems at Norton.

At all sites, the limiting factor in high recovery operation was calcium sulfate insolubility. Generally, calcium sulfate fouling occurred when  $\sqrt{P_{mc}/(2.16 \times 10^{-4})}$  exceeded 2.0, where  $P_{mc}$  = product of the molar concentrations of calcium and sulfate in the brine stream.

In all tests, product water was of near potable quality. Neutralization was required in all cases to elevate pH and, in some cases, to remove residual iron and manganese.

A "neutrolosis" process was developed in the course of these investigations and constituted a major technological advance in reverse osmosis treatment of acid mine drainage. The neutrolosis process, a combination of reverse osmosis and neutralization, achieved water recoveries near 99 percent at the Norton site while producing a high quality product.

At Mocanaqua, the hollow-fiber and spiral systems exhibited comparable performance. Tubular performance, though adequate, was not quite equal to the other systems.

At Norton, the spiral-wound system performed normally but the hollow-fiber system experienced major colloidal and iron fouling problems which were never completely overcome.

Operation of both hollow-fiber and spiral-wound systems at Mocanaqua under optimized flow conditions at 75 percent recovery

yielded log-log flux decline slopes near  $-0.01$  for 2,000 hours of operation.

Pretreatment at all sites consisted of ten micron filtration. Ultraviolet disinfection, acid injection, or both, were necessary at some sites to inhibit iron oxidation and precipitation.

This report was submitted in fulfillment of Environmental Protection Agency Project 14010 TMC. Work was completed as of June 1972.

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## SECTION I

### CONCLUSIONS

The following conclusions summarize the results observed from tests of spiral-wound, hollow-fiber, and tubular reverse osmosis systems made on acid mine drainage discharges at four sites (Norton, W. Va., Morgantown, W. Va., Ebensburg, Pennsylvania, and Mocanaqua, Pennsylvania):

1. Reverse osmosis has been shown to be an effective method of treating acid mine drainage with the production of high quality water.

2. Product water from all sites would require neutralization to increase pH and, in some cases, to remove residual iron before potable standards could be met. At sites where manganese concentrations exceeded 10 mg/l, product quality would require neutralization to pH 9-10 to effect manganese removal to meet U. S. Public Health Service potable standards. Reacidification would then be required to reduce pH to acceptable limits.

3. Recovery was limited at each site by calcium sulfate insolubility. In general, calcium sulfate fouling occurred when  $\sqrt{P_{mc}/(2.16 \times 10^{-4})}$  was greater than 2.0 where  $P_{mc}$  = product of molar concentrations of calcium and sulfate in the brine stream.

4. All test sites considered, performance of the spiral-wound system was superior to that of the hollow-fiber and tubular units. Although the hollow-fiber performed on a par with spiral-wound at Mocanaqua, the hollow-fiber system had considerable difficulty in treating the Norton ferric iron surface water acid mine drainage because of iron and colloidal fouling problems.

5. Neutrolosis (the blending of neutralized brine supernatant from the reverse osmosis unit back into the feed to the unit) has been shown to be a promising process for obtaining maximum recoveries and solving the brine disposal problem.

6. Unless the neutrolosis concept were used, treatment of the brine before discharge would be required in all cases of reverse osmosis treatment of acid mine drainage.

7. Operation of the spiral system at 400 psi with brine/product (b/p) flow ratios in excess of 10:1 per module provided significant improvements in flux stability as compared to higher pressure, lower b/p ratio operation.



## SECTION II

### RECOMMENDATIONS

It is recommended that additional research be implemented in the following areas:

1. Determination of membrane life under acid mine drainage conditions and development of reliable cost figures.
2. Development of a calcium sulfate precipitation inhibitor which would allow significant increases in attainable reverse osmosis recovery levels.
3. Development of techniques for fouling removal (i.e., removal of iron and calcium sulfate precipitation and organic deposition).
4. Optimization of neutrolosis process and testing under a variety of conditions to determine scope of application.
5. Evaluation of reverse osmosis for removal of heavy metals commonly found in "hard rock" type mine drainage.

It is also recommended that future system comparison evaluation work not correct flux for pressure losses from internal piping and intrinsic brine flow resistance since such values are characteristics of the system involved and deleting these considerations would only tend to cover up losses in process efficiency.

## SECTION III

### INTRODUCTION

Between 1968 and 1972, the staff of the U. S. Environmental Protection Agency's (EPA) Norton Mine Drainage Treatment Field Site investigated reverse osmosis (RO)\* treatment of acid mine drainage (AMD).

Beginning in 1968, EPA (then Federal Water Pollution Control Administration - FWPCA) cooperated with the Office of Saline Water (OSW) in research at Norton, West Virginia to demonstrate the feasibility of reverse osmosis treatment of a ferric iron acid mine drainage water.<sup>1,2</sup> During these initial studies, OSW supplied the spiral-wound RO equipment and a consultant. EPA provided analytical support and assisted in operating the unit. Most of these studies were conducted at water recovery rates between 50 and 75 percent, although one test was as high as 80 percent, because of the fear of fouling the membranes with iron and/or calcium sulfate precipitation. At recoveries greater than 70 percent, calcium sulfate exceeded the theoretical saturation concentration and a potential danger of fouling the membranes was present.

It was concluded from these studies that water recoveries up to 80 percent could be achieved on the Norton ferric water with no uncontrollable iron or  $\text{CaSO}_4$  fouling. Salt rejections between 97 and 99 percent were obtained.

The Environmental Protection Agency was deeply concerned with the waste brine which constituted from 20 to 25 percent of the water treated by an RO unit operating at 75-80 percent recovery. One approach to decreasing this problem would be to increase the recovery rate to a maximum, thus producing a minimum volume of brine. Towards

\*See Glossary for definition of terms.

this goal, EPA entered into a contract with Gulf Environmental Systems Company in 1969 to continue tests at Norton<sup>3</sup> with emphasis on high recovery operation. OSW supplied a portion of the RO equipment. EPA conducted the tests with consultation of Gulf Environmental Systems and portions of the results are discussed in this report. Recoveries above 90 percent were obtained during these studies in short duration runs.

Concurrent with the Gulf contract, EPA, through a grant to the Commonwealth of Pennsylvania, contracted with Rex Chainbelt, Inc., to study the feasibility of reverse osmosis treatment of a ferrous AMD discharge at Mocanaqua, Pennsylvania, using a tubular RO unit. Although the water quality characteristics of the Mocanaqua discharge were similar to the Norton water except for the ionic state of the iron, severe fouling was observed at moderate recovery levels at Mocanaqua.<sup>4</sup> The implication therefore existed that ferrous iron was, for some unknown reason, more difficult to treat than a comparable ferric discharge. Although Riedinger and Shultz<sup>5</sup> in 1966 had studied spiral-wound type RO treatment of a ferrous discharge near Kittanning, Pennsylvania, and reported no severe fouling, it was desirable that ferrous situations be more thoroughly investigated. For this purpose, the scope of work of the on-going Gulf Environmental Systems contract was modified by mutual agreement to include studies on ferrous waters in addition to the Norton ferric site.

The first ferrous site studied by EPA was a severely polluted AMD discharge near Morgantown, West Virginia. Even at 50 percent recovery, severe fouling occurred at this site. Due to the extreme concentrations at Morgantown, the situation was not comparable to that at Mocanaqua. A site with conditions comparable to Mocanaqua was located near Ebensburg, Pennsylvania, and the spiral-wound unit was tested there in 1970. No fouling was observed at 50 percent recovery and only minor fouling occurred at 84 percent recovery.

Following the Ebensburg test, the spiral unit was returned to Norton for a long-term, 75 percent recovery study which lasted 3,012 hours and in which some major fouling occurred.

The Norton Mine Drainage Field Site also had an active research program concerned with neutralization of AMD. The staff conceived that the reverse osmosis process could be combined with the neutralization process to produce a maximum amount of high quality water with a minimum volume of waste. The process conceived was operation of the reverse osmosis unit at maximum recovery (90 percent at Norton), neutralization of the brine, and recycle of the neutralized brine supernatant water back into the feed to the reverse osmosis unit. Thus, this system would produce only product water plus a small amount of neutralized sludge containing the iron, calcium, sulfate, aluminum, etc. This process was named neutrolosis (combination of reverse osmosis and neutralization) and was tested by EPA at Norton during 1970.

In 1971, EPA, again through a grant to the Commonwealth of Pennsylvania, contracted with Rex Chainbelt to further evaluate the fouling observed in the 1969 Mocanaqua studies. Rex Chainbelt returned to Mocanaqua with an improved tubular unit and a hollow-fiber unit. EPA installed a spiral-wound unit to operate alongside the other two under identical conditions. Severe fouling occurred only on the tubular system equipped with a membrane with a salt rejection of 96-98 percent. Both the spiral-wound and hollow-fiber units performed extremely well at 75 percent recovery. Very small flux losses were observed for the spiral and hollow-fiber units.

After the 1971 Mocanaqua studies, both the spiral-wound and hollow-fiber units were returned to EPA's Norton facility for final tests.

Results of the EPA studies are presented in this report.

## SECTION IV

### PROCEDURES

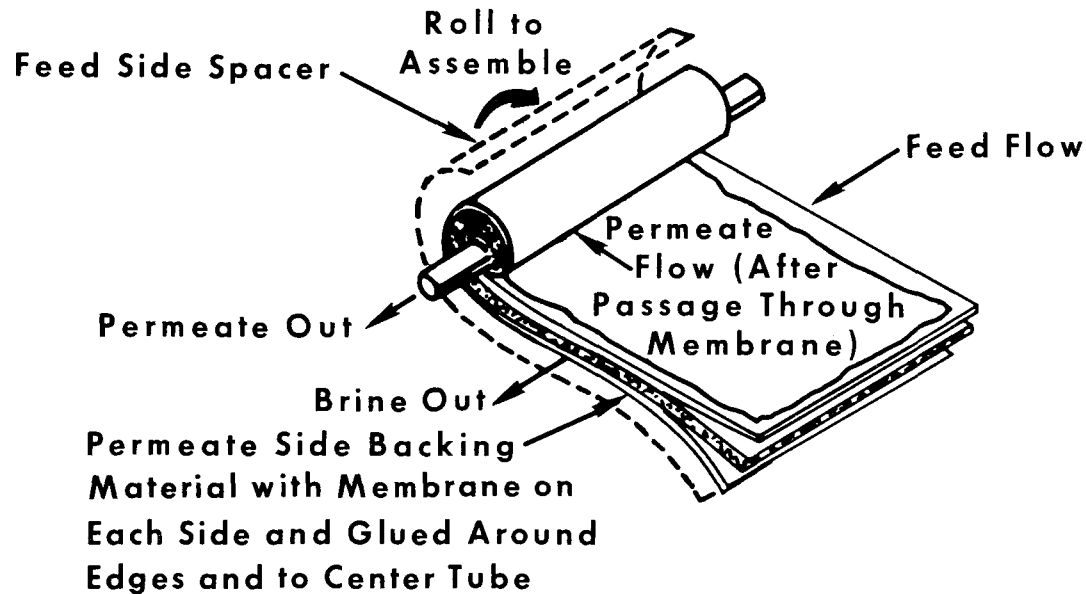
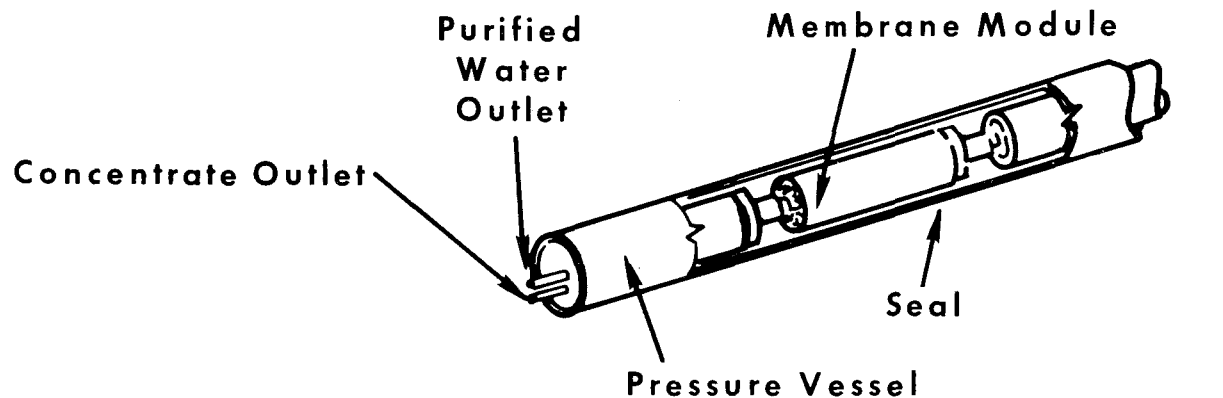
#### TEST EQUIPMENT

Two spiral-wound type reverse osmosis units were used in the course of these studies. Both were manufactured by Gulf Environmental Systems. The initial unit (owned by OSW) was a 37,850 liter per day (10 K - 10,000 gallons per day nominal product flow) unit consisting of five 4 in x 10 ft (1.58 cm x 3.05 m) Schedule 40 steel pipe pressure vessels which had been lined with an epoxy to prevent corrosion. A Moyno high pressure progressive cavity stainless steel pump was used to supply water to the unit at pressures up to 5,517 kilonewtons per square meter -  $\text{kN/m}^2$  (800 psig).

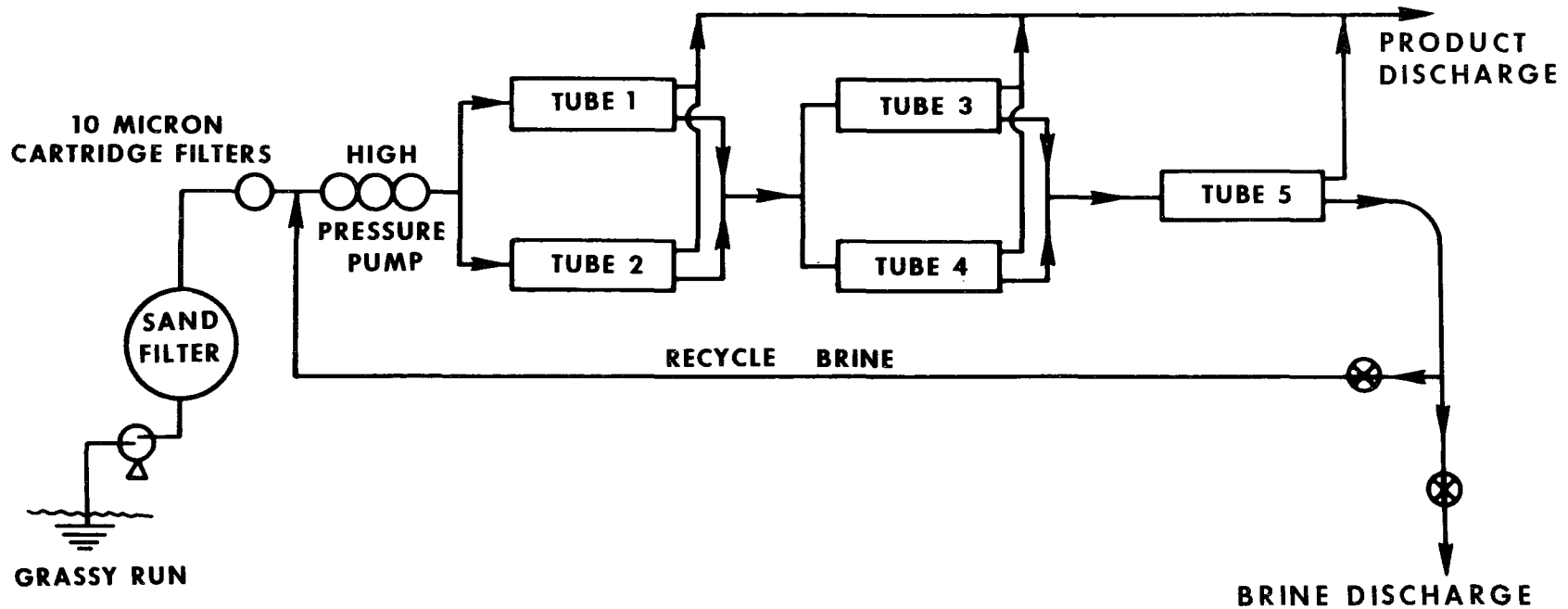
Each of the five pressure vessels contained three spiral-wound modules (Figure 1). Each module was 0.92 meters long (3 ft), 9.53 centimeters (3.75 in) in diameter, and contained  $4.65 \text{ m}^2$  ( $50 \text{ ft}^2$ ) of modified cellulose acetate membrane. The three modules were placed in series in each pressure vessel (tube). There were two effluents from each module (or tube of modules), i.e., brine and product water. Typically, the brine from one module (or tube of modules) served as the feed to the next module (or tube of modules) and was progressively dewatered in this manner. Each vessel therefore contained  $13.96 \text{ m}^2$  ( $150 \text{ ft}^2$ ) of membrane for a five vessel unit total of  $69.8 \text{ m}^2$  ( $750 \text{ ft}^2$ ).

The flow diagram for the 10 K unit is presented in Figure 2. Pressurized sand filters and 10 micron cartridge filters were used to remove suspended solids from the feed water before the water entered the RO unit. Filtration was necessary as suspended solids can clog the narrow brine channels and foul the RO membranes.

For these studies, the pressure vessels were arranged in a 2-2-1 array in order to maintain, as nearly as possible, a uniform



**Figure 1**  
**Spiral-wound module configuration (3)**



**Figure 2. Flow diagram for 37850 l/day (10,000 gpd)  
spiral-wound reverse osmosis unit.**

brine flow through each vessel. The first two vessels were in parallel. Brines from these vessels were combined to serve as the feed to vessels 3 and 4, which were in parallel. Brines from vessels 3 and 4 were then combined to serve as feed to vessel 5.

In order to increase recovery beyond 70 percent and yet maintain sufficient brine flow velocity and turbulence in each module to prevent 'boundary layer' precipitation, it was necessary to recycle a portion of the brine into the feed to the RO unit. In this case, the spiral unit membranes were actually treating a blended feed (mixture of raw water and recycled brine) rather than the raw water.

Inlet pressure and pressure drops across each tube were measured on pressure and differential pressure gages. Internal flow measurements were made using venturies and differential-pressure flow gages. External flows were measured volumetrically. As product flow was strongly temperature dependent, careful temperature measurements were made using a laboratory thermometer. The spiral 10 K unit was not mobile and therefore was used solely at Norton.

The second spiral-wound unit produced 15,140 liters per day (4,000 gpd) of product water (4 K unit) and consisted of three 4 in x 10 ft (1.58 m x 3.05 m) pressure vessels arranged in a 2-1 array. Operation and construction of this unit was the same as the 10 K unit previously described. This 4 K unit was owned by EPA and due to its size, was especially suited to portable field testing. Several feed pumps were tried on the 4 K system with the ultimate selection of a Goulds MB 13600 stainless steel-ceramic, multi-stage, centrifugal pump which had been especially designed for reverse osmosis applications. For field applications, the 4 K unit was mounted in a portable 2.44 m x 6.10 m (8 ft x 20 ft) metal building. In addition to tests at Norton, the studies at Morgantown, Ebensburg, and Mocanaqua were made on this 4 K unit.

For the Mocanaqua study, a hollow-fiber unit manufactured by DuPont was tested alongside the spiral-wound 4 K system. Initial



Mocanaqua hollow-fiber tests were made on a single permeator on loan to Rex Chainbelt from the manufacturer. EPA later purchased two additional permeators to enlarge the hollow-fiber system to 6 K (22,710 l/day or 6,000 gpd of product flow) in order to more effectively compare hollow-fiber results with spiral-wound.

Approximately 139.6 m<sup>2</sup> (1,500 ft<sup>2</sup>) of 8-9 modified nylon hollow-fiber membrane<sup>6</sup> were packed in each 15.2 cm x 1.22 m (6 in x 4 ft) stainless steel pressure vessel as illustrated in Figure 3. The three permeators were arranged in a 2-1 array. System arrangement will be more thoroughly discussed in the section on the Mocanaqua testing. All flows were measured volumetrically.

#### ANALYTICAL PROCEDURES

Acidity was determined according to the Salotto<sup>7</sup> method of adding hydrogen peroxide and titrating potentiometrically to a pH 7.3 end point. Total iron, calcium, magnesium, manganese, and aluminum concentrations were determined by atomic absorption spectrophotometry.<sup>8</sup> EPA Methods<sup>8</sup> was used for the sulfate determination. The pH was measured potentiometrically. Ferrous iron was determined by colorimetrically titrating potassium dichromate against a p-Diphenylamine sulfonic acid sodium salt indicator.<sup>9</sup> A YSI Model 51 dissolved oxygen meter was used for dissolved oxygen measurements.

For field studies, acidity, ferrous iron, pH, conductivity, and dissolved oxygen determinations were made on-site. Acidified samples were returned to Norton for the remainder of analyses.

#### CALCULATIONS

Recovery was defined as the percentage of water resulting as product as compared to the initial volume entering the unit. Therefore, recovery equalled product flow ÷ feed flow expressed as a percentage. Since accurate measurements could be made of the brine and product flow rates, feed flow was calculated as the sum of the brine and product flow.

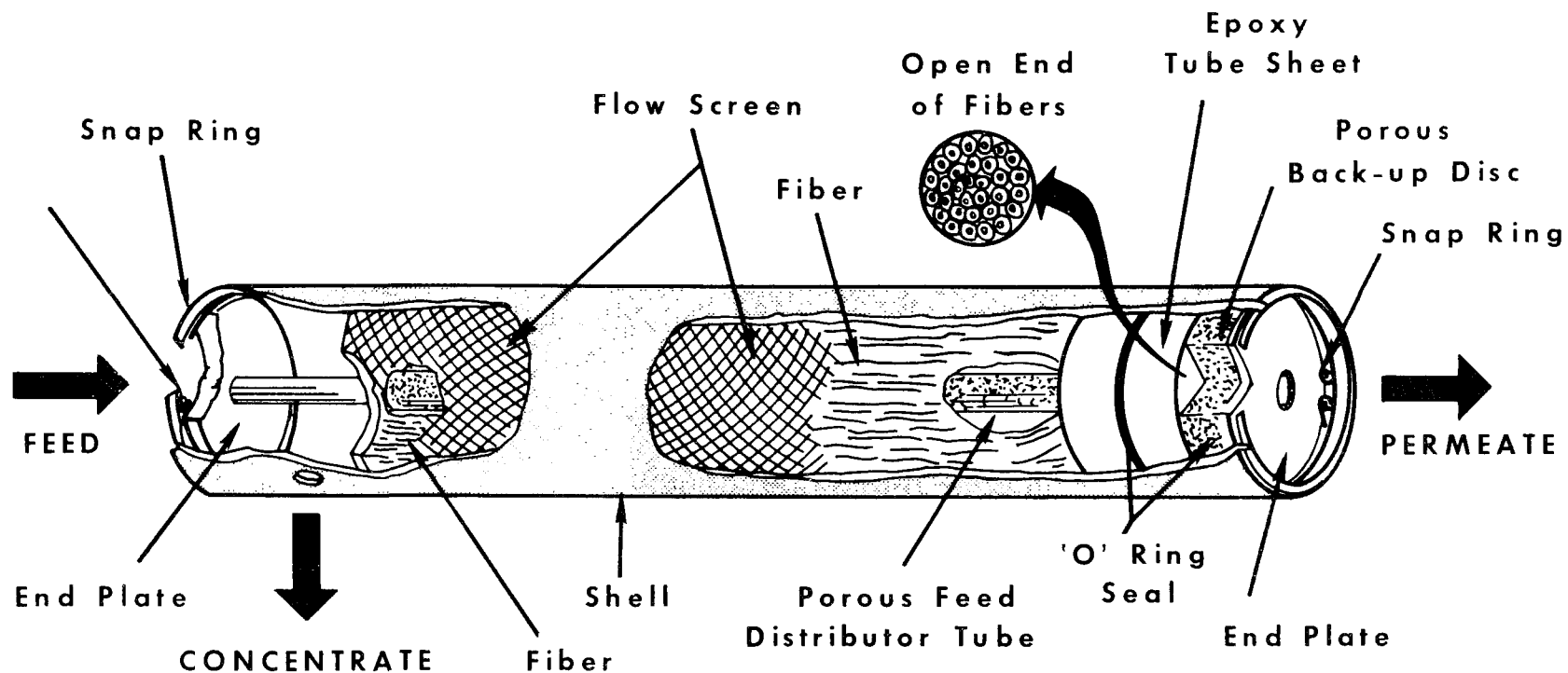
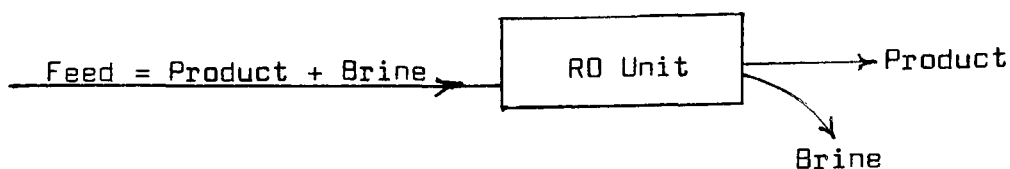


Figure 3  
Hollow-fiber reverse osmosis module<sup>(6)</sup>



Since very little of the original pollutants appear in the product stream, virtually all remain in the brine stream. As recovery increases, progressively less water is available for dilution of these pollutants. Figure 4 illustrates the recovery and concentration factor relationship. Above 75 percent recovery, small changes in recovery level produce large changes in brine concentration.

The standard way of expressing membrane performance is flux rate; i.e., gallons of product flow per square foot of membrane per day at a specified temperature and net pressure. To obtain these values, product flow was corrected from the observed temperature to 77° F by a correction chart supplied by each manufacturer. The 77° F temperature was used since it is the standard of the reverse osmosis industry; however, a more realistic value for mine drainage studies would be 50° F. In general, product flow increased roughly 1.5 - 2 percent per degree Fahrenheit. Factors for correcting flux rates from English to metric units are supplied at footnotes for Figures and Tables in this report.

Average pressure was determined by reading gage pressures in and out of each vessel and averaging them. Osmotic pressure, which in this study was mathematically correlated to conductivity, was subtracted from the average applied pressure to give net driving pressure.

Therefore, flux rates were determined according to the following equation:

$$\text{Flux (gal/ft}^2\text{/day @ 77° F and desired net pressure)} = \frac{\text{Product flow (gpm) at observed temperature} \times \text{correction factor to 77° F}}{\text{membrane area (ft}^2\text{)} \times 1440 \text{ minutes/day} \times \text{desired net pressure}} \times (\text{Average pressure} - \text{osmotic pressure}) \text{ psi net}$$

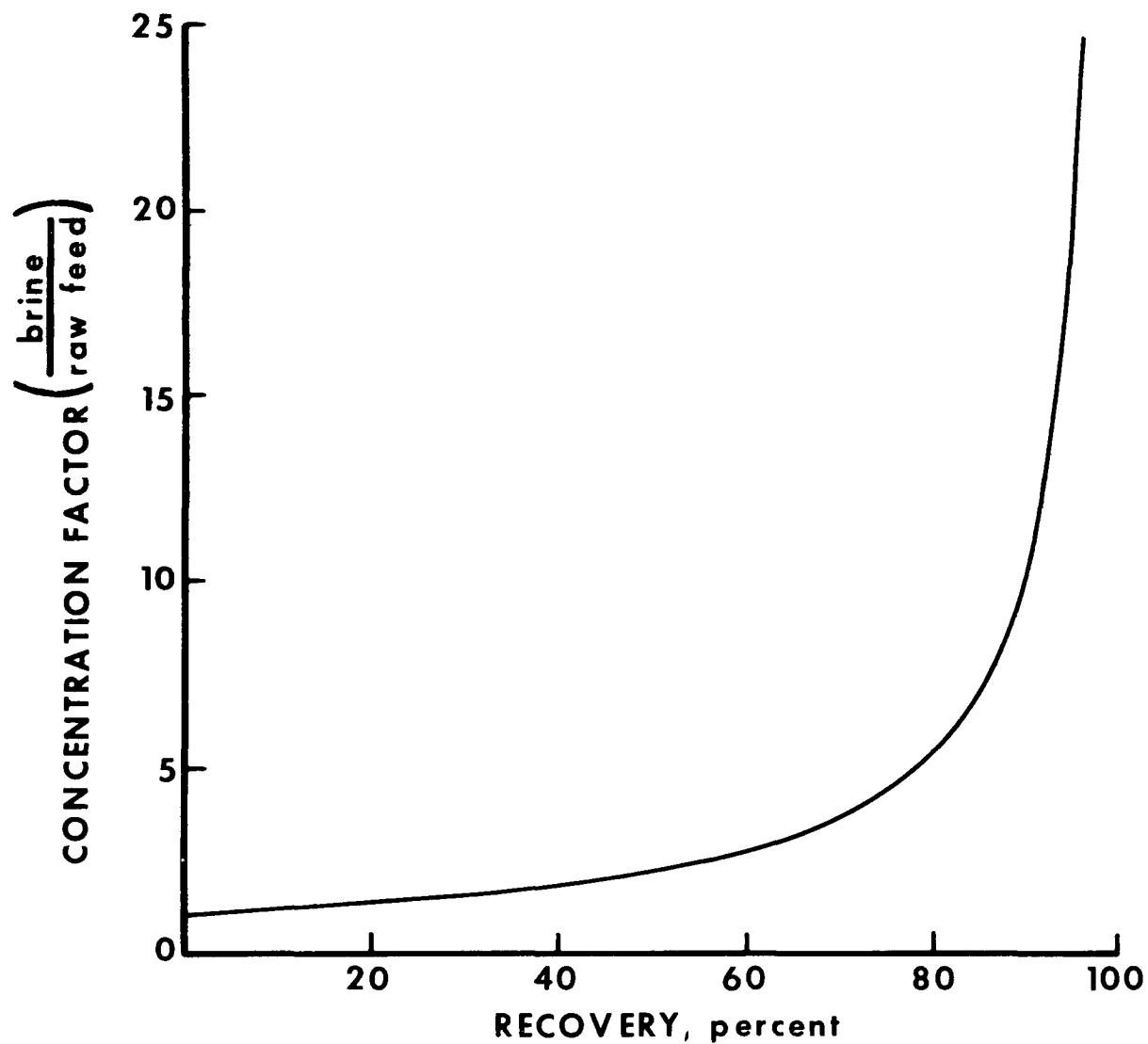


Figure 4. Effect of recovery on brine concentrations.

Salt rejection measures the ability of a membrane to reject specific ions; therefore, rejection is a measure of the efficiency of a membrane in separating pollutants from the product water by being relatively impermeable to the passage of salts. This measurement is generally made in reference to ion concentrations in the water entering the reverse osmosis unit as compared to the treated water discharged. For these studies, percent salt rejection equalled (concentration of influent - concentration of product) x 100/ concentration of influent. In the case of the hollow-fiber unit at Mocanaqua, the influent was raw acid mine drainage. For all spiral-wound studies, blended feed was the influent to the unit.

Loss in flux has been observed on RO membranes which were treating high purity water. This flux loss phenomena in pure water systems is due to compaction of the membrane and/or its porous support structure.<sup>3,14</sup> In systems free of fouling, this flux loss follows a linear log-log plot in respect to time. Under actual treatment conditions, some fouling occurs in every application and the flux trend may approximate a straight log-log line for varying lengths of time until a significant buildup of fouling occurs. At that time, an obvious deviation occurs as the flux line begins to curve downward. Also, the slopes of flux loss trends are steeper than for compaction losses alone.

The log-log slope is very important in analysis of reverse osmosis operation as it is an indicator of the severity of fouling and a rough predictor of membrane life. Figure 5 illustrates the effect of various log-log slopes upon flux in respect to time. Flux decline slopes in excess of -0.05 are felt to be intolerable.<sup>10</sup>

Therefore, membrane performance, deterioration, and fouling were evaluated by plotting observed flux values on log-log paper and calculating log-log flux decline slopes from the line of best fit. Taking values from the graph, the slope was calculated by the following equation:

$$\text{Slope} = \frac{\text{Log Flux}_2 - \text{Log Flux}_1}{\text{Log Time}_2 - \text{Log Time}_1}$$

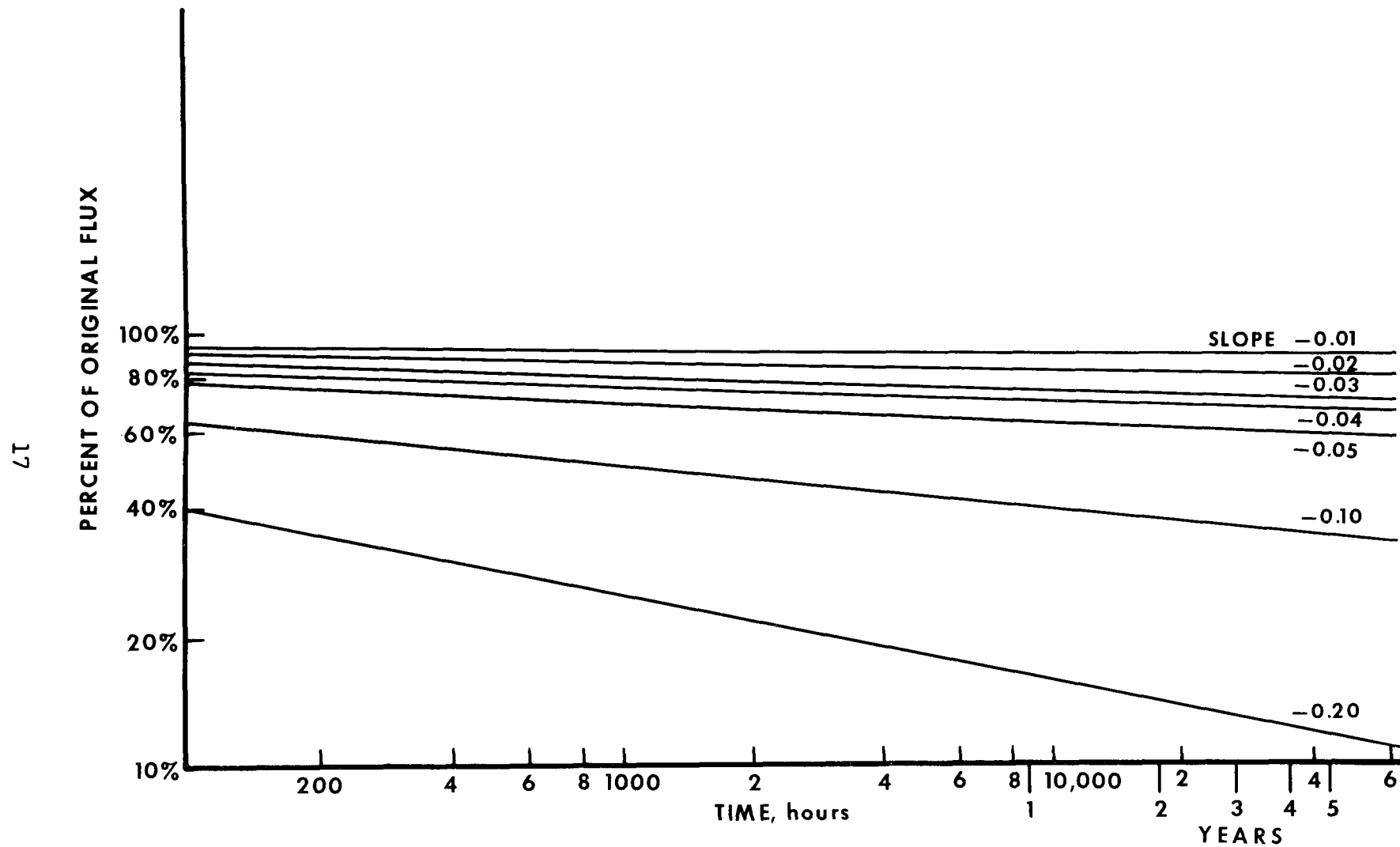


Figure 5. Effect of log-log slopes on flux (all fluxes were 100% @ 1 hour).

## SECTION V

### RESULTS

#### MAXIMUM RECOVERY STUDIES, REVERSE OSMOSIS AND NEUTROLOSIS

As previously mentioned, the main thrust of EPA's 1969 contract with Gulf Environmental Systems was toward increasing recoveries in order to produce the smallest possible volume of waste brine. These studies were conducted at EPA's Norton Mine Drainage Field Site at Norton, West Virginia.

The acid water source for these studies was Grassy Run, a surface stream of which 90 percent of the flow emanated from abandoned coal mines. Due to surface flow and biological influence, the ferrous iron was rapidly oxidized to ferric. By the time the water reached the Norton Facility, more than 90 percent of the iron was in the ferric state. As a surface flow, wide variations in temperature were observed in relatively short periods of time. In addition to the AMD, Grassy Run also contained sewage from approximately 30 residences upstream of the EPA Facility.

Typical water quality of Grassy Run during 1969 is presented in Table 1.

The 10 K spiral-wound reverse osmosis unit was used for these tests. As shown in Figure 2, sand filtration and 10 micron cartridge filtration served as pretreatment for the RO unit. Osmotic pressure was assumed to equal  $70 \text{ kN/m}^2$  (10 psi) per 1000 micromhos conductance.

Five tests were made during the high recovery stage of RO testing:

Test Number One: A 100 hour, 91 percent recovery reverse osmosis run. This test was monitored 24 hours per day.

Table 1. TYPICAL GRASSY RUN WATER QUALITY - 1969

Parameter	Units	Mean	Maximum	Minimum	Standard Deviation
pH	pH	2.8 <sup>(a)</sup>	3.1	2.4	-
Specific Conductance	Mmhos/cm	1300	1600	800	255
Acidity as CaCO <sub>3</sub>	mg/l	550	1700	300	288
Calcium	mg/l	120	170	56	30
Magnesium	mg/l	33	52	16	8.8
Aluminum	mg/l	32	50	13	9.0
Sulfate	mg/l	690	1100	350	168
Iron (Total)	mg/l	120	330	52	64
Temperature	°F	51	66	35	11
Flow	CFS	4.5	13.0	1.0	3.3

(a) Median Value.

Note: To convert from CFS to m<sup>3</sup>/s, divide by 35.314.



Test Number Two: A 96.5 hour reverse osmosis test in which the recovery was maintained at 91 percent during the day (7 hr/day) and was lowered to 85 percent during the night (17 hr/day). This test was monitored only during the normal 8 hr work day.

Test Number Three: A 29.5 hour feasibility test of the neutrolosis system. In neutrolosis, the brine was lime neutralized, the solids were removed, and the supernatant water was recycled into the feed to the reverse osmosis unit. The results of this test were previously reported<sup>11</sup> and indicated that further tests of neutrolosis should be made.

Test Number Four: A 99.6 hour neutrolosis test with the reverse osmosis unit operating at a recovery rate of 91 percent. The recovery rate of the neutrolosis system was 98.8 percent. The test was monitored around the clock.

Test Number Five: A 130.6 hour neutrolosis test with the reverse osmosis recovery rate lowered to 80 percent. The neutrolosis system recovery rate was 98.7 percent and the test was monitored continuously.

#### Test Number One (Reverse Osmosis)

This 100 hr reverse osmosis test was made at 91 percent water recovery. The operational and chemical data are given in Tables 2 and 3. Salt rejections were uniformly above 99 percent on all multi-valent ions. Figure 6 presents the history of membrane performance during the test run. Both the unit flux and the tube 5 flux values decreased with time as the run progressed due to membrane fouling. An explanation for the up and down flux variation is not available. The tube 5 fouling rate was somewhat more severe than that for the total unit as tube 5 was the last one and was subject to the highest ion concentrations. A greater risk of precipitation would be expected. Calcium sulfate precipitation appeared to be the predominant fouling mechanism as  $\text{CaSO}_4$  crystals formed in brine samples within one hour after sampling. The rate of fouling was severe

Table 2. OPERATING PARAMETERS FOR 10K NORTON RO STUDY AT 91 PERCENT RECOVERY, TEST NUMBER ONE

Parameter	Unit	Value
Raw Water Feed Flow	gpm	5.75
Product Water Flow	"	5.24
Brine Water Discharged	"	0.51
Brine Water Recycled	"	3.69
Minimum Brine/Product Flow Ratio	ratio/module	9:1
Maximum Brine/Product Flow Ratio	"	17:1
Water Recovery	percent	91.2
Recovery of Blended Feed	"	55.5
Feed Pressure	psi	600.6
Feed Temperature	°F	44
Unit Flux, gal/ft <sup>2</sup> /day @ 600 psi & 77° F		20.50
*Tube Five Flux, gal/ft <sup>2</sup> /day @ 600 psi & 77° F		19.55
Length of Run	hours	100.2
Date of Run	March 9-13, 1970	

All Values are Means from 26 Data Sets

\* Last tube in unit

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77° F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25° C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 3. CHEMISTRY ANALYSES FOR TEST NUMBER ONE

	Cond- uctance	pH	Acid- ity	Calc- ium	Magne- sium	Alum- inum	Total Iron	Sul- fates
Raw Feed	1200	2.7	630	110	33	35	110	810
Blended Feed	4200	2.2	2600	480	180	170	530	4000
Brine	9500	2.0	5900	1100	410	400	1200	9500
Product	250	3.4	115	3.0	0.7	1.1	2.8	17
Rejections <sup>(a)</sup>	94.1%	-	95.5%	99.4%	99.6%	99.4%	99.5%	99.6%

All units are mg/l except pH and conductance (Mmhos/cm)

(a) Rejection Equals  $\frac{\text{Blended Feed Concentration} - \text{Product Concentration}}{\text{Blended Feed Concentration}} \times 100.$

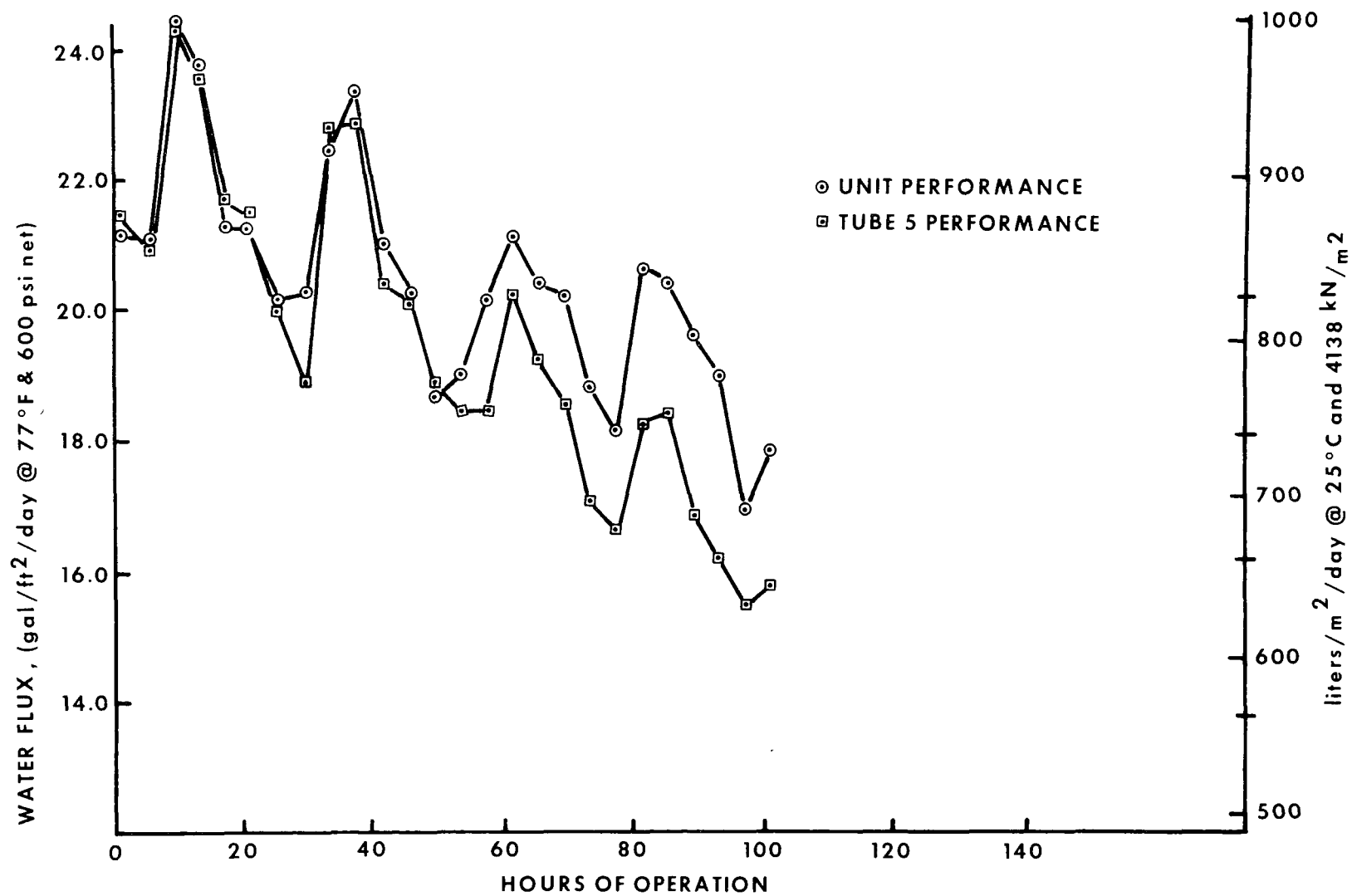


Figure Number 6

Membrane performance during R.O. Test Number One at 91 percent recovery

enough that once per week flushing would be required to maintain membrane performance. Long-term operation of this system with the incorporation of flushes appeared possible.

#### Test Number Two (Reverse Osmosis)

During this 96.5 hr reverse osmosis test run, the unit operated at 91 percent recovery during the day (7 hr/day) and was lowered to 85 percent recovery at night (17 hr/day). Table 4 presents a comparison of typical operational data at the two recovery rates.

Flux values were higher at 85 percent than at 91 percent recovery due to less fouling at the lower recovery.

In Table 5, the chemical analyses show that the salt rejections were virtually identical at both recovery rates and were comparable to the rejections of Test Number One. The concentration of pollutants in the brine at 91 percent recovery was roughly 1.2 times the respective concentrations at 85 percent recovery.

As lowering the recovery tended to reduce the fouling, a test was made to determine if the fouling mechanisms could be detected by chemical analyses and subsequent material balances. During the run, samples were taken immediately before and 30 min after lowering the recovery from 91 to 85 percent. At 91 percent recovery, the quantity of all constituents entering the unit agreed within 10 percent with the quantity leaving the unit. When the recovery was lowered to 85 percent, the mass balance indicated approximately 30 percent more of each ion (calcium, sulfate, iron, aluminum, and magnesium) was coming out of the unit than was going in. These results clearly showed that the in-unit precipitate consisted of more than calcium sulfate alone and that the precipitate could be at least partially flushed from the unit by lowering recovery and increasing brine flow.

A spectrochemical analysis of material scraped from the surface of a membrane used in another test was reported by Sleigh<sup>3</sup> to be predominately chromium (from the high pressure pump), copper (from

Table 4. OPERATING PARAMETERS FOR SPLIT RECOVERY REVERSE OSMOSIS TEST (TEST NUMBER TWO)

Parameter	91 Percent Recovery	85 Percent Recovery
Hours per Day	7	17
Raw Feed Water Flow, gpm	5.42	5.63
Product Flow, gpm	4.94	4.94
Brine Flow Tube Five, gpm	4.09	4.11
Brine Flow Discharged, gpm	0.48	0.69
Brine Flow Recycled, gpm	3.61	3.42
Water Recovery Percent	91.1	84.4
Recovery of Blended Feed, Percent	54.7	54.6
Feed Pressure, psi	600.0	602.5
Feed Temperature, °F	45°	44°
Unit Flux, gal/ft <sup>2</sup> /day @ 600 psi Net & 77° F	18.32	18.79
Tube Five Flux, gal/ft <sup>2</sup> /day @ 600 psi Net & 77° F	16.80	17.86
Length of Run, Hours	96.5	
Date of Run	March 24-27, 1970	

All Values are Means from Six Data Sets

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77° F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25° C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 5. CHEMISTRY ANALYSES - SPLIT RECOVERY 10K REVERSE OSMOSIS

	Con- ductance	pH	Acid- ity	Cal- cium	Magne- sium	Alum- inum	Total Iron	Sul- fates
				<u>90.7% Recovery</u>				
Raw feed	1100	2.8	490	100	37	31	80	820
Blended feed	3600	2.5	2000	500	190	160	380	2600
Brine	7000	2.3	4300	1050	440	360	860	8500
Product	240	3.1	40	4.0	1.0	1.0	2.0	14
Rejections <sup>(a)</sup>	93.3%	-	98.0%	99.2%	99.5%	99.4%	99.5%	99.5%
				<u>84.8% Recovery</u>				
Raw feed	1200	2.7	540	110	37	31	80	850
Blended feed	3000	2.5	1700	410	160	130	320	1800
Brine	6000	2.3	3900	890	380	290	680	7100
Product	240	3.1	37	3.2	0.7	1.0	2.0	12
Rejections <sup>(a)</sup>	92.0%	-	98.0%	99.2%	99.5%	99.2%	99.4%	99.3%

All units are mg/l except conductance (Mmhos/cm) and pH.

(a) Rejections equal  $\frac{\text{Blended Feed Concentration} - \text{Product Concentration}}{\text{Blended Feed Concentration}} \times 100.$

bronze fittings), sodium (from NaCl test solution), silicon (from pump packing), and iron. Iron was the only element that could be directly attributed to the acid mine water. This module had been thoroughly acid washed before the analysis was made, and it must be assumed that the absence of calcium and sulfur on the membrane implies that  $\text{CaSO}_4$  can be totally removed by prolonged flushing whereas iron cannot. Possibly iron deposition may prove to be the long-term threat to flux. However, calcium sulfate precipitation is the immediate threat as massive  $\text{CaSO}_4$  precipitation was observed in high recovery brine samples within one hour of sampling.

### Test Number Three (Neutrolosis)

Brine disposal from an RO system is a severe problem. Even at 91 percent recovery, 9 percent of the water treated resulted as a highly polluted liquid brine. Because of  $\text{CaSO}_4$  fouling, 91 percent was near the maximum attainable recovery under the test conditions at Norton.

Previously, the Norton Mine Drainage Field Site had conducted extensive research on neutralizing acid water and RO brine.<sup>12</sup> Originally, the plan for controlling brine was to lime neutralize the brine at 91 percent recovery and then blend the neutralized supernatant with the product water from the reverse osmosis unit, fully realizing that the neutralized supernatant would degrade the high quality product water.

The idea of "neutrolosis" was then conceived. Instead of blending the neutralized brine supernatant with the product, blend the neutralized supernatant back into the feed to the RO unit. In this manner, the only effluents from the process would be RO product of a high quality and a neutralized sludge. The major concern was that the higher pH of the neutralized supernatant would increase the pH of the blended feed to a point where ferric iron would hydrolyze and precipitate (around pH 4).



Test Number Three was an initial 30 hour feasibility test of the neutrolosis concept. As the results of this test have been previously reported,<sup>11</sup> it will suffice to mention that the reverse osmosis unit recovery was 91 percent, the brine was neutralized, and the supernatant did not raise the blended feed pH enough to cause iron precipitation and the overall neutrolosis water recovery was 98.3 percent.

The apparent success of this feasibility test showed that the neutrolosis concept had great potential and that further tests were in order.

#### Test Number Four (Neutrolosis)

The neutrolosis concept was used for this test. A complete flow diagram of neutrolosis (reverse osmosis-neutralization) is presented in Figure 7. For the neutrolosis test, brine from the RO unit passed directly into a 189 liter (50 gal) stainless steel reaction tank where lime was added. The neutralized brine then was pumped from the reactor to a 4542 liter (1200 gal) upflow settling tank. In the settling tank, the majority of the solids was removed as sludge and the supernatant was filtered and returned to the feed to the RO unit. Thus, the only effluents from the process were (1) RO product water and (2) neutralized brine sludge.

For this 99.6 hr test, the RO unit operated at 91 percent recovery. Total recovery was 99.0 percent. Table 6 presents the operational data for the test run and Table 7 presents the chemical analyses.

As in Tests One and Two, the salt rejections in Test Number Four were better than 99 percent on all multivalent ions. Lime neutralization, as seen in Table 7, removed virtually all the iron from the brine. However, pH 4.7 was not high enough to accomplish total aluminum removal and 460 mg/l of acidity remained in the supernatant. Even though calcium (lime) was added, there was a net loss in calcium and in sulfate indicating that a significant amount of calcium sulfate was removed during the neutralization process.

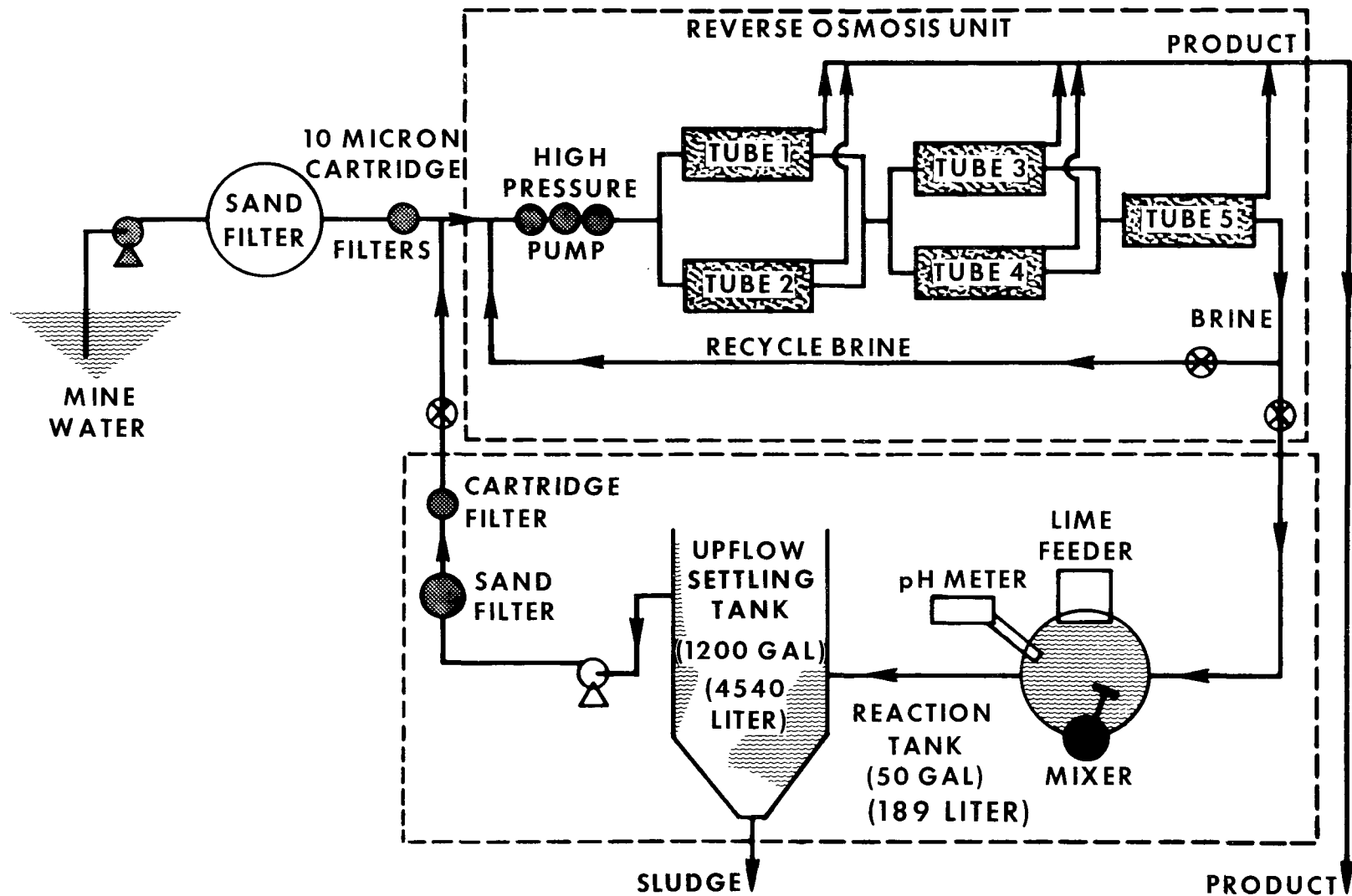


Figure 7

Flow diagram for neutrolysis tests

Table 6. OPERATING PARAMETERS\* FOR NEUTROLOSIS STUDY AT 91 PERCENT REVERSE OSMOSIS RECOVERY (TEST NUMBER FOUR).

Parameter	Unit	Value
Raw water feed flow	gpm	5.02
Product water flow	"	4.97
Brine water discharged (flow to neutralizer)	"	0.48
Brine water recycled	"	3.49
Minimum brine/product flow ratio	ratio/module	6.3:1
Maximum brine/product flow ratio	"	24:1
Neutralized brine supernatant recycled	gpm	0.43
Neutralized brine sludge discharged	"	0.05
Reverse osmosis water recovery	percent	91.2
Recovery of blended feed	"	55.6
Total system recovery - neutrolosis	"	99.0
Percent sludge (by volume of discharged brine)	"	10.4
Feed pressure	psig	602.2
Feed temperature	°F	58
Unit flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77°F		15.43
Tube five flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77°F		9.83
Length of run	hours	99.6
Date of run	May 11-15, 1970	

\*All values are means from 82 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77°F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25° C, multiply by 40.67; to convert gallons per minute to liters/minute, multiply by 3.785; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 7. CHEMISTRY ANALYSES FOR NEUTROLOSIS TEST AT 91 PERCENT RO RECOVERY  
(TEST NUMBER FOUR)

	Cond. Mmhos/cm	pH	Acid- ity	Cal- cium	Magne- sium	Alum- inum	Total Iron	Sul- fates	Alk. as CaCO <sub>3</sub>
Raw Feed	1700	2.7	660	100	38	38	120	980	0
Blended Feed	5200	2.2	2700	470	270	190	520	4700	0
Brine	10000	2.0	6000	1100	550	410	1200	11000	0
Neutralized Brine Recycled	3700	4.7	460	760	310	65	1.5	2200	1.0
Product	340	3.4	130	3.0	1.5	1.1	1.6	21	0
Rejections	93.5%		95.1%	99.4%	99.4%	99.4%	99.7%	99.6%	

R. D. Recovery at 91 Percent

All units are mg/l except conductance (Mmhos/cm) and pH

Rejection equals  $\frac{\text{Blended feed concentration} - \text{product concentration}}{\text{blended feed concentration}} \times 100.$

Comparing the product quality of this neutrolosis test with that of Test Number One, (91 percent recovery RO test, Table 3) the product qualities were virtually identical. The only effects of recycling the neutralized supernatant were seen in the blended feed concentrations. The neutrolosis blended feed had increased concentrations of magnesium and aluminum due to insufficient removal during neutralization. Previous studies<sup>12</sup> indicated both these constituents could be removed around pH 7. If the magnesium and aluminum are not removed, a long-term buildup would occur and neutralization should be taken close to pH 7 to alleviate this problem. Any ions which would not precipitate might be removed by occasionally increasing pH and "blowing down" the system.

Figure 8 illustrates membrane performance during the run. The sharp decrease in tube 5 flux in respect to the unit flux indicated severity of the fouling. Calcium sulfate precipitation was substantially worse in tube 5 than in the rest of the unit as tube 5 was subject to the heaviest concentration of pollutants.

Four low-recovery (50 percent) flushes were required during the first 90 hr of the test to remove the severe fouling. Flush number five was a 3 hr flush at low pressure ( $690 \text{ kN/m}^2$  or 100 psi) and low recovery (40 percent) using BIZ enzyme detergent. The BIZ flush was more successful in increasing flux than were low recovery acid flushes.

The severe fouling observed in Test Number Four would prohibit feasible operation under these conditions.

#### Test Number Five (Neutrolosis)

By operating the RO unit near 80 percent recovery and employing the neutrolosis concept, it was hoped that the severe fouling observed in Test Number Four (neutrolosis test at 91 percent recovery) could be reduced to tolerable levels. As lowering the RO recovery increased the volume of brine discharged, the flow of neutralized supernatant also increased and again the possibility of the supernatant increasing the blended feed pH to the point where ferric iron would precipitate was feared.

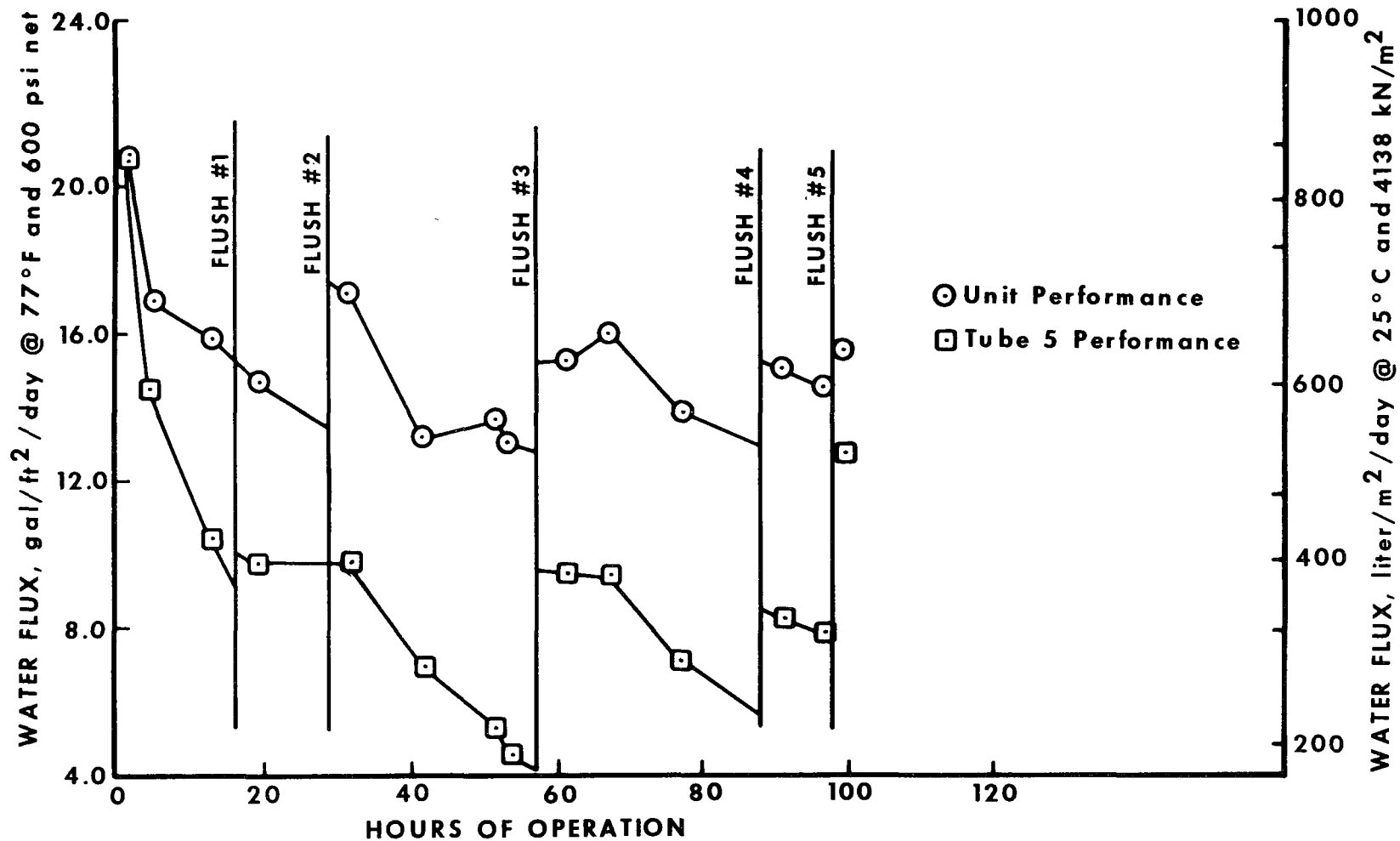


Figure 8. Membrane performance during neutrolysis test (Number Four) operating at 91 percent unit recovery and 98.8 percent system recovery.

Table 8 presents operational data for the run and Table 9 presents chemical data. The recycled neutralized brine flow was 4.731 l/m (1.25 gpm) at 80 percent RO recovery as compared to 1.628 l/m (0.43 gpm) in Test Number Four (91 percent RO recovery). However, the pH of the blended feed was still only pH 2.5, far from the danger of ferric iron precipitation.

Total recovery during this 130.6 hr test was 98.8 percent at 78 percent RO recovery as compared to 99.0 percent recovery (91 percent RO recovery) in Test Number Four. Figure 9 shows the membrane performance for the test. The rate of flux decline was significantly less at 80 percent RO recovery (Test Five) as compared to Test Four (91 percent RO recovery). Both the unit flux values and the tube 5 flux values declined at approximately equal rates during this 80 percent test, indicating the fouling was uniformly distributed throughout the unit. In the earlier tests, the tube 5 fouling rate was noticeably more severe than the unit fouling rate.

Comparing this neutrolosis test at 80 percent RO recovery with Test Number One (reverse osmosis test at 91 percent recovery - Figure 5), the fouling rates were almost identical.

As in the previous tests, salt rejections were near 99 percent on all multivalent ions.

A 2.5 hr low-recovery (50 percent) flush improved the flux rate 7 percent for the unit and 38 percent for tube 5, indicating that the majority of earlier fouling had occurred in tube 5.

Operation of this neutrolosis system at 80 percent RO recovery and 98.8 percent total recovery appeared feasible for long-term use if periodic flushes were incorporated to control fouling and sustain membrane performance.

#### Discussion of Five Maximum Recovery Tests

The chemical analyses of the blended feed (water actually entering RO unit) and brine were compared in an attempt to determine the cause of Test Four's severe fouling as compared with Tests One and Five.

Table 8. OPERATING PARAMETERS\* FOR NEUTROLOSIS STUDY @ 78 PERCENT RO RECOVERY (TEST NUMBER FIVE)

Parameter	Unit	Value
Raw Water Feed Flow	gpm	4.83
Product Water Flow	"	4.77
Brine Water Discharged (Flow to Neutralizer)	"	1.31
Brine Water Recycled	"	2.65
Minimum Brine/Product Flow Ratio	ratio/module	6:1
Maximum Brine/Product Flow Ratio	"	23:1
Neutralized Brine Supernatant Recycled	gpm	1.25
Neutralized Brine Sludge Discharged	"	0.06
Reverse Osmosis Water Recovery	percent	78.5
Recovery of Blended Feed	"	54.6
Total System Recovery-Neutrolosis	"	98.8
Percent Sludge (by Volume of Discharged Brine)	"	4.6
Feed Pressure	psig	600.0
Feed Temperature	°F	61.5
Unit Flux, gal/Ft <sup>2</sup> /day at 600 psi Net & 77" F		12.28
Tube 5 Flux       "       "       "		9.99
Length of Run	hours	130.6
Date of Run		June 3-8, 1970

\*All values are means from 34 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77° F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25° C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.



Table 9. CHEMISTRY ANALYSES FOR NEUTROLOSIS TEST AT 78% RO RECOVERY (TEST NUMBER FIVE)

	pH	Cond.	Acidity	Calcium	Magnesium	Aluminum	Total Iron	Sulfate	Alk. as CaCO <sub>3</sub>
Raw feed	2.7	1660	590	130	32	43	100	1340	0
Blended feed	2.5	3000	1150	460	120	91	210	3000	0
Brine	2.3	5600	2400	940	250	190	460	6400	0
Neutralized brine recycled	4.9	2500	180	850	130	30	7.7	3500	7
Product	3.7	210	36	2.1	0.6	1.0	1.2	18	0
Rejections <sup>(a)</sup>		92.9%	96.9%	99.5%	99.4%	98.9%	99.4%	99.4%	

All units are mg/l except conductance (Mmhos/cm) and pH.

(a) Rejection equals  $\frac{\text{Blended feed concentration} - \text{product concentration}}{\text{Blended feed concentration}} \times 100.$

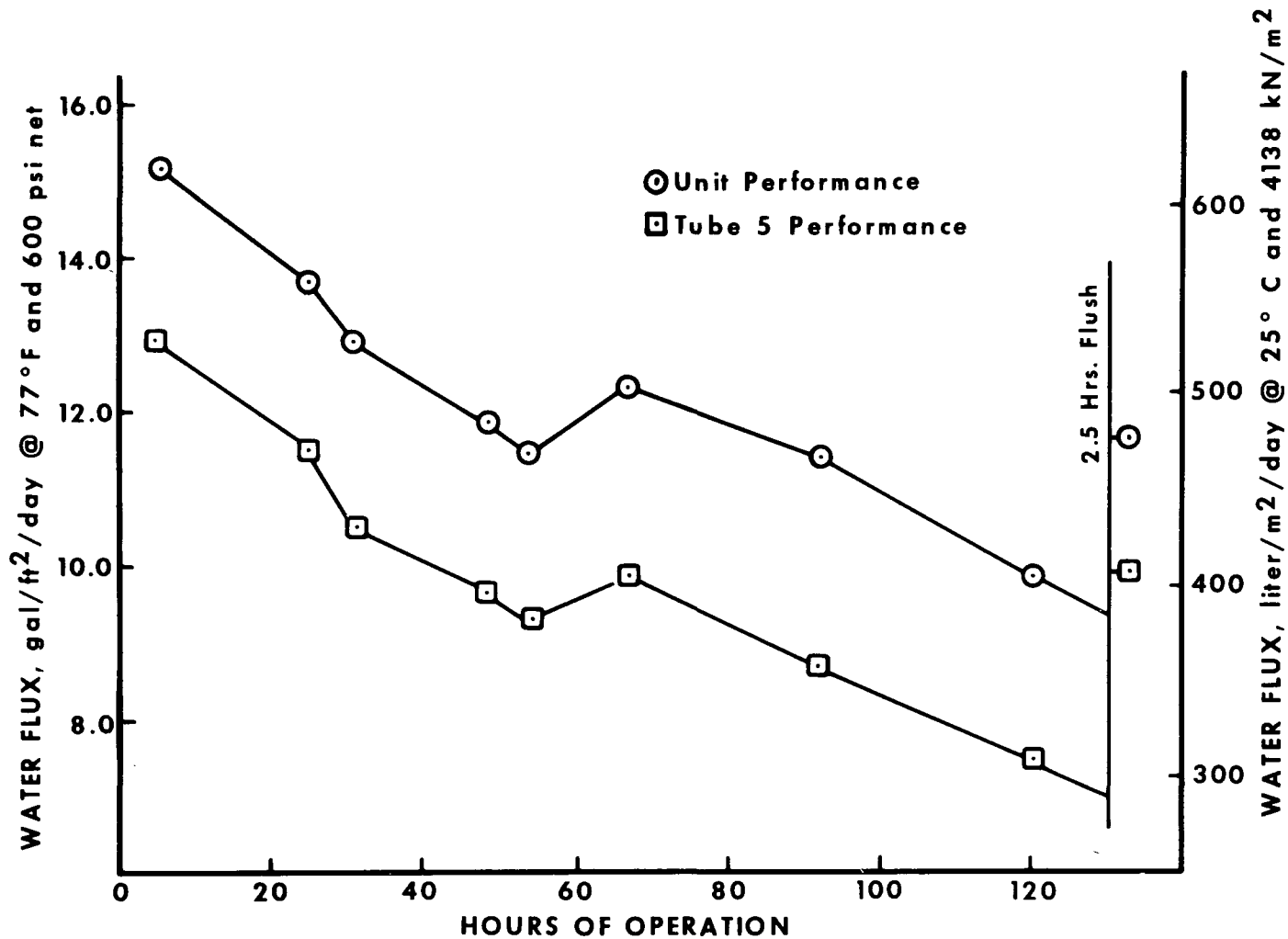


Figure 9. Membrane performance during neurolysis test (Number Five) operating at 78 percent unit recovery and 98.7 percent system recovery.

These analyses, as shown in Table 10, indicated that the water characteristics were identical between Tests One and Four, except for magnesium and sulfate concentrations which were slightly higher in Test Four, yet only Test Four fouled severely. All constituents were much lower in concentration in Test Five than in either Test Four or Test One as the reverse osmosis unit recovery was only 78 percent as compared to 91 percent on the other two tests. Still, Test Five fouled at the same rate as Test One.

The conclusions drawn from these data were that the fouling in all tests was due to precipitation, but this precipitation apparently was not directly related to chemical concentration (as the concentrations in Test Five were significantly less than Test One, yet the fouling rates were similar; and the concentrations were approximately equal in Tests Four and One, yet Test Four fouled severely). Instead, the physical properties of the recycled neutralized brine supernatant appeared to promote precipitation. Since the neutralized recycle was already above saturation for calcium sulfate, it was assumed that minute  $\text{CaSO}_4$  seed crystals existed in the recycled supernatant and these promoted precipitation in the unit.

Product water quality, as shown in Table 10, was much superior in Test Five as compared to Tests One or Four as the lower RO unit recovery (78 percent) did not concentrate the pollutants as much as the higher recovery (91 percent) runs. Since salt rejections were approximately the same in all these tests, lowering the brine concentrations improved product quality. None of the product waters were of potable quality. Further treatment with lime to increase the pH and remove the iron would be required to increase the quality to potable standards.

In conclusion, the feasibility of 91 percent recovery reverse osmosis operation under the conditions at Norton was borderline. If periodic flushing would continue to control fouling, operation would be feasible. Disposal of the 9 percent highly polluted liquid brine would still be a major problem.

Table 10. BLENDED FEED, BRINE AND PRODUCT CHEMISTRY ANALYSES FOR 10K STUDIES

Test	RO recovery	Total recovery	Cond.	pH	Acidity	Ca	Mg	Al	Total iron	Sulfate
<u>BLENDED FEED</u>										
#1 Reverse osmosis	91.2	91.2	4200	2.2	2580	480	180	170	530	4000
#4 Neutrolosis	91.2	99.0	5200	2.2	2700	470	270	190	520	4700
#5 Neutrolosis	78.5	98.8	3000	2.5	1150	460	120	91	210	3000
<u>BRINE</u>										
#1 Reverse osmosis	91.2	91.2	9540	2.0	5900	1100	410	400	1200	9500
#4 Neutrolosis	91.2	99.0	10,000	2.0	6000	1100	550	410	1200	11,000
#5 Neutrolosis	78.5	98.8	5600	2.3	2400	940	250	190	460	6400
<u>PRODUCT</u>										
#1 Reverse osmosis	91.2	91.2	250	3.4	115	3.0	0.7	1.1	2.8	17
#4 Neutrolosis	91.2	99.0	340	3.4	130	3.0	1.5	1.1	1.6	21
#5 Neutrolosis	78.5	98.8	210	3.7	36	2.1	0.6	1.0	1.2	18

All units are mg/l except for recovery (percent), conductance (Mmhos/cm), and pH.

The use of neutrolosis at 91 percent RO unit recovery produced a total recovery around 99 percent and one percent of the initial volume resulted as a dense sludge which could be landfilled. Unfortunately, the fouling rate of the RO membranes under these conditions was too severe for feasible long-term operation.

By employing the neutrolosis concept at 80 percent RO unit recovery, fouling was minimized to levels where continuous long-term operation appeared feasible. Periodic flushes should be able to control membrane fouling. Total recovery by this system was 98.7 percent. The remaining 1.3 percent of the original water resulted as sludge.

The neutrolosis concept is a significant breakthrough in RO technology. Converting 99 percent of the acid water treated into a high quality product water and the remaining one percent into a dense sludge is a dramatic result. The reverse osmosis problem of brine disposal was eliminated in the Norton application by this neutrolosis process. We see no reason why this process or modifications of it could not be used to treat most types of acid mine drainage. Ferrous iron sites may have to include aeration and higher pH neutralization to remove the iron prior to recycling. At such sites, it may be possible to inject acid to lower the pH of the neutralized brine supernatant before recycling it into the feed. Sludge dewatering devices would increase the recovery even further. Development of calcium sulfate precipitation inhibitors would reduce membrane fouling problems. In brief, neutrolosis is a very promising method for the treatment of acid mine drainage.

#### TWO-STAGE REVERSE OSMOSIS SYSTEM

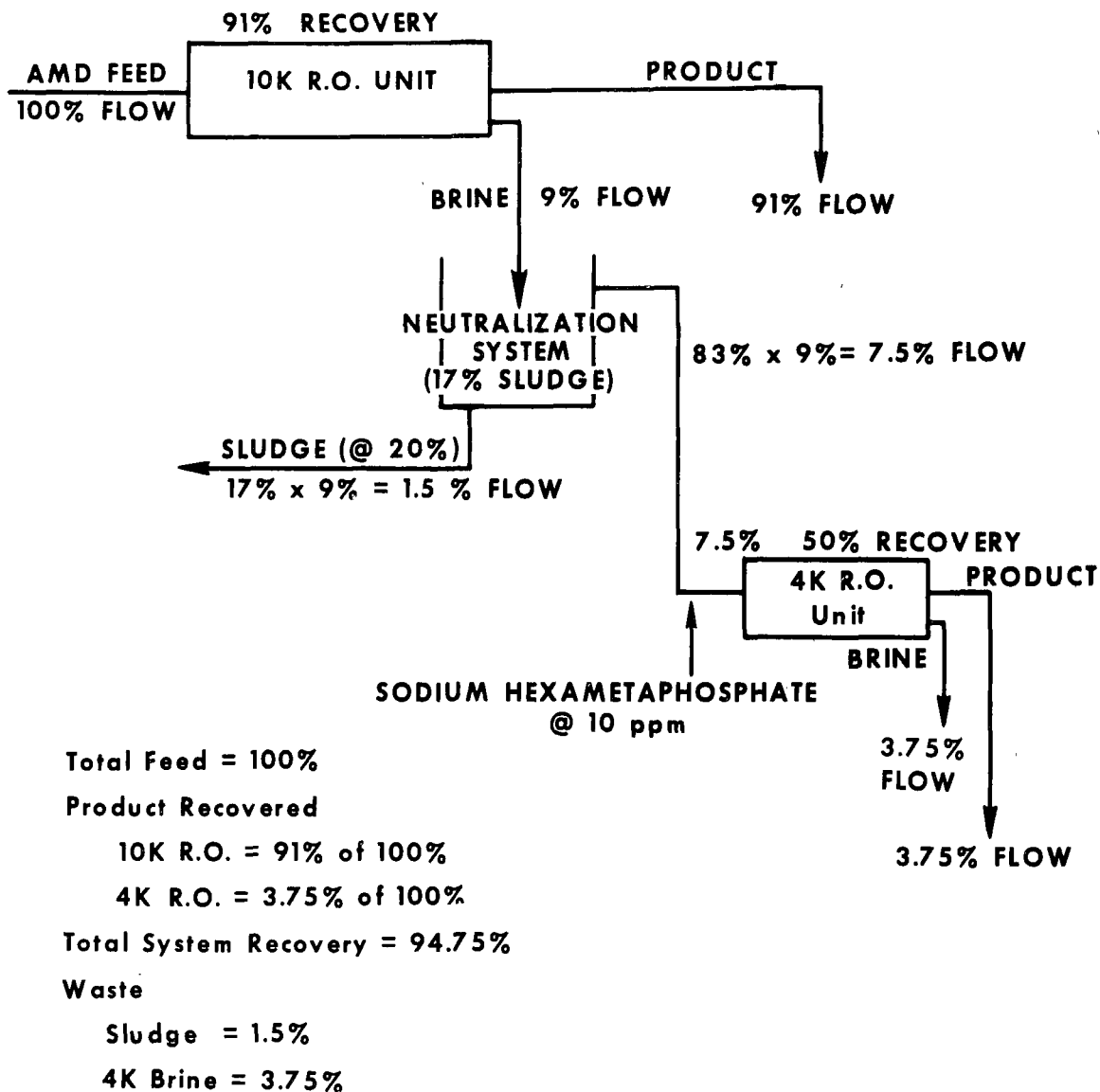
Gulf Environmental Systems had investigated several calcium sulfate precipitation inhibitors (chelating agents) which had been successfully applied to sea water desalination<sup>3</sup>. If the precipitation of  $\text{CaSO}_4$  could be delayed, then maximum recovery could be significantly increased. Unfortunately, the chelating agents tested were ineffective due to either acidic pH or high iron concentrations, or both.

In order to utilize sodium hexametaphosphate as a  $\text{CaSO}_4$  precipitation inhibitor, the water must first be neutralized. Neutralization of the entire volume of water to be treated by the reverse osmosis unit was impractical. A more feasible scheme was to operate the 10 K RO unit on raw AMD at 91 percent recovery and to neutralize the brine (9 percent of the original volume - therefore neutralization costs would be less). After settling the solids, the neutralized supernatant water would be fed into a smaller, second, RO unit in which sodium hexametaphosphate could be used as a chelating agent since the pH would be close to neutral.

To test this arrangement, a 4 K unit, which was supplied under the terms of a Gulf Environmental Systems Contract<sup>(3)</sup>, was used as the second-stage RO unit. The 4 K unit consisted of three 1.58 m x 3.05 m (4 in x 10 ft) pressure vessels arranged in a 2-1 array where the brines from tubes one and two combined to serve as the feed to tube three.

Two tests were made of the proposed process. Brine from the 10 K unit operating at 91 percent RO recovery was collected, neutralized, and stored. From the storage tank, the neutralized water was pumped into the 4 K RO unit which operated at 50 percent recovery. A schematic drawing of the process is presented in Figure 10; in Table 11 are the data for the second test of the process. Overall system recovery was 94.75 percent. As seen in Table 11, a continual decrease in product flow was observed during the 2.6 hr 4K run on brine supernatant water which had been neutralized to pH 4.8. A rapid increase in pressure loss across the unit occurred indicating immediate and severe fouling and terminating the test. Sodium hexametaphosphate was ineffective at pH 4.8 in controlling  $\text{CaSO}_4$  precipitation. As very little iron was present in the neutralized feed (Table 12), the inability of the chelating agent to perform successfully was probably the result of the acidic pH (4.8). No further tests were made at higher pH's, however.

Salt rejections during this test were unexplainably low (Table 12).



**Figure 10. Two stage RO treatment with intermediate brine neutralization.**

Table 11. OPERATING PARAMETERS FOR 50 PERCENT RECOVERY 4K RO STUDY ON NEUTRALIZED BRINE

Elapsed Time, hr	Product, gpm	Brine, gpm	Recycle, gpm	Pressure, psi	Recovery	$\Delta p^{(a)}$ System, psi	$\Delta p$ Tubes 1 & 2, psi	$\Delta p$ Tube 3, psi
0	2.19	2.90	2.50	410	37.1%			
0.1	2.19	2.63	2.50	410	45.4%			
0.1	2.19	2.19	3.00	410	50.0%			
0.2	2.17	2.17	3.00	415	50.0%			
0.2	Samples taken				50.0%	17.5	6.5	11.3
1.0	2.15	2.17	3.25	420	51.3%			
1.1	Samples taken then pressure lowered				51.3%	19.0	7.8	11.7
1.5	2.00	2.11	3.00	400	48.6%			
1.6	2.04	2.00	3.25	400	50.4%			
1.8	2.00	1.94	3.25	400	50.7%	20.3	8.5	12.2
2.1	2.00	1.95	3.25	400	50.6%			
2.3	1.96	1.92	3.25	400	50.5%	22.1	9.4	13.2
2.5	1.96	1.92	3.25	400	50.5%			
2.6	Unit shut down and flushed with $H_3PO_4$							

pH of influent = 4.8.

Temperature of water = 52° F (11° C).

Total operating time = 2 hr, 35 min.

Neutralized brine sludge volume = 17% (after 24 hours).

Total recovery (including 91% 10K recovery, 17% neutralized brine sludge, and 50% 4K recovery) = 94.75% of original feed.

Sodium hexametaphosphate injected at 10 ppm rate.

Date of run - March 20, 1970.

(a)  $\Delta p$  = Pressure drop.

To convert gpm to l/s, multiply by 0.065, and to convert from psi to  $kN/m^2$ , multiply by 6.90.



Table 12. CHEMISTRY ANALYSES FOR 50% RECOVERY 4K RO STUDY ON NEUTRALIZED 10K BRINE

Parameter	Neutralized brine (Feed to 4K unit)	Blended feed	Brine	Product	Rejections (a)
pH	4.8	4.9	4.9	4.5	--
Conductivity	3200	4000	5000	200	93.8%
Acidity	66	73	110	3.9	94.1%
Calcium	400	540	800	10	97.5%
Magnesium	170	210	300	4.0	97.7%
Iron	1.3	1.6	2.0	0.1	92.3%
Aluminum	4.5	4.8	8.0	0.3	93.3%
Sulfate	3100	4800	6000	60	98.1%

All units are mg/l except for pH and conductivity (micromhos/cm).

(a) Rejection equals  $\frac{\text{raw feed concentration} - \text{product concentration}}{\text{raw feed concentration}} \times 100$ .

## MORGANTOWN 4 K FERROUS IRON SPIRAL-WOUND STUDY

Up to this time, the RO studies had been conducted on ferric iron mine drainage. The next series of studies was conducted on ferrous iron. The first ferrous site was the acid mine discharge into Indian Creek located 10 miles south of Morgantown, West Virginia, at the Arkwright Mine of Christopher Coal Company.

The 4 K unit and support wiring were housed in a 2.4 m x 6.1 m (8 ft x 20 ft) metal building so that the entire system was portable. On-site chemical analyses (acidity, ferrous iron, pH, and conductivity) were performed in this building and the samples then acidified and returned to the Norton Laboratory for the remainder of the analyses. Dissolved oxygen (D.O.) determinations, which were made at the site, were unstable but in the 4.5 ppm range. Attempts at using a modified Winkler Method on the brine were unsuccessful because of the high ferrous iron concentration.

The flow diagram for the 4 K unit and support facilities is shown in Figure 11. Neither brine recycle or pH control was used during this study.

The 1890 liter (500 gal) holding tank was necessary as the mine water was pumped only intermittently from the borehole (on 8 minutes, off 5 minutes). Pressured sand filters and 10 micron cartridge filters were used to remove any suspended solids from the feed water before the water entered the RO unit.

Initially, tubes 1 and 2 contained standard-flux, high-selectivity modules and tube 3 contained high-flux, intermediate-selectivity modules. These modules had been in operation approximately 180 hr prior to this study. After the first test run, the modules were badly fouled and were replaced. The loading for the second test was: tube 1, new high-flux modules; tube 2, new standard-flux modules; and tube 3, used high-flux modules.

The histories of the two Morgantown tests are presented in Table 13 and the chemical analyses are reported in Table 14.

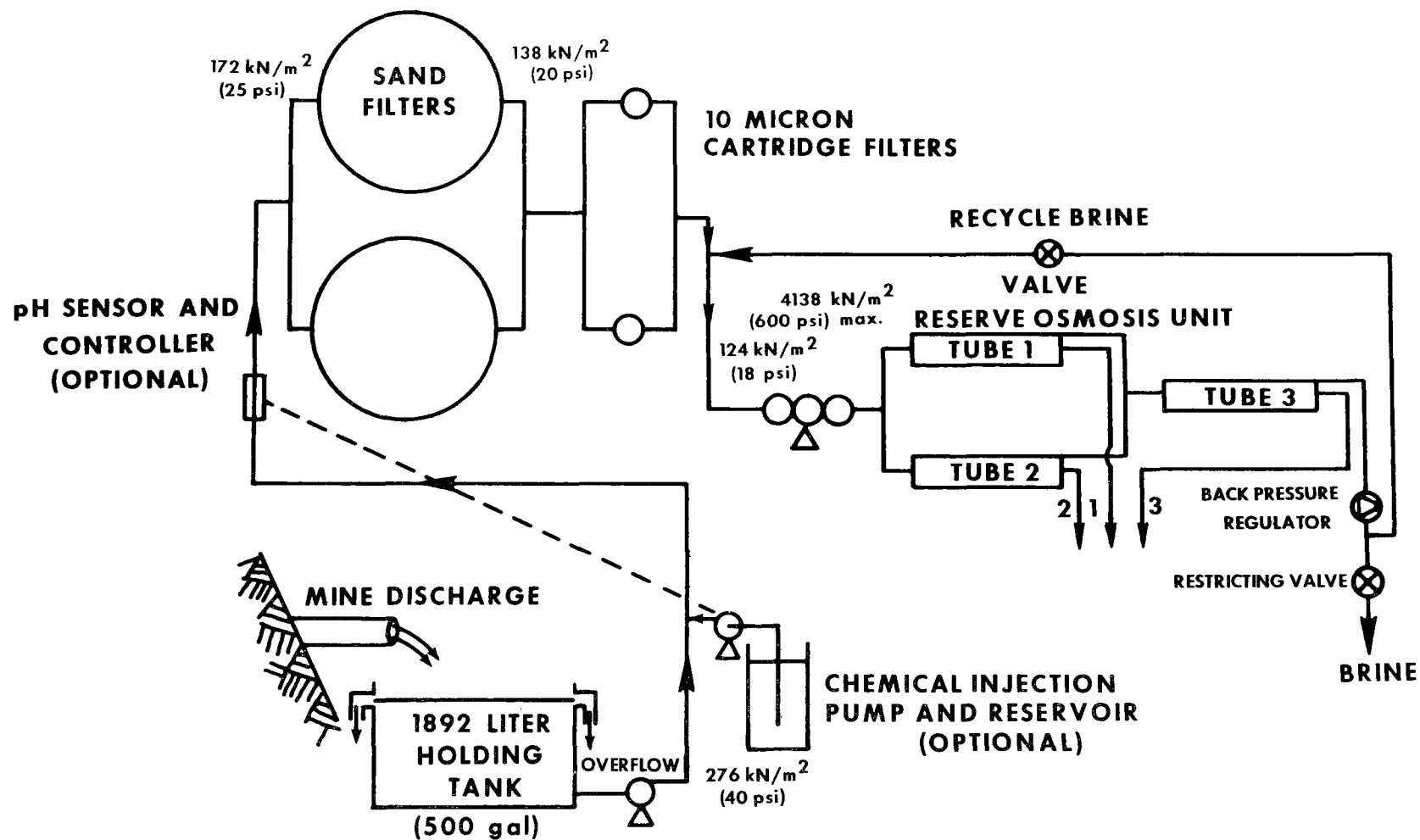


Figure 11. Flow diagram for 4K spiral-wound reverse osmosis unit.

Table 13. 4K REVERSE OSMOSIS OPERATIONAL HISTORY FOR MORGANTOWN FERROUS IRON STUDY AT THE ARKWRIGHT MINE

Date	Time, hours	Elapsed time, hours	Pressure, psi	Recovery, percent	Product flow, gpm	Brine flow, gpm	$\Delta P^{(a)}$ , psi	Temp. °F	Unit <sup>(b)</sup> flux
Run #1									
5/13/70	0	0	400	Unit started					
5/13/70	3.6	3.6	400	39.5	2.30	3.52	9.9	68	16.38
5/13/70	4.1	4.1	500	47.0	3.33	3.75	11.0	68	18.43
5/14/70	22.0	22.0	500	43.5	2.86	3.70	11.0	64	16.99
5/14/70	27.8	27.8	600	49.1	3.57	3.70	11.1	67	16.09
5/14/70	28.8	Power failure							
5/15/70	45.7	Unit shut down - no feed pressure - pump air lock							
		Modules badly fouled							
		Replacement modules installed (some used)							
5/21/70	0	0	400		2.50	4.00			
		Unit shut down for inspection of tubes 1 & 3 (high cond.)							
5/21/70	1.7	1.7	Probed tubes for leaky modules						
5/21/70	9.8	9.8	Shut down again for inspection						
		Replaced modules and O-Rings							
5/21/70	21.7	21.7	Feed pump leaking, unit flushed with acidified product water						
		Replaced pump and 3 more modules							
		Restarted unit							
Run #2									
5/22/70	22.7	0	400	41.6	2.64	3.70	10.5	68.5	19.23
5/22/70	23.8	1.1	600	52.5	3.87	3.48	-	68	17.16
5/22/70	25.0	2.3	600	51.4	3.84	3.64	11.1	68	17.05
5/23/70	40.5	17.8	600	50.0	3.45	3.46	10.3	62	17.01
5/24/70	65.2	42.5	600	47.5	3.23	3.57	11.3	64	15.36
5/24/70	69.1	46.4	600	46.7	3.13	3.57	11.2	70	13.48
5/25/70	88.8	66.1	600				12.0		
5/25/70	89.3	Begin low-pressure flush							
5/26/70	111.6	88.9	240	20.7	1.05	4.00	No change	63	14.40
	111.7	Terminate testing							

(a) Pressure drop across unit = pressure in - pressure out

(b) Flux = gal/ft<sup>2</sup>/day @ 77° F and 600 psi net

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77° F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25° C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 14. CHEMICAL ANALYSES FOR 4K REVERSE OSMOSIS STUDY AT ARK-WRIGHT FERROUS IRON SITE (UNIT RECOVERY 50 PERCENT)

Parameter	Feed	Brine	Product	Rejections*
pH	2.24	2.00	3.14	
Dissolved oxygen	4.50	4.50	-	
Conductance	7000	12,000	420	94.0%
Acidity as CaCO <sub>3</sub>	5200	10,000	150	97.1%
Calcium	530	930	9.6	98.2%
Magnesium	420	810	7.6	98.2%
Aluminum	320	600	5.0	98.4%
Sulfate	10,900	20,500	190	98.3%
Iron (Ferrous)	1300	2450	29	97.8%
Iron (Total)	2300	4460	39	98.3%
% Ferrous	56.5%	54.9%	74.4%	

\*Rejection =  $\frac{\text{Feed concentration} - \text{product concentration}}{\text{Feed concentration}} \times 100.$

All units are mg/l except for conductance (micromhos) and pH.

The first run, lasting 45.7 hr, was begun at low pressure and 40 percent water recovery. The recovery was gradually increased by raising the pressure until 50 percent recovery was established. Unfortunately, data were available for only the first 27.8 hr of operation. The differential pressure, which indicates rapid fouling, increased initially but levelled off after four hours of operation. However, performance of the membrane, as illustrated by the water flux rate, showed a definite decreasing trend as shown in Table 15.

The second test was begun at 50 percent water recovery and lasted 66.1 hours, but data were available for only the first 46.4 hr. At the end of 66.1 hr, the unit was badly fouled by precipitation which occurred when a brass valve corroded and diminished the water supply to the unit, thus the unit was receiving only recirculated brine. As shown in Table 15, the water flux decreased 21 percent in 46.4 hr of operation. The flux value for tube 3 (where the precipitation problems are most acute due to the higher concentration of ions) decreased only 19 percent. A 35 percent flux loss occurred in tube 1, 5 percent in tube 2, and 19 percent in tube 3. The high flux decrease in tube 1 (loaded with new high-flux modules) was difficult to explain, especially since tube 2 was in parallel to tube 1 and was subject to the same conditions. After termination of the test run, an explanation for the tube 1 flux loss was found. The brine seal on the last module of the tube had failed and allowed water to bypass the module. The module produced progressively less water until it became severely fouled by precipitates.

If results from tube 1 are ignored and flux declines between tubes 2 and 3 are compared, the decrease appears to be a concentration related phenomena, as a much greater decrease was observed in tube 3 where the concentration was the greatest.

There was no significant increase in the differential pressure for the unit or for the individual tubes. This indicated that the rate of fouling was not too severe to prohibit short-term operation

Table 15. FLUX\* AND  $\Delta P$  VALUES FOR ARKWRIGHT FERROUS IRON STUDY

Run No.	Elapsed Time	Tube 1 Flux	Tube 2 Flux	Tube 3 Flux	Unit Flux
1	3.6	14.58	14.58	20.29	16.38
	22.0	14.75	15.31	24.94	16.99
	27.8	13.55	14.23	19.52	16.09
DIFFERENT MODULES					
2	2.3	19.20	14.00	19.03	17.05
	17.8	16.04	15.24	20.48	17.01
	42.5	14.00	14.57	16.27	15.36
	46.4	12.53	13.32	15.33	13.48

		Tubes 1 & 2 $\Delta P$ (psi)	Tube 3 $\Delta P$ (psi)	Unit $\Delta P$ (psi)
1	3.6	3.4	6.7	9.9
	22.0	4.0	7.2	11.0
	27.8	4.3	7.1	11.1
2	2.3	4.0	7.5	11.1
	17.8	3.5	7.0	10.3
	42.5	3.5	8.0	11.3
	46.4	3.5	8.0	11.2

\*Flux = gal/ft<sup>2</sup>/day at 77°F and 600 psi. Since the osmotic pressure of this water was unknown and recovery was relatively constant, osmotic pressure was ignored for these calculations.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77° F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25° C, multiply by 40.67; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

on this water at the 50 percent recovery level. Rejections of the various ions by the membranes were relatively high (98 percent on all multivalent ions). Rejection of ferrous iron was somewhat lower than the rejection of ferric iron as trivalent ions are better rejected than are divalent ions. Maximum brine/product (b/p) flow ratios during the study were near 9.4:1. Minimum b/p ratios were 5.1:1.

#### Discussion of Morgantown Study

Chemical composition of the feed water at the Arkwright Site was similar to that of the 91 percent recovery brine from the RO unit at the Norton Site (Table 3). Attempts to further treat the brine from the Norton test by RO had revealed that calcium sulfate fouling occurred at 50 percent recovery. Therefore, it was not surprising that 50 percent recovery was the maximum attainable at Arkwright.

The two test runs, though short-lived, were terminated by equipment and facility problems, rather than module or membrane failure. However, membrane fouling was evident. Fifty percent recovery was about the maximum recovery possible before  $\text{CaSO}_4$  deposition began to rapidly foul the membranes.

Effects of fouling were easily seen during the study by the decrease in flux values for the membranes. Unfortunately, the exact cause of fouling was difficult to determine. All evidence pointed to calcium sulfate deposition, but the role of ferrous iron could not be determined.

During the study, a sample of brine at 50 percent recovery was collected and a precipitate formed within an hour. Analysis of the precipitate<sup>(3)</sup> (Table 16) indicated the composition to be virtually  $\text{CaSO}_4$ . Trace amounts of iron were present.

A sample of the precipitate that lined the pressure vessel was analyzed (Table 17). The composition of the in-unit precipitate was similar to the external brine precipitate (Table 16).



Table 16. CHEMICAL ANALYSIS OF ARKWRIGHT STUDY BRINE PRECIPITATE

	<u>Percent</u>
CO <sub>3</sub>	0.5
Fe	0.7
Mg	0.5
SO <sub>4</sub> <sup>(a)</sup>	63.0
Ca <sup>(a)</sup>	25.0
Al	0.3
Clay and silica	1.5
Other	8.5
	<u>100.0</u>

(a) Present in stoichiometric amounts found in CaSO<sub>4</sub>.

Sample: 5/23/70, 50 percent recovery.

Data from reference 3.

Table 17. CHEMICAL ANALYSIS OF SOLIDS IN ARKWRIGHT STUDY UNIT AFTER SHUTDOWN<sup>3</sup>

	<u>Percent</u>
CO <sub>3</sub>	1.
Fe	0.3
Mg	1.6
SO <sub>4</sub>	60.8
Ca	21.7

Date: 5/17/70, tube 3 pressure vessel.

The majority of the precipitation in the unit occurred during the last few hours before the runs were terminated. In both test runs, mechanical problems caused the recovery to soar to undetermined levels (probably greater than 90 percent) before the unit shut down and thus the brine was very concentrated and precipitation occurred. As calcium sulfate is the first salt to exceed solubility, it was expected that the precipitate would be largely calcium sulfate. The results in Table 17 confirm this conclusion.

However, this predominance of  $\text{CaSO}_4$  deposition may not be representative of what occurred during successful operation. The possibility of ferrous iron fouling cannot be ruled out nor can it be substantiated by these results.

Contrasting the salt rejections at Arkwright with those at Norton, the rejections at Norton were slightly higher in most cases. This difference in rejection rates was due to the high ionic concentration at Arkwright whose higher osmotic pressure resulted in less product flow while the salt flow remained essentially the same. This conclusion was valid since osmotic pressure is directly related to ionic concentrations and increases in ionic concentrations elevate osmotic pressure.

In conclusion, it does not appear that RO would be a feasible method for treatment of water of this quality based upon the problem of membrane fouling which severely limited recovery (50 percent) resulting in disposal of an equal volume of brine for each gallon of water reclaimed.

#### EBENSBURG 4 K FERROUS IRON SPIRAL-WOUND STUDY

A ferrous iron test site with concentrations more typical of AMD commonly encountered was located near Ebensburg, Pennsylvania, at the 32-33 discharge of Bethlehem Mines Corporation Cambria Division. The 4 K spiral-wound test system was installed there in July 1970. The study included tests to determine if iron fouling could be controlled by pH adjustment, i.e., the lower the pH, the less likelihood of iron precipitation.

A new, improved version of Gulf Environmental System's standard flux, high-selectivity module was used in this Ebensburg study. In these modules, the membrane was cast directly upon the backing material and the old glue joints were eliminated. The glue joints may have contributed to small "leakage" problems in the past and the manufacturer felt that their elimination should insure high rejection rates.

The system flow arrangement was the same as that at Arkwright (Figure 11) except for acid injection which was used during this study. Osmotic pressure was assumed to equal 10 psi per 1,000 micromhos of conductance. Water quality of the Ebensburg site was similar to that at Norton (except for ferrous iron).

Four tests were made during this study. These were:

Test Number One: A 191 hour, 80-85 percent recovery, recycle brine run utilizing injection of sulfuric acid into the feed water to lower the pH from pH 3.6 to pH 2.5. Acid injection was used since it was feared that ferric iron might precipitate at pH 3.6. The amount of acid injected was gradually diminished toward the end of the test. The last module in tube 3 was removed at the end of the test and returned to Gulf Environmental Systems for post mortem analysis.

Test Number Two: An 86 hr, 80-85 percent recovery, recycle brine run with no pH control of the feed (i.e., no acid injection).

Test Number Three: An 18 hr, 80-85 percent recovery, recycle brine run utilizing injection of sodium hydroxide to increase the pH of the blended feed (blended feed = raw feed plus recycled brine; blended feed is the water actually entering the RO unit) to pH 3.6. The purpose of this test was to simulate the raw water pH to determine if ferric iron precipitation would occur in a unit with no brine recycle.

Test Number Four: A 94 hr, 50-55 percent recovery run without brine recycle and no pH control. A new module had been installed in tube 3 at the start of this run. After the test, the module was re-

moved and returned to Gulf Environmental System for post mortem analysis. This test investigated the fouling rate at lower recoveries.

### Test Number One

As the pH of the AMD at Ebensburg was 3.6, the possibility of ferric iron precipitation was feared. Sulfuric acid was, therefore, injected automatically into the water before it entered the RO unit in order to lower the pH to 2.5. The test run lasted 191 hr and the amount of acid injected was gradually diminished toward the end of the run. The recovery during the test was maintained near 84 percent by recycling a portion of the brine into the feed to the unit.

As tube 3 was subject to the most polluted water, it was more prone to fouling than tubes 1 and 2. As shown in Figure 12, the pressure drop ( $\Delta P$ ) across tube 3 after 100 hr of operation had increased significantly, thus indicating membrane fouling. The recovery was then reduced for three hours in an effort to remove the fouling. The flush was successful in restoring the  $\Delta P$  across tube 3 to normal values. Significantly, the  $\Delta P$  across tubes 1 and 2 decreased during the run while tube 3 increased, indicating that the fouling was a concentration-related phenomenon.

The flux history of the run is shown on a linear basis in Figure 13. Very little fouling was observed in tubes 1 or 2 as their log-log slopes were -0.043. An excessive flux decline was observed in tube 3. A rapid change in log-log slope for tube 3 occurred after approximately 40 hr of operation on the Ebensburg water.

It is felt that the tube 3 flux loss was due to calcium sulfate fouling. Although acid injection was diminished as the run progressed, very little change occurred in the tube 3 pH as shown in Table 18. Thus, the decrease in acid injection probably had no significant effect on tube 3 behavior.

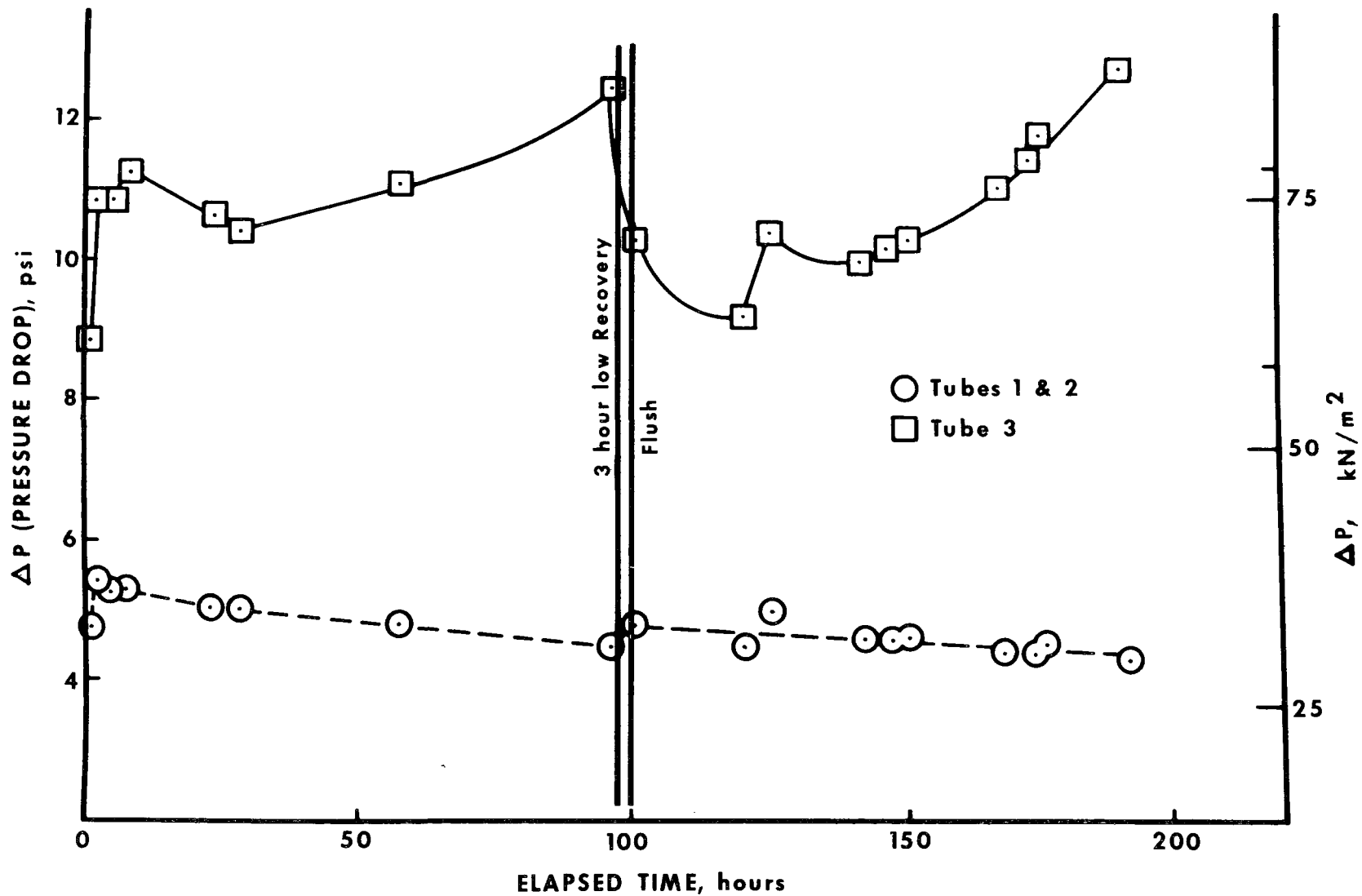


Figure 12. ( $\Delta P$ ) Pressure drop across tubes during Test Number One.

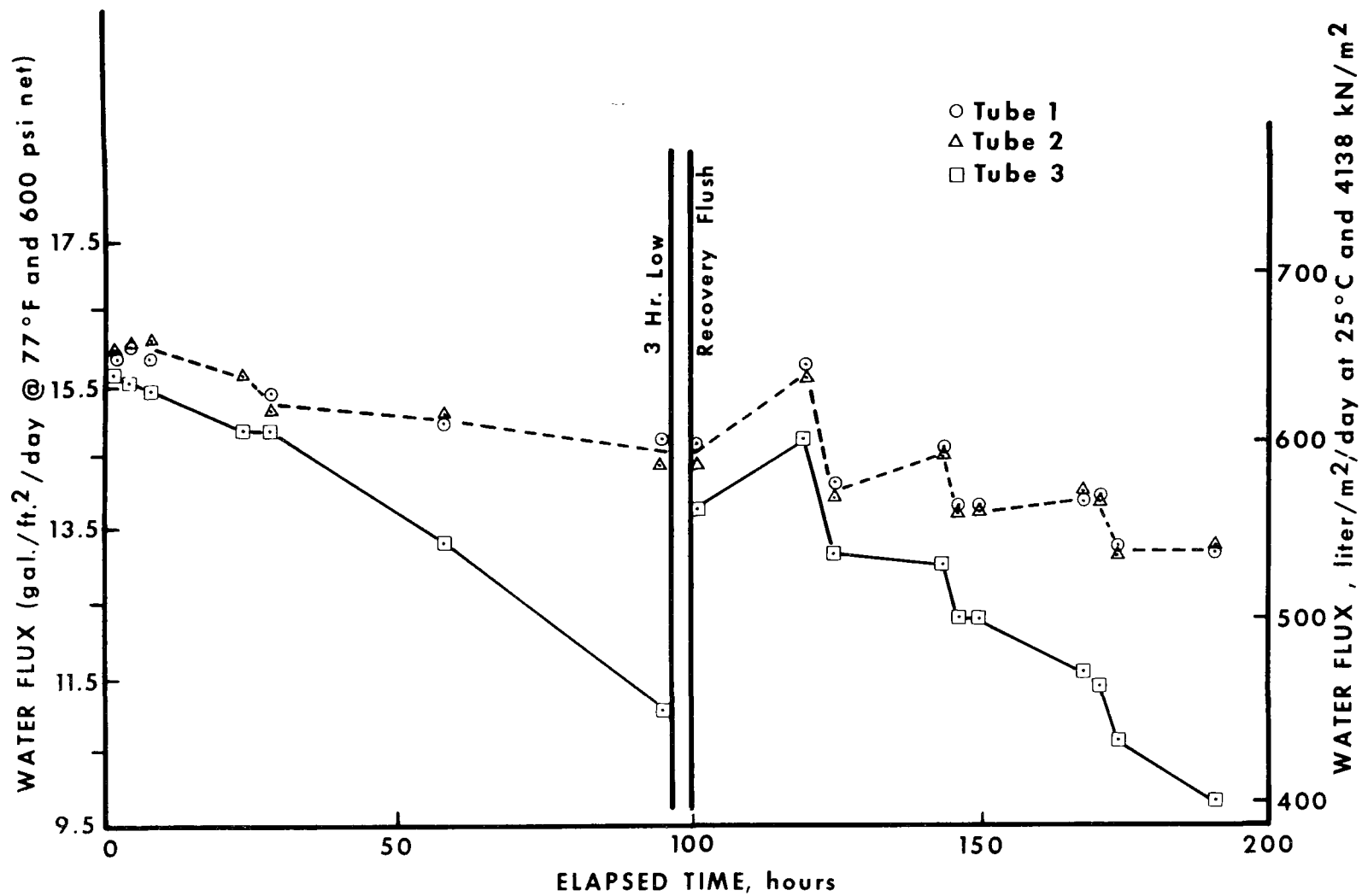


Figure 13. Membrane performance during Ebensburg test at 84 percent recovery.

Table 18. BLENDED FEED AND BRINE pH'S AT EBENSBURG

Elapsed time, hr	Blended feed pH	Elapsed time, hr	Brine pH (tube 3)
0-28	2.7	0-100	2.3
28-57	2.75	100-191	2.6
57-96	2.8		
96-100	3.2		
100-191	3.1		

On the log-log graph, there appeared to be a slight tendency for the tube 1 flux values to tail off from the linear log-log slope of -0.043 between hours 100 and 191. Unfortunately, the run did not continue long enough to substantiate this suspicion. If some fouling were occurring in tubes 1 and 2 during that time period, it would likely have been due to iron precipitation as the pH (Table 18) had increased to 3.1 during that portion of the test.

A module was removed from the downstream end of tube 3 at the end of the test and returned to Gulf Environmental Systems for post mortem analysis. Sleigh<sup>3</sup> reported the presence of a white flaky precipitate in the module:

"Analyses of this material showed it to be 23.7 percent calcium, 55.1 percent sulfate, and 22.6 percent loss of weight at 600° C. The theoretical amount of  $\text{CaSO}_4$  in gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is 79.1 percent; therefore, this material was almost pure gypsum. The precipitate could easily be washed from the membrane which is what takes place in the unit when the recovery level is lowered."

No tests were made to determine the presence of iron.

Table 19 presents the physical data for the test run and Table 20 shows the chemical analyses. Salt rejections were uniformly greater than 99 percent on all multivalent ions.

Table 19. OPERATING PARAMETERS FOR TEST NUMBER ONE AT EBENSBURG, PENNSYLVANIA

Average recovery, percent	83.6 Avg.	85.7 Max.	81.2 Min.
Average feed rate, gpm		3.57	
Average brine flow rate, gpm		0.59	
Average recycle brine flow rate, gpm		3.79	
Average temperature, °F	63.6 Avg.	67.5 Max.	59.0 Min.
Average feed pressure, psi		399.2	
Average product flow rate, gpm		2.98	
Normalized to 50°F, gpm		2.32	
Normalized to 77°F, gpm		3.72	
Average flux rate, gal/ft <sup>2</sup> /day @ 50°F and 400 psi net		7.44	
Average flux rate, gal/ft <sup>2</sup> /day @ 77°F and 400 psi net		11.90	
Maximum brine/product flow ratio		19.6:1	
Minimum brine/product flow ratio		7.5:1	
Dates of test	: July 30 - August 7, 1970		
Length of run	: 191 hours		
Number of shutdowns:	0		

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25° C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.



Table 20. CHEMISTRY ANALYSES FOR TEST NUMBER ONE WHERE AVERAGE RECOVERY = 83.6%

	Raw feed	Acidified feed	Blended feed	Brine	Product	Rejections*
pH	3.6	3.0	2.7	2.5	4.1	
Conductivity	1500	1825	5100	6900	92	98.2%
Acidity	380	450	1270	2360	56	95.6%
Calcium as Ca	190	190	600	920	1.2	99.8%
Magnesium as Mg	54	54	190	340	0.4	99.8%
Aluminum	32	32	100	180	0.9	99.1%
Total iron	135	135	430	730	1.7	99.6%
Ferrous iron	100	100	310	540	<2	99.4%
Sulfates	1640	1620	5100	9300	14	99.7%
Dissolved oxygen	2.0	-	-	2.0	2.0	-

All units are mg/l except for conductivity (Mmhos/cm) and pH.

\*Rejection equals  $\frac{\text{Blended feed concentration} - \text{product concentration}}{\text{Blended feed concentration}} \times 100.$

## Test Number Two

The injection of sulfuric acid to control the influent pH was not used in this test as it was observed that, at 80-85 percent recovery, the recycled brine lowered the pH of the resulting "blended feed" from pH 3.6 to pH 3.1.

This test was plagued with shutdowns. In a total run time of 86.3 hr, the longest continuous run was 22.5 hr and the longest continuous period of data available was for only 17.3 hr. The shutdowns were all caused by pump problems.

Table 21 shows the flux and  $\Delta P$  value for Test Number Two.

Each accidental shutdown acted as a flux rejuvenator. Planned full pressure shutdowns have long been used at Norton to dislodge precipitates and restore membrane performance. In essence, each of these accidental shutdowns served to clean and relax the membrane.

Considering the data between shutdowns as individual runs, the flux values in most cases decreased as the run progressed. As in Test Number One, the flux decline in tube 3 was significantly greater than the decline in tubes 1 or 2.

The  $\Delta P$  value over the entire test run did not change appreciably for tubes 1 and 2 but did show a continuous increase across tube 3. This was analagous to the results of Test Number One.

Flux rates for tubes 1 and 2 were greater at the end of the test than at the beginning. The tube 3 flux decreased 9.2 percent over the entire run.

Overall, there was significantly less fouling in Test Number Two than in Test Number One, due to the shutdowns which acted as precipitation removers.

The physical data for Test Number Two are shown in Table 22 and the chemical analyses are given in Table 23. As in Test Number One, the salt rejections of all multivalent ions were greater than 99 percent.

Table 21. FLUX AND  $\Delta P$  VALUES FOR EBENSBURG TEST NUMBER TWO

Elapsed Time (Hours)	Flux Tube 1	Flux Tube 2	Flux Tube 3	$\Delta P$ Tubes 1&2 (psi)	$\Delta P$ Tube 3 (psi)
0.7	14.95	14.92	15.25	4.75	8.70
2.8	14.73	14.70	15.02	4.70	8.75
5.9	14.50	14.58	15.02	4.75	8.80
22.5	-----Shutdown - Pump Failed				
22.9	15.53	15.40	15.63	4.75	8.90
24.7	14.74	14.71	14.91	4.75	8.90
27.8	14.62	14.71	14.68	4.75	8.90
45.0	-----Shutdown - Pump Failed				
46.5	15.47	15.32	15.44	4.75	8.90
48.5	14.56	14.41	14.15	4.75	8.90
51.0	14.28	14.24	13.84	4.75	8.90
62.5	-----Shutdown - Pump Failed				
63.5	15.35	15.32	14.53	4.70	8.90
66.0	14.98	14.95	14.23	4.70	9.10
68.5	14.31	14.28	13.18	4.70	9.20
69.0	-----Shutdown - Pump Failed				
70.4	15.32	15.19	14.37	4.70	9.2
72.5	14.95	14.82	13.74	4.70	9.3
86.3	15.59	15.35	13.85	4.70	9.8
	-----End Test				

Note: Flux expressed as gal/ft<sup>2</sup>/day @ 77°F and 400 psi net. To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77° F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25° C, multiply by 40.67 and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 22. OPERATING PARAMETERS FOR TEST NUMBER TWO AT EBENSBURG, PENNSYLVANIA

Average recovery, percent	84.0 Avg.	84.5 Max.	82.8 Min.
Average feed rate, gpm		3.81	
Average brine flow rate, gpm		0.61	
Average recycle brine flow rate, gpm		3.29	
Average temperature, °F	63.3	60.0 Min.	68.0 Max.
Average feed pressure, psi		400	
Average product flow rate, gpm		3.20	
Normalized to 50°F		2.42	
Normalized to 77°F		3.87	
Average flux rate, gal/ft <sup>2</sup> /day @ 50°F and 400 psi net		7.74	
Average flux rate, gal/ft <sup>2</sup> /day @ 77°F and 400 psi net		12.38	
Maximum brine/product flow ratio		13.4:1	
Minimum brine/product flow ratio		6.8:1	
Dates of test	: August 17-21, 1970		
Length of run	: 86.3 hours		
Number of shutdowns	: 4		

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 23. CHEMISTRY ANALYSES FOR TEST NUMBER TWO WHERE AVERAGE RECOVERY = 84.0%

	Raw feed	Blended feed	Brine	Product	Rejections <sup>(a)</sup>
pH	3.6	3.1	3.0	4.6	
Conductivity	1470	4000	6800	85	97.9%
Acidity	385	1160	2150	58	95.0%
Calcium as Ca	210	650	1200	1.8	99.7%
Magnesium as Mg	63	200	390	1.1	99.4%
Aluminum	37	110	220	1.1	99.0%
Total iron	150	460	870	1.9	99.6%
Ferrous iron	98	280	550	<2	99.3%
Sulfates	1700	5200	10,000	23	99.6%
Dissolved oxygen	2.0	-	2.0	2.0	-

All units are mg/l except for conductivity (Mmhos/cm) and pH.

(a) Rejection equals  $\frac{\text{Blended feed concentration} - \text{product concentration}}{\text{Blended feed concentration}} \times 100$ .

### Test Number Three

Without brine recycle or acid injection, the RO unit would have to treat pH 3.6 AMD at this site. It was the intent of Test Number Three to simulate pH 3.6 influent conditions to the 4 K unit by injecting sodium hydroxide to increase the pH of the blended feed.

The point of injection was highly critical in this application. Referring to Figure 10, if the NaOH were injected into the blended feed, and overtreatment occurred, the ferric iron would precipitate directly in the RO unit. To protect the RO unit, the NaOH was injected into the raw feed prior to the sand filters. As the recycled brine lowered the blended feed pH from pH 3.6 to pH 3.1, the NaOH increased the raw feed pH to counteract the effect of the recycled brine. This meant the raw feed must be increased to approximately pH 3.9 to obtain the desired result. At pH 3.9, however, the ferric iron rapidly precipitated in the sand filter. The clogged sand filter prevented water flow to the unit so the test was discontinued. The collected data were not sufficient to establish any definite trends.

### Test Number Four

By eliminating brine recycle, the pH conditions which Test Number Three was trying to produce were achieved. With no recycled brine, the raw AMD was fed directly into the RO unit at pH 3.6. Unfortunately, without the use of brine recycling, the small 4 K unit was limited to approximately 55 percent recovery.

Figure 14 shows the  $\Delta P$  and flux history for the 94 hr, 50-55 percent recovery test. The  $\Delta P$  remained constant throughout the test run. Flux values, though somewhat erratic, were identical for tubes 1, 2, and 3. Flux history (Figure 14) did not indicate fouling in any of the tubes. This was quite different from the readily apparent fouling seen in Tests Number One and Two. Peaks in the flux value graph all occurred during periods of lowest water temperature which indicate some discrepancies may exist between the manufacturer's temperature-flux normalization curve and the behavior of the Ebensburg water.

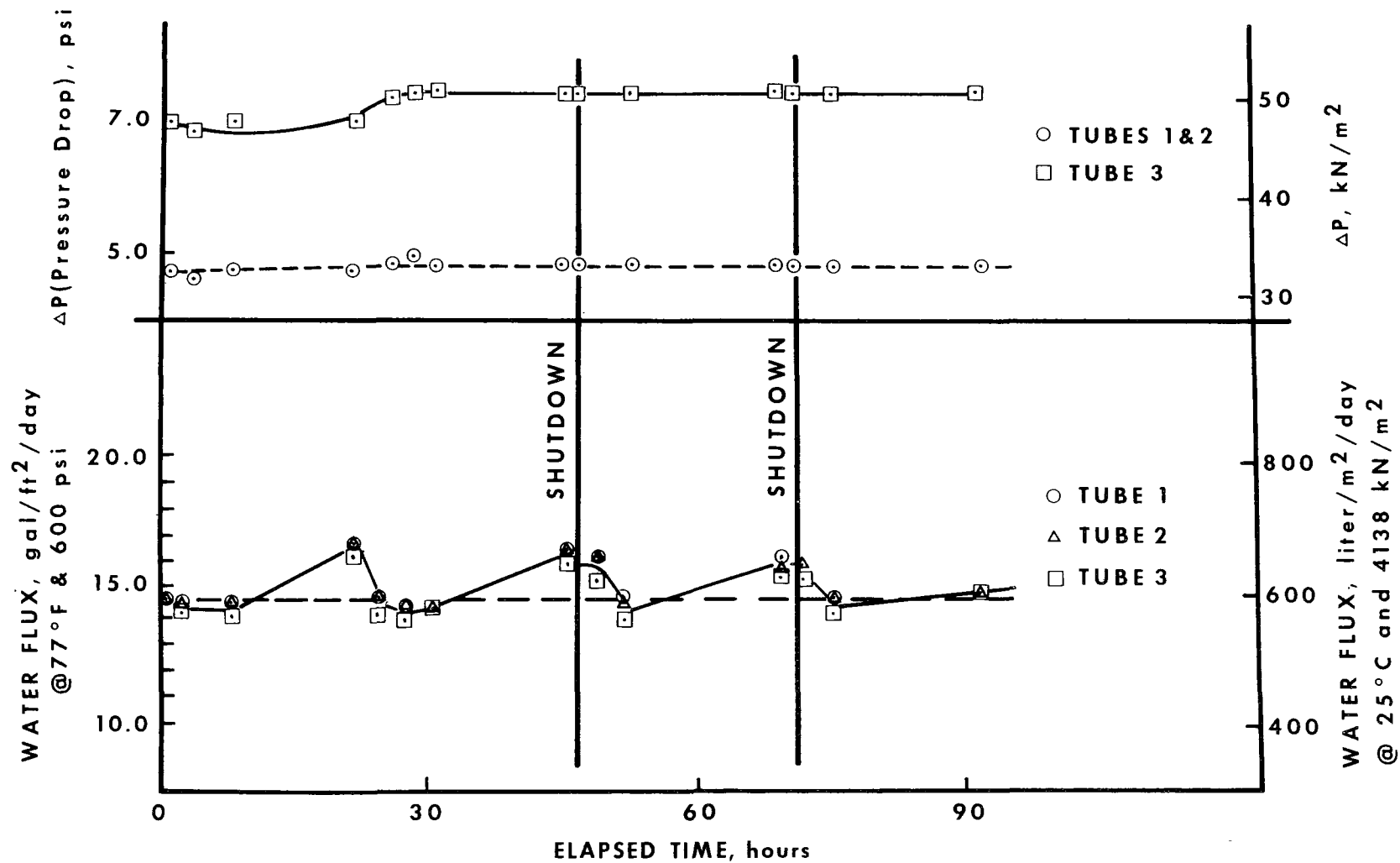


Figure 14.

Membrane performance and  $\Delta P$  history for Ebensburg RO Test Number Four at 50 percent recovery

Physical data for Test Number Four are presented in Table 24 and the chemical analyses are given in Table 25. Salt rejections (Table 25) were greater than 99 percent on all multivalent ions except aluminum.

The downstream module in tube 3, which had been installed at the beginning of Test Number Four, was removed and a post mortem analysis made. Sleigh<sup>3</sup> reported that the module had been damaged during shipment. He observed some iron present on the membrane surface but was unable to quantify it. There was no calcium sulfate present on the membrane.

#### Discussion of Four Ebensburg Tests

At this site, it was seen that pretreatment of the feed to lower the pH was not necessary for short-term tests as long as the pH was near 3.1 and/or the recovery was near 50 percent.

Product water quality, though uniformly good, would require slight addition of lime and filtering to be of potable quality.

As the fouling at 85 percent recovery could be removed successfully by a weekly 3 hr low-recovery flush, fouling would not prohibit operation at that recovery level. The flux at 50 percent recovery (Test Number Four), however, was roughly 15 percent greater than the flux during the 85 percent recovery runs (Tests Number One and Two). Therefore, obvious improvements in membrane performance can be obtained by operating below the  $\text{CaSO}_4$  fouling level.

Table 26 compares the results of the first Ebensburg test with those of Rex Chainbelt at Mocanaqua.<sup>4</sup> The spiral wound unit was operating at Ebensburg under more severe conditions in terms of concentrations than the tubular unit at Mocanaqua, yet it produced significantly superior results in terms of flux stability and product quality. Due to the apparent success of the spiral unit at Ebensburg, it was not possible to determine if the fouling observed at Mocanaqua was peculiarly due to the tubular RO system or whether some unknown characteristic of the Mocanaqua water was responsible.



Table 24. OPERATING PARAMETERS FOR TEST NUMBER FOUR AT EBENSBURG, PENNSYLVANIA

Average recovery, percent	53.2 Avg.	54.8 Max.	52.3 Min.
Average feed rate, gpm		6.33	
Average brine flow rate, gpm		2.97	
Average recycle brine flow rate, gpm		0	
Average temperature, °F	60.2 Avg.	54.0 Min.	63.0 Max.
Average feed pressure, psi		401.1	
Average product flow rate, gpm		3.36	
Normalized to 50°F, gpm		2.78	
Normalized to 77°F, gpm		4.45	
Average flux rate, gal/ft <sup>2</sup> /day @ 50°F and 400 psi net		8.90	
Average flux rate, gal/ft <sup>2</sup> /day @ 77°F and 400 psi net		14.24	
Maximum brine/product flow ratio		8.7:1	
Minimum brine/product flow ratio		5.5:1	
Dates of test	: August 31 - September 4, 1970		
Length of run	: 93.5 hours		
Number of shutdowns	: 2		

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 25. CHEMISTRY ANALYSES FOR TEST NUMBER FOUR WHERE AVERAGE RECOVERY = 53.2%

	Raw feed	Brine	Product	Rejections*
pH	3.6	3.4	4.8	
Conductivity	1180	2160	27	97.7%
Acidity	390	770	24	93.9%
Calcium as Ca	160	330	1.1	99.3%
Magnesium as Mg	51	110	0.3	99.4%
Aluminum	30	61	1.1	96.3%
Total iron	130	250	0.4	99.5%
Ferrous iron	96	210	1.0	99.0%
Sulfates	1300	2900	1.0	99.9%
Dissolved oxygen	2.0	2.0		

All units are mg/l except for conductivity (Mmhos/cm) and pH.

\*Rejection equals  $\frac{\text{Feed concentration} - \text{product concentration}}{\text{Feed concentration}} \times 100$ .

Table 26. COMPARISON OF MOCANAQUA<sup>4</sup> AND EBENSBURG RO TEST RESULTS

<u>Operating Parameters</u>		
Location	Mocanaqua	Ebensburg
Investigator	Rex Chainbelt	EPA & Gulf Environmental Systems
Type of unit	Tubular	Spiral-wound
Date of test	1969	1970
Length of test	813 hours	191 hours
Flux loss in 190 hours	≈40 percent (total unit)	≈25 percent (total unit)
Operating recovery (190 hours)	≈70 percent	≈84 percent
<u>Chemical Parameters</u>		
	Mocanaqua	Ebensburg
	Feed      Product	Feed      Product
pH	3.6      4.1	3.6      4.1
Acidity	--      --	380      56
Calcium	140      2.8	190      1.2
Sulfates	790      36	1640      14
Total iron	100      3.7	135      1.7
Ferrous iron	100      3.7	100      >2
Dissolved oxygen	4.9      --	2.0      --
Magnesium	100      1.9	54      0.4

All units are mg/l except for pH.

Plans were made to take the spiral RO unit to the Mocanaqua site in the spring of 1971 to further investigate the situation.

#### NORTON FERRIC IRON LONG-TERM SPIRAL-WOUND STUDY

Following the Ebensburg study, the 4 K spiral unit was returned to Norton for a long-term winter study before going to Mocanaqua in the spring of 1971.

This Norton study lasted 3,013 hr at 73 percent recovery. The flow arrangement (Figure 10) was the same as previous studies except that no pH control was used. New high-flux modules with membrane cast directly on the backing material were used for this test. One of the major problems prior to this investigation was the unreliability of high pressure pumps to operate on AMD. A Gould MB 13600, ceramic-stainless steel, multi-stage, centrifugal pump was tested on this study and performed flawlessly.

Flux history for the 3,013 hr test is shown on a log-log basis in Figure 15. Tube 3, whose performance was usually below that of tubes 1 or 2 due to its higher concentrations, exhibited superior performance to tubes 1 and 2. Log-log slope changes occurred in all tubes after approximately 300 hr. Until that time, tube 3 had followed a log-log slope of  $-0.031$  and tube one's slope was  $-0.058$ .

Several flushing techniques, which are individually discussed later, were successful in restoring flux to values in excess of those predicted by the initial slope. However, rapid flux losses immediately recurred following each flush. The loss in tubes 1 and 2 was more severe than tube 3's loss. At the end of 3,013 hr, tubes 1 and 2 had each lost 58 percent of their initial flux and tube 3 had lost 38 percent.

The operating parameters for this study are given in Table 27 and chemistry analyses are presented in Table 28.

The data in Table 27 provide a possible explanation for the poor performance of tubes one and two in respect to tube 3. Brine/product flow ratios for this study were extremely low in general and

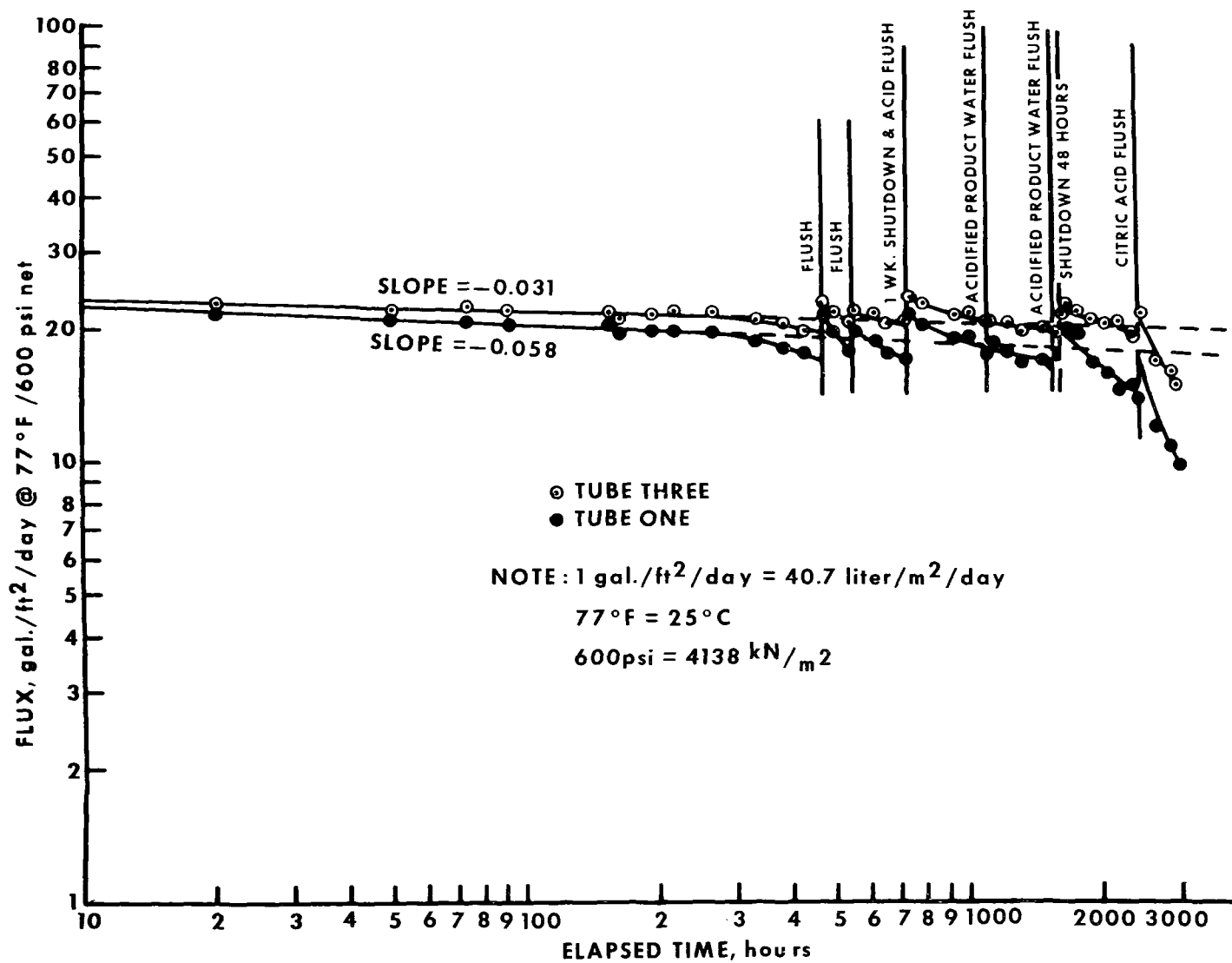


Figure 15

Flux trends for Norton 3000 hour spiral-wound R.O. study at 13 percent recovery

Table 27. OPERATING PARAMETERS FOR 3000 HR 4K NORTON STUDY AT 73 PERCENT RECOVERY

Parameter	Unit	Value
Raw water feed flow	gpm	5.00
Product water flow	gpm	3.64
Brine water discharged	gpm	1.36
Brine water recycled	gpm	1.46
Minimum brine/product flow ratio	ratio/module	2.8:1
Maximum brine/product flow ratio	ratio/module	6.6:1
Water recovery	percent	72.8
Recovery of blended feed	percent	56.3
Feed pressure	psig	600.2
Feed temperature	°F	54.4
Tube one flux	gal/ft <sup>2</sup> /day @ 77°F & 600 psi net	17.43
Tube two flux	gal/ft <sup>2</sup> /day @ 77°F & 600 psi net	17.25
Tube three flux	gal/ft <sup>2</sup> /day @ 77°F & 600 psi net	20.41
Length of run	hours	3012.6
Date of run	November 16, 1970 - April 13, 1971	

All values are means from 130 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77°F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 28. NORTON 4K 3000 HR CHEMICAL ANALYSES

Parameter	pH	Cond.	Acidity	Ca	Mg	Fe	Al	SO <sub>4</sub>
Raw feed	2.9	970	440	120	39	130	40	680
Blended feed	2.7	1600	660	180	71	210	63	1100
Brine	2.5	2900	1600	420	140	480	150	2600
Product	3.9	77	22	1.1	.40	1.1	1.5	1.2
Rejections		95.2%	96.7%	99.4%	99.4%	99.5%	97.6%	99.9%

Rejection equals  $\frac{\text{Blended feed concentration} - \text{product concentration}}{\text{Blended feed concentration}} \times 100.$

All units are mg/l except for conductance (micromhos/cm) and pH.

were at a minimum in tubes one and two (b/p minimum ratios of 2.8:1). The b/p ratio in tube 3 was significantly higher with a maximum ratio of 6.6:1. It was felt that the low brine/product ratios did not provide sufficient turbulence in the brine stream in the modules and thus did not effectively control boundary layer precipitation.

Salt rejections (Table 28) were uniformly above 99 percent on all multivalent ions except aluminum.

Near the end of the test, copper sulfate was injected directly into the raw feed water to determine the capability of the membrane to reject copper. Concentrations of copper in the feed were varied from 2.8 to 44 mg/l resulting in blended feed concentrations from 4.4 to 60 mg/l. The membrane rejected an average of 99.5 percent (based upon blended feed), yielding product copper levels below 0.16 mg/l and brine copper concentrations up to 150 mg/l at 75 percent recovery.

The severe fouling which occurred during this study afforded an opportunity to investigate the effectiveness of various flushing techniques. The flux history through 2,500 hr is shown on a linear basis in Figure 16 to illustrate more clearly differences in flush results.

The type of flush and its success in fouling removal should yield some insight into the nature of the fouling. A list of the flushing tried and their expected results follows:

1. Low-recovery Flush - Mainly scours the membranes due to higher brine velocities and corresponding increases in turbulence. Should remove some loose precipitation such as flocculated ferric hydroxide or calcium sulfate. May dislodge particulate matter. Mainly a physical flushing technique.
2. Acidified Product Flush - Product water is stored and acidified to pH 2.5 and then pumped through the RO unit.



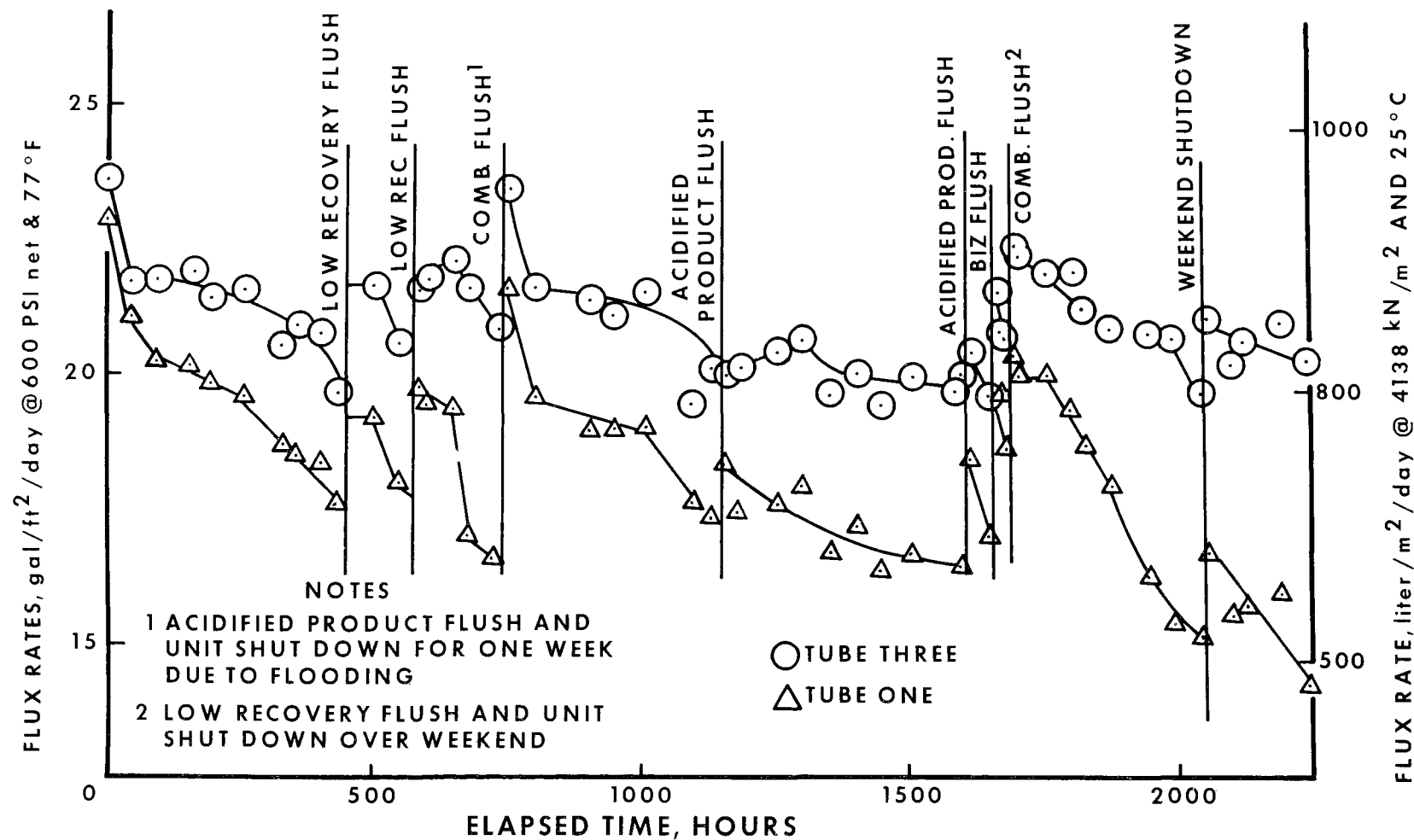


Figure 16

Membrane performance during 4K reverse osmosis 3000-hr study at Norton

This type flush should chemically redissolve those minerals which are acid soluble (i.e., iron, aluminum, calcium, and some calcium sulfate) if the fouling is not too severe before the flush is attempted.

3. BIZ flush - The catalytic action of enzymes should mainly remove organics by breaking down protein-containing materials. BIZ also contains wetting agents that should aid in the resolubilization of precipitates and phosphates that should be quite effective in sequestering iron, calcium, and magnesium as well as in emulsifying oils.
4. Shutdowns - Immediate depressurization should tend to dislodge precipitates that have been held against the membrane by pressure and RO flow through the membrane. During long periods of depressurization, the membrane tends to relax and the effects of compaction are reduced. Also, normal osmotic flow (from product side into brine side) takes place during this period and should tend to dislodge precipitates from the brine side of the membrane.

Although all the flushes attempted (Figure 16) were successful in improving flux, the most dramatic increase occurred using a two-step flush. First, the unit was flushed with acidified product water, and then it was shut down for one week because of flooding which overloaded the filtration equipment. This accidental combination acid flush-shutdown at 725 hours elapsed time significantly improved flux. However, after each flush, flux again rapidly declined. As each of the previously mentioned flushes were successful, the flux decline was attributed to a combination of compaction, iron fouling, and organic deposition.

Samples were taken during the citric acid flush at 2,500 hours elapsed time. Recovery during the flush was maintained at 50 percent so the brine concentrations should have been twice that of the raw feed. The resulting analyses indicated that the brine contained

twice as much magnesium, aluminum, and sulfate as was in the acidified feed (normal for 50 percent recovery); however, eleven times more iron and three times more calcium were in the brine than in the feed. The predominance of iron in the flush brine indicated iron precipitation was the major inorganic fouling mechanism.

A module was removed from tube 1 after 3,013 hr of operation at Norton and dissected for membrane deposit analyses. An algal slime covered the outside of the module. The membrane removed had an obvious coating on it which, from its red-brown appearance, was tentatively identified as ferric hydroxide.

For chemical analyses, the membrane was cut into small rectangles (approximately 0.79 cm x 1.18 cm or 2 in x 3 in). Various reagents were used to attempt to dissolve the coating from the membrane patches. Table 29 lists the reagents used and chemical analyses of the resulting solution. Initial analyses were made on each of the reagents to determine background levels and to identify possible interferences with the analytical procedures. Membrane patches were weighed before and after immersion in the dissolving solution in an attempt to correlate the resulting concentrations to a gravimetric reference base (weight of coating). In most cases, however, the solutions dissolved the membrane as well as the coating and only the fabric backing material remained; therefore, the gravimetric reference base was ineffective as it was not possible to ascertain the amount of membrane removed when only partial membrane destruction occurred. The membrane coating appeared to consist mainly of iron and sulfate (Table 29). Presence of sulfate without calcium was not completely understood.

Samples of the membrane were sent to Rex Chainbelt and Gulf Environmental Systems for analysis. Mason<sup>13</sup> of Rex Chainbelt found two distinct layers of fouling material on the membrane:

"The first layer closest to the membrane was an iron oxide coating. The second layer was a clay-like substance which was approximately 65 percent organic ma-

Table 29. CHEMISTRY ANALYSES OF COATING MATERIAL ON 4K REVERSE OSMOSIS MEMBRANE

Sample designation	Ca	Mg	Fe	Al	SO <sub>4</sub>	Membrane area in <sup>2</sup>	Membrane Weight		
							Wet mg	Dry mg	Difference mg
Blank									
Stannous chloride	<.1	.1	4.4	<.1	<.1				
Blank									
Sodium hydrosulfite	23	1.0	8.8	<.1	10900				
Blank									
Citric acid	.4	<.1	3.0	<.1	27				
Blank									
Hydrochloric acid	<.1	<.1	<.1	<.1	<.1				
Blank									
Phosphoric acid	<.1	<.1	<.1	<.1	<.1				
Stannous chloride (b,c)	2.8	.1	73	1.4	3900	8.75	.7830	.5830	.2000
Stannous chloride (c)	2.8	.1	90	.1	2950	9.38	.8220	.5930	.2290
Sodium hydrosulfite (b)	26	1.1	83	<.1	10900	7.88	.7820	.7380	.0440
Sodium hydrosulfite (a)	23	<.1	45	<.1	10900	6.00	.5260	.5230	.0030
Citric acid (b)	3.0	<.1	89	<.1	340	6.00	.5990	.5930	.0060
Citric acid (c)	3.0	<.1	24	<.1	160	6.00	.5910	.5800	.0110
Hydrochloric acid (b)	3.0	<.1	110	.9	63	6.50	.6510	.4250	.2260
Hydrochloric acid	3.0	<.1	110	<.1	27	6.50	.5940	.5170	.0770
Phosphoric acid (b)	10	<.1	110	<.1	220	6.75	.6270	.4930	.1340
Phosphoric acid (a)	10	<.1	80	<.1	27	6.50	.5800	.4000	.1800

(a) Precipitate did not dissolve completely off membrane.

(b) Heat to temperature of 90° C.

(c) Dissolved stannous chloride in hydrochloric acid.

All units expressed as mg/100 ml unless otherwise noted.

To convert in<sup>2</sup> to cm<sup>2</sup>, multiply by 6.45.

mg = Milligram

ml = Milliliter

terial. This second layer adhered to the membrane very loosely, and was easily removed by slight agitation. The ease of removal may have been due to the handling of the membrane when removed from the pressure vessel and shipped to Milwaukee. The membrane flux, tested with both layers of fouling material, was 12.7 gal/ft<sup>2</sup> day at 415 psi and 77° F. Salt rejection was approximately 96 percent sodium chloride. The membrane was flushed with a 2 wt. percent of sodium hydrosulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) in water. The pH of this solution was approximately 6.0. This chemical solution provided a strong reducing environment which converted the ferric iron to soluble ferrous iron, and thus allowed cleaning of iron oxides from the membrane. This cleaning can generally be effected with a two-hour flush. After cleaning by the above procedure, the membrane had a flux of 16.6 gal/ft<sup>2</sup> day at 415 psi and 77° F. The salt rejection remained unchanged at 96 percent, and therefore the membrane surface was not damaged.

It should be noted that the second layer of fouling material was not dissolved by the sodium hydrosulfite solution, and therefore must be removed by other methods, such as normal osmosis flushing, enzyme solutions, and high velocity flushing."

Sleigh<sup>14</sup> reported the analysis of the coating material to be ferric hydroxide and mud.

Since the product water was not of potable quality, a feasibility test was made for lime neutralization to increase pH and remove residual iron.

During the test, product from the RO unit was diverted to a 200 gal reaction tank equipped with a mixer. A pH controller automatically controlled the addition of a 1 percent slurry of lime to maintain a pH between 7.4 and 7.8 in the reaction chamber. Neutralized product water was then pumped through a 10 micron cartridge filter.

Table 30 shows the effectiveness of product neutralization.

Table 30. CHEMISTRY ANALYSES FOR RO PRODUCT NEUTRALIZATION

Water	pH	Alk.	Cond.	Acid- ity	Ca	Mg	Fe	Al	SO <sub>4</sub>
Product	3.7	0	55	9.3	0.37	0.20	0.25	0.19	0.33
Neutral product	7.4	5	27	0	5.1	0.20	0.04	0.10	0.40

All units expressed as mg/l except conductance (Mmhos/cm) and pH.

An increase in calcium was expected since lime  $[\text{Ca}(\text{OH})_2]$  was used as the neutralizing agent. With the decrease in iron and acidity, the neutralized product was of potable quality.

Continuous RO product neutralization required (9.83 gram/m<sup>3</sup>) 0.082 pounds of lime per 1,000 gal.

#### Discussion of Norton Study

Fouling, which was observed during this long-term study, was severe toward the end of the run. The fouling mechanism was diagnosed as a combination of organic and colloidal deposition and ferric hydroxide precipitation. Several flushing techniques were successful in short-term flux restoration, but rapid degradation recurred after each flush.

The apparent reason for the fouling was operation of the spiral system at insufficient brine flow rates thus allowing boundary layer

precipitation. This conclusion was confirmed by superior flux stability of tube 3 as compared to tubes 1 and 2. Tube 3 performance normally would be inferior since it was subject to the most severe concentration of pollutants. In this study, however, the superiority of tube 3 was attributed to a brine/product flow ratio which was up to 2.4 times the b/p ratio in tubes 1 and 2.

Injection of copper sulfate into the RO feed water determined that the membrane would reject copper at a 99.5 percent rejection rate.

RO product water was not of potable quality due to iron and pH. Lime neutralization of the product water resulted in a potable quality effluent.

Further testing was necessary at higher brine/product flow ratios to provide more representative long-term flux trends. Additional tests along this line were made after the 4 K unit returned from Mocanaqua in Fall 1971.

#### MOCANAQUA FERROUS IRON STUDIES COMPARING SPIRAL-WOUND, HOLLOW-FIBER, AND TUBULAR UNITS (15,16)

To investigate the Mocanaqua fouling phenomena, EPA and the Commonwealth of Pennsylvania contracted with Rex Chainbelt in 1971 to evaluate the iron fouling problem in the laboratory, to modify the 1969 tubular system, and to conduct additional studies at Mocanaqua. In order to make these studies more comprehensive, EPA was to conduct simultaneous studies with the 4 K spiral-wound RO unit at the same site. A hollow-fiber RO permeator was also obtained for this study, and EPA later enlarged it to a three permeator array for a hollow-fiber system of comparable size to the spiral-wound system.

For the ensuing study, all three systems operated side by side on the same water; the only exception was the acid injection to the feed during the last phase of spiral-wound testing. Thus, a unique opportunity was provided for direct comparison of systems and for investigation of the Mocanaqua iron fouling phenomenon.

Typical water quality characteristics of the Mocanaqua discharge are presented in Table 31.

Table 31. TYPICAL RAW WATER QUALITY CHARACTERISTICS  
OF MOCANAQUA DISCHARGE

Parameter	Units	Value
pH		3.4
Conductance	Mmhos/cm	1100
Acidity	mg/l as $\text{CaCO}_3$	230
Calcium	mg/l	120
Magnesium	"	90
Total iron	"	80
Ferrous iron	"	68
Aluminum	"	11
Sulfate	"	800
Manganese	"	15
Silica	"	10
TDS	"	1200
Dissolved oxygen	"	1
Temperature	°Fahrenheit	54

The Rex Chainbelt Laboratory, in addition to the normal EPA determinations, analyzed for silica by atomic absorption. A Hach Kit was used by Rex Chainbelt for on-site determinations of calcium, total hardness, total iron, ferrous iron, and sulfates. A Myron L TDS meter was used for total dissolved solids measurements.

As a prelude to actual field investigations, laboratory studies were performed by Rex Chainbelt to attempt to isolate possible causes for the severe iron fouling seen at Mocanaqua during their 1969 tests. From the results of these batch tests, Mason<sup>16</sup> postulated that the most probable cause of the observed fouling was bacterial oxidation of ferrous iron at the membrane surface and subsequent precipitation of the resulting ferric iron which had been hydrolyzed.

For this reason, ultraviolet (UV) disinfection lights were installed as part of the pretreatment system for all three field units tested in the belief that the UV light would kill most of the iron oxidizing bacteria and thus inhibit or prevent bacterial oxidation of  $\text{Fe}^2$  to  $\text{Fe}^3$ .



Iron oxidation studies were performed during the actual field study to evaluate the effectiveness of the UV light. Sixteen sets of samples were taken for one of these tests. Twelve of the 16 were raw feed samples that had passed through 10 micron filters. The remaining four sets were blended feed samples from the spiral RO unit. Each individual set of samples consisted of five duplicates. Ferrous iron was determined once per day on each set of samples for a period of five days. To prevent contamination from the pH probes and stirrers which were used to determine ferrous concentrations, only one of the duplicates was analyzed per day. Following analysis, the sample was considered contaminated and was discarded.

All samples were kept in a mine discharge at a 11°C (53°-54°F) temperature to eliminate environmental changes. Those samples to be kept dark were placed in opaque plastic bags, placed in the creek, and covered with brush to provide shade. Sulfuric acid was added to those samples in which the pH was lowered. Formaldehyde was used for a disinfectant where required. The results of the test are given in Table 32. Specific conclusions relative to possible oxidation control techniques from the oxidation study were:

- ultraviolet disinfection inhibited oxidation;
- lowering the pH to 2.5 inhibited oxidation;
- some oxidation occurred in blended feed samples which had been exposed to UV and kept in dark;
- at creek temperature (54° F), virtually no oxidation took place in 24 hours; and
- the oxidation mechanism was bacteria since the above variations in treatment inhibited oxidation.

Since some oxidation occurred in two of the blended feed samples that had been exposed to ultraviolet treatment, it was probable that the UV did not effect a 100 percent kill. If bacteria were present in the blended feed, it was assumed that significant growth was probable at the membrane surface in the RO units.

Table 32. FERROUS IRON OXIDATION CONTROL STUDY, MOCANAQUA, PA.

Sample Number	Initial	Ferrous concentration after:				Description (a,c)
		24 hours	48 hours	72 hours	96 hours	
1	56	56	56	56	56	Raw feed - light
2	56	56	45	22	1.8	Raw feed - dark
3	56	56	56	56	56	Raw, ultraviolet-light
4	56	56	56	56	56	Raw, ultraviolet-dark
5	56	56	56	56	56	Raw, pH 2.5 - light
6	56	56	56	56	56	Raw, pH 2.5 - dark
7	56	56	56	56	56	Raw, UV, pH 2.5 - light
8	56	56	56	56	56	Raw, UV, pH 2.5 - dark
9	56	56	39	28	28	Raw, UV, disinfect <sup>(b)</sup> - light
10	56	56	56	56	56	Raw, UV, disinfect <sup>(b)</sup> - dark
11	56	56	39	34	28	Raw, disinfect <sup>(b)</sup> - light
12	56	56	56	56	56	Raw, disinfect <sup>(b)</sup> - dark
13	118	118	118	118	118	Blended feed, UV - light
14	118	112	112	79	39	Blended feed, UV - dark
15	118	118	112	96	96	Blended, disinfect <sup>(b)</sup> , UV - light
16	118	118	118	118	118	Blended, disinfect <sup>(b)</sup> , UV - dark

Note: Results expressed as mg/l.

(a) All samples passed through 10 micron filter prior to collection.

(b) Disinfection consisted of addition of 2 ml of formaldehyde to 400 ml/sample.

(c) All temperatures 53-54°F except for initial blended feed sample temperature of 64° F.

Another series of oxidation tests at air temperatures 15.6° to 23.9° C (68-75° F) resulted in significantly faster oxidation rates as is typical in most biological growth.

Two sets of spiral-wound modules were used in the 4 K unit during the study. During Phase I, each module contained 4.65 m<sup>2</sup> (50 ft<sup>2</sup>) of standard percholate-modified cellulose acetate membrane for a total unit membrane area of 41.9 m<sup>2</sup> (450 ft<sup>2</sup>). The modules used for Phase II contained 5.77 m<sup>2</sup> (62 ft<sup>2</sup>) of Formamid-modified cellulose acetate for a total unit membrane area of 51.9 m<sup>2</sup> (558 ft<sup>2</sup>).

Figure 17 presents the system arrangement and flow diagram for the spiral unit. Acid mine water was pumped through ten micron cartridge filters and a UV disinfection light before entering the reverse osmosis unit. UV disinfection was believed necessary to inhibit bacteriological oxidation of the ferrous iron which had presumably contributed to fouling observed in earlier studies.<sup>4</sup>

During Phase II, sulfuric acid was injected to lower the blended feed pH to 2.9 and thus inhibit both ferrous oxidation and ferric precipitation.

The second unit tested was a hollow-fiber system, manufactured by DuPont; initially, it consisted of one permeator on loan from DuPont to Rex Chainbelt. As illustrated in Figure 3, approximately 139.6 m<sup>2</sup> (1500 ft<sup>2</sup>) of 8-9 hollow-fiber nylon membrane were packed in a 15.2 cm x 1.22 m (6 in x 4 ft) stainless steel pressure vessel. During Phase I, the single DuPont permeator operated at 2758 kN/m<sup>2</sup> (400 psi) from a Moyno high pressure pump which also supplied feed water to the tubular unit. Phase I DuPont tests were successful so EPA purchased two additional permeators for Phase II and formed a three permeator array, 6 K unit, as shown in Figure 18. The brine from both new permeators in parallel served as the feed to permeator number 3 (the original Phase I permeator). Flow control orifices were placed in each brine line from permeators 1 and 2 to ensure equal brine flows and prevent system unbalance. Because high brine flows are not required for hollow fiber systems, it was not necessary

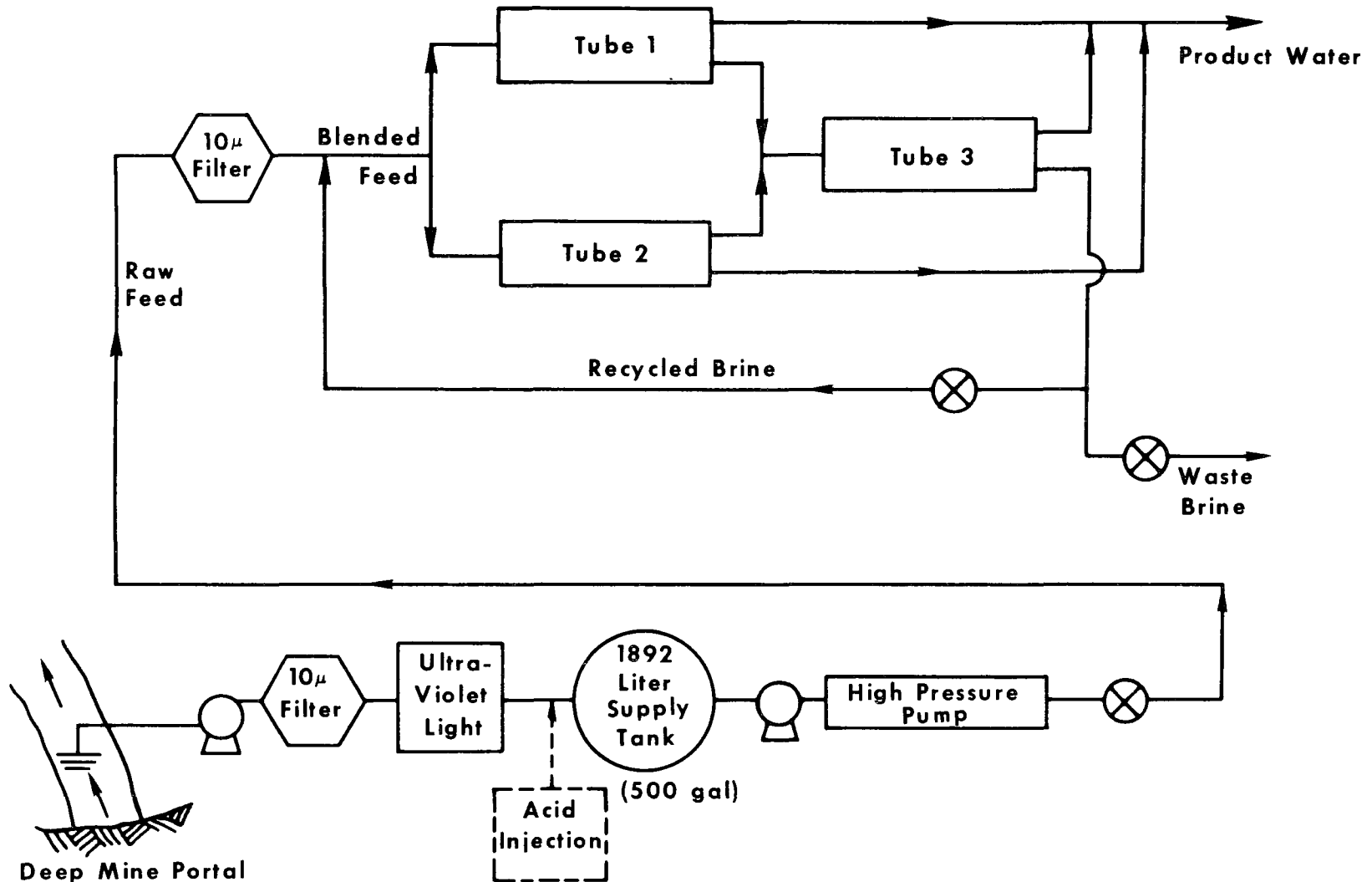


Figure 17. Spiral -wound reverse osmosis system arrangement at Mocanaqua, Pa.

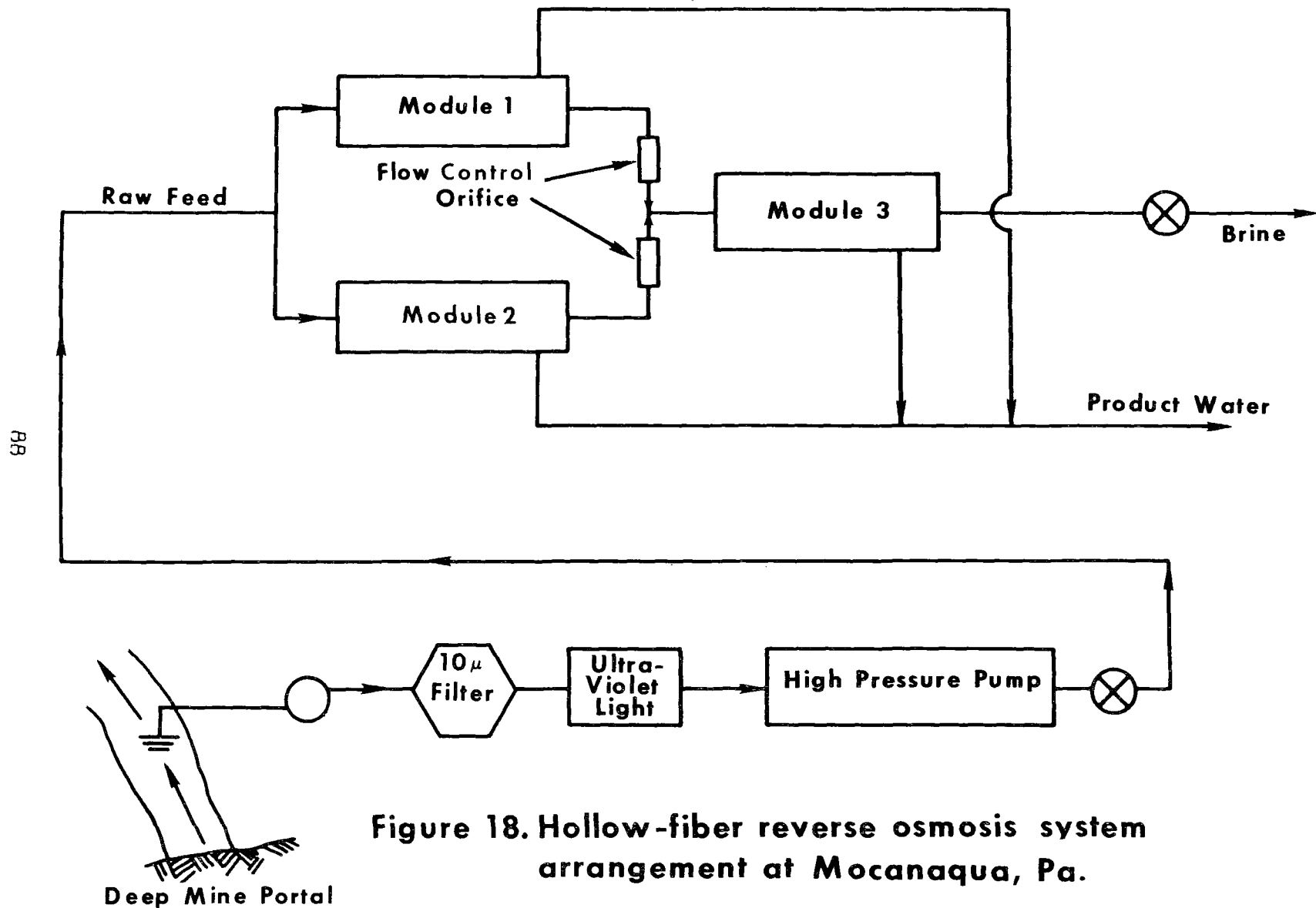


Figure 18. Hollow-fiber reverse osmosis system arrangement at Mocanaqua, Pa.

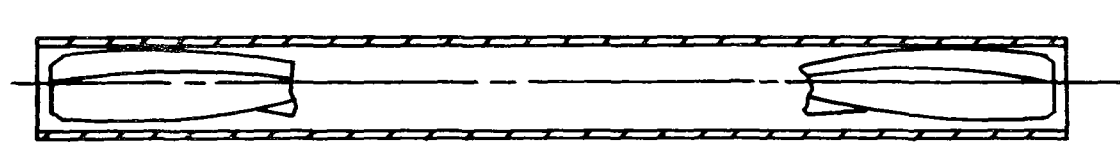
to recycle brine. Therefore, the unit received raw acid mine water that had been filtered and had passed through the ultraviolet light for disinfection.

Phase I tubular studies<sup>15,16</sup> utilized a unit consisting of sixty 7.6 cm x 2.39 m (3 in x 7 ft 10 in) plastic tubular #310 modules illustrated in Figure 19 and arranged as shown in Figure 20. The tubular system was manufactured by Calgon-Havens Company. Each module contained eighteen 1/2 in (1.27 cm) i.d. porous fiberglass tubes that were lined with cellulose acetate membrane and connected in series. Membrane area was 1.57 m<sup>2</sup> (16.9 ft<sup>2</sup>) per module for a total system membrane area of 94.4 m<sup>2</sup> (1014 ft<sup>2</sup>). Pretreatment was the same as that for Phase I Gulf and DuPont, i.e., 10 micron filtration and UV disinfection.

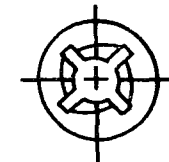
Turbulence promotion rods were placed in modules where brine flow was lowest to inhibit 'boundary layer' precipitation and fouling. Unfortunately, use of turbulence promoters also resulted in high pressure drops across the modules in which they were installed, thus reducing the average applied pressure.

During Phase II, the sixty #310 modules were replaced with five #610 modules for a total membrane area of 7.87 m<sup>2</sup> (84.5 ft<sup>2</sup>).

It was necessary to determine the osmotic pressure of the water in order to compensate for variations in water quality and recovery. The spiral-wound unit was modified<sup>14</sup> to enable measurement of osmotic pressure by pressure differences between the brine and product side of the membrane. By varying recovery, osmotic pressure measurements were made over a complete range of concentrations and a correlation was developed between brine conductivity and osmotic pressure. Since acid injection was utilized in Phase II spiral-wound studies and since acid affects conductivity, a different correlation was necessary for Phase II. Both equations and plots are shown in Figure 21.



SINGLE TUBE WITH TURBULENCE PROMOTER ROD



TURBULENCE  
PROMOTER  
ROD END VIEW

U6

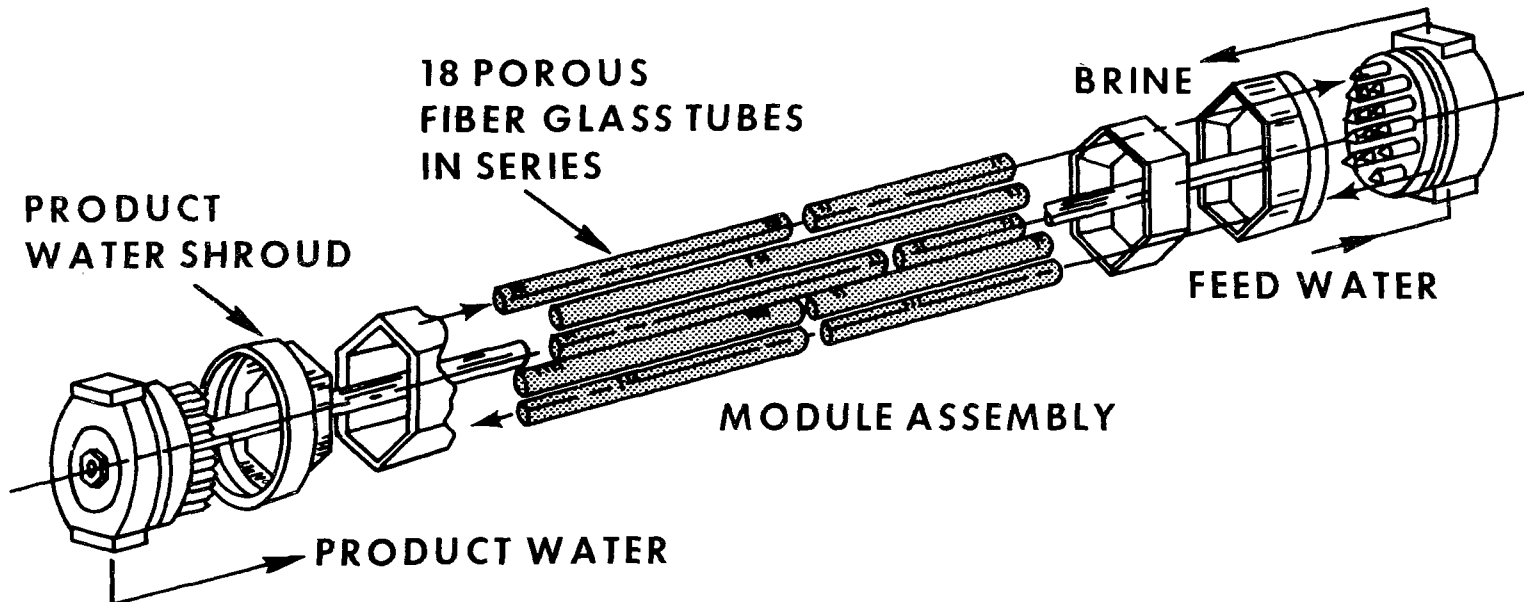


Figure 19

Tubular reverse osmosis module configuration<sup>(16)</sup> at Mocanaqua, Pa.

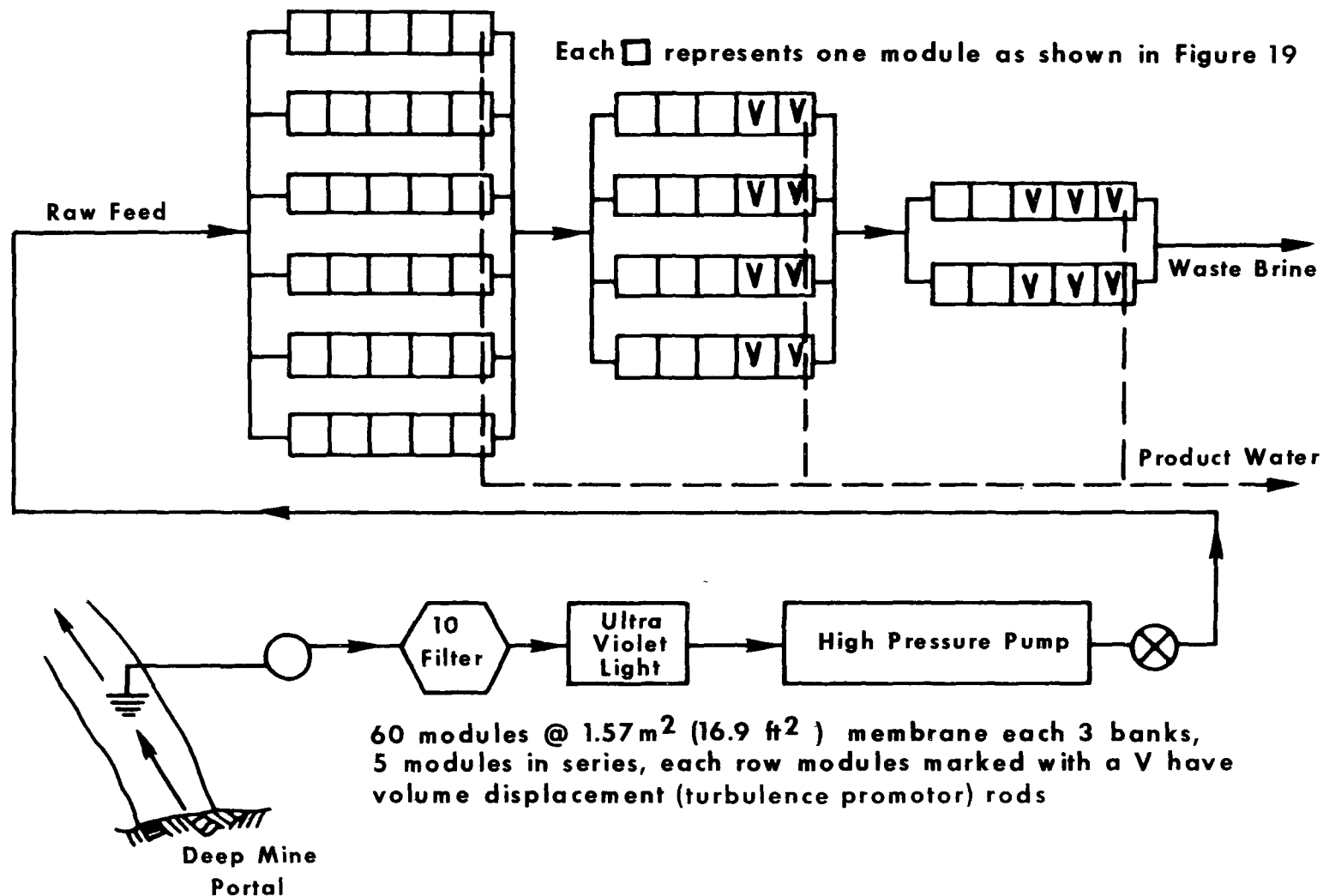
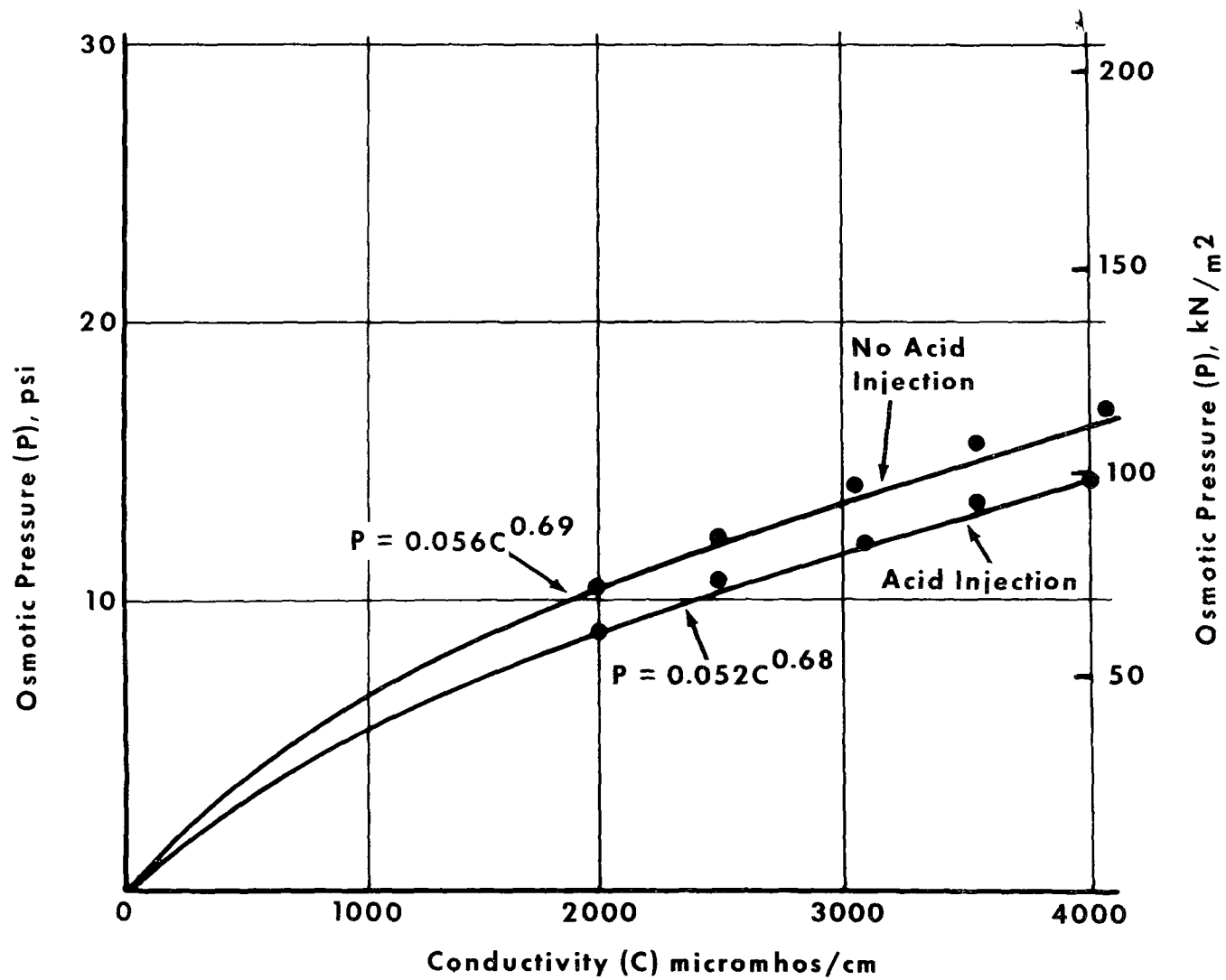


Figure 20. Phase I module arrangement <sup>(16)</sup> for tubular reverse osmosis study at Mocanaqua, Pa.





**Figure 21**  
Osmotic pressure - conductivity relationships at Mocanaqua, Pa.

## Spiral-Wound Phase I Studies

Phase I of the spiral-wound studies was made at a unit recovery of 75 percent and system operating pressure of  $4138 \text{ kN/m}^2$  (600 psi). A summary of operating parameters for this study is given in Table 33. Water temperatures of  $63^\circ \text{ F}$  were caused by the Gould high-pressure pump that imparted energy to the  $54^\circ \text{ F}$  raw AMD. The necessity of brine recycle only aggravated the temperature rise since a portion of the water was continually recycled through the pumps. The increased temperature benefitted observable flux rates since product flow was strongly temperature dependent. Since all data were corrected for temperature, the higher operating temperature was not a factor in data evaluation. In actual operation, however, the higher the temperature, the higher the flux. Overall system recovery during Phase I was maintained at 75 percent during the first 1,054 hr of operation. The log-log flux decline slope was -0.034 for tube 1 and -0.032 for tube 3 during this period. At 1,054 hr elapsed time, the ultraviolet light was turned off to determine its effectiveness in controlling flux decline. As shown in Figure 22 (linear plot) and Figure 23 (log-log plot), the increase in flux decline was dramatic with the log-log slope increasing to near -0.2 even though recovery remained at 75 percent. Following a phosphoric acid flush, the UV was turned on again but recovery was increased to 84 percent. Flux decline was so severe at 84 percent recovery (log-log slope greater than -4.0) that the run was terminated after only 70 hours at that recovery level and flushed again with phosphoric acid. Though the acid flush improved flux, it did not stabilize on the original slope, presumably indicating all the fouling had not been removed. Total operating time during Phase I was 1,922 hr.

Fouling observed at 84 percent recovery was attributed to calcium sulfate precipitation. Analysis of the acid flush water confirmed the presence of large amounts of both iron and calcium after the 84 percent recovery run. A loss of calcium, sulfate, and iron

Table 33. OPERATING PARAMETERS FOR SPIRAL-WOUND PHASE I STUDY AT 75 PERCENT RECOVERY AT MOCANAQUA, PENNSYLVANIA

Parameter	Value
Raw water feed flow, gpm	6.02
Product water flow, gpm	4.50
Brine water discharged, gpm	1.52
Brine water recycled, gpm	4.26
Minimum brine/product flow ratio (Tubes 1 and 2), ratio/module	5:1
Maximum brine/product flow ratio (Tube 3), ratio/module	12:1
Water recovery, percent	74.8
Recovery of blended feed, percent	43.8
Feed pressure, psig	602
Feed water temperature, °F	62.6
Tube one flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77° F	19.56
Tube two flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77° F	19.52
Tube three flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77° F	18.77
Length of run, hours	1672
Date of run	May 1 - July 12, 1971

All values are means from 73 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77°F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

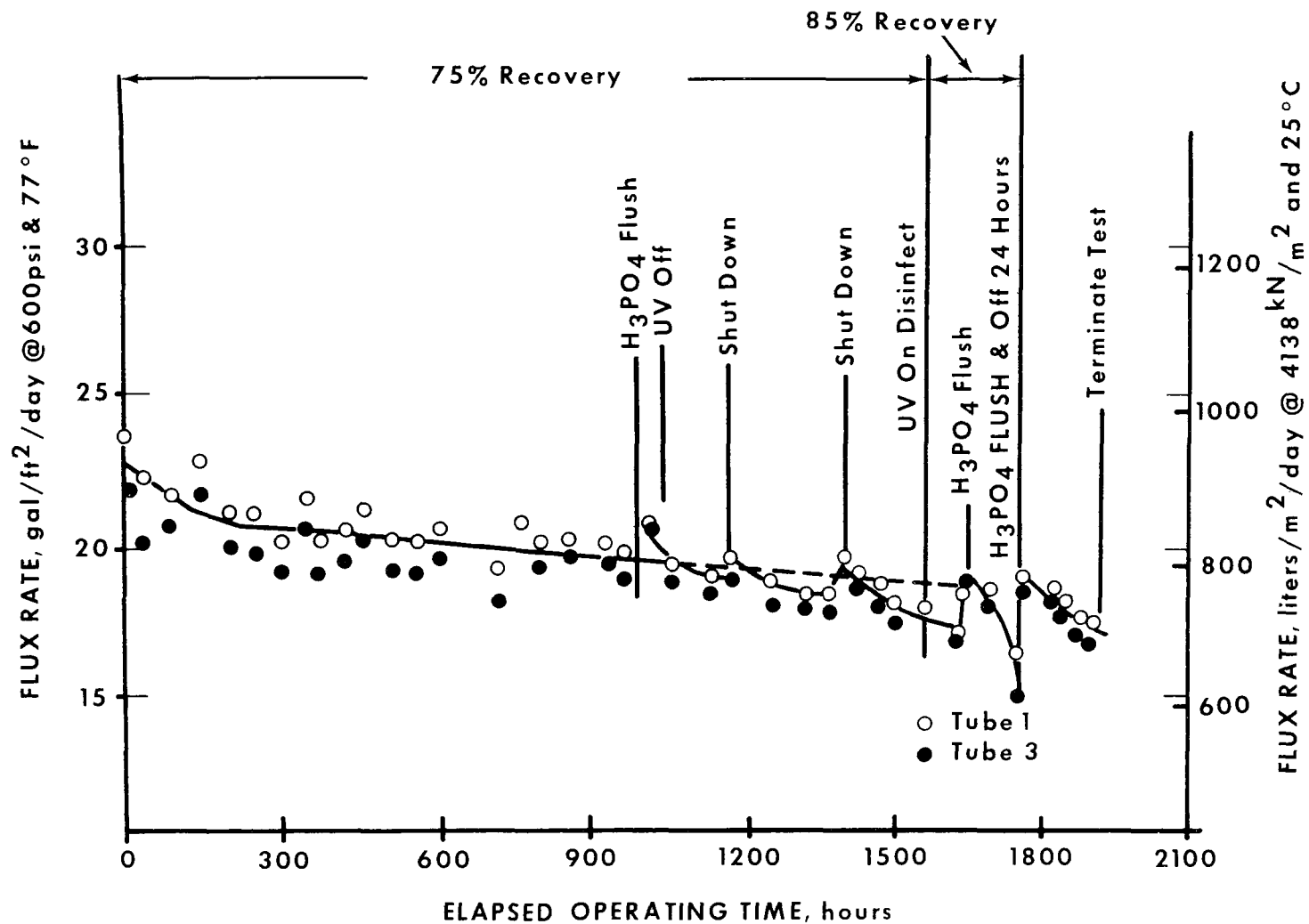


Figure 22

Phase I spiral-wound reverse osmosis unit flux rates at Mocanaqua, Pa.

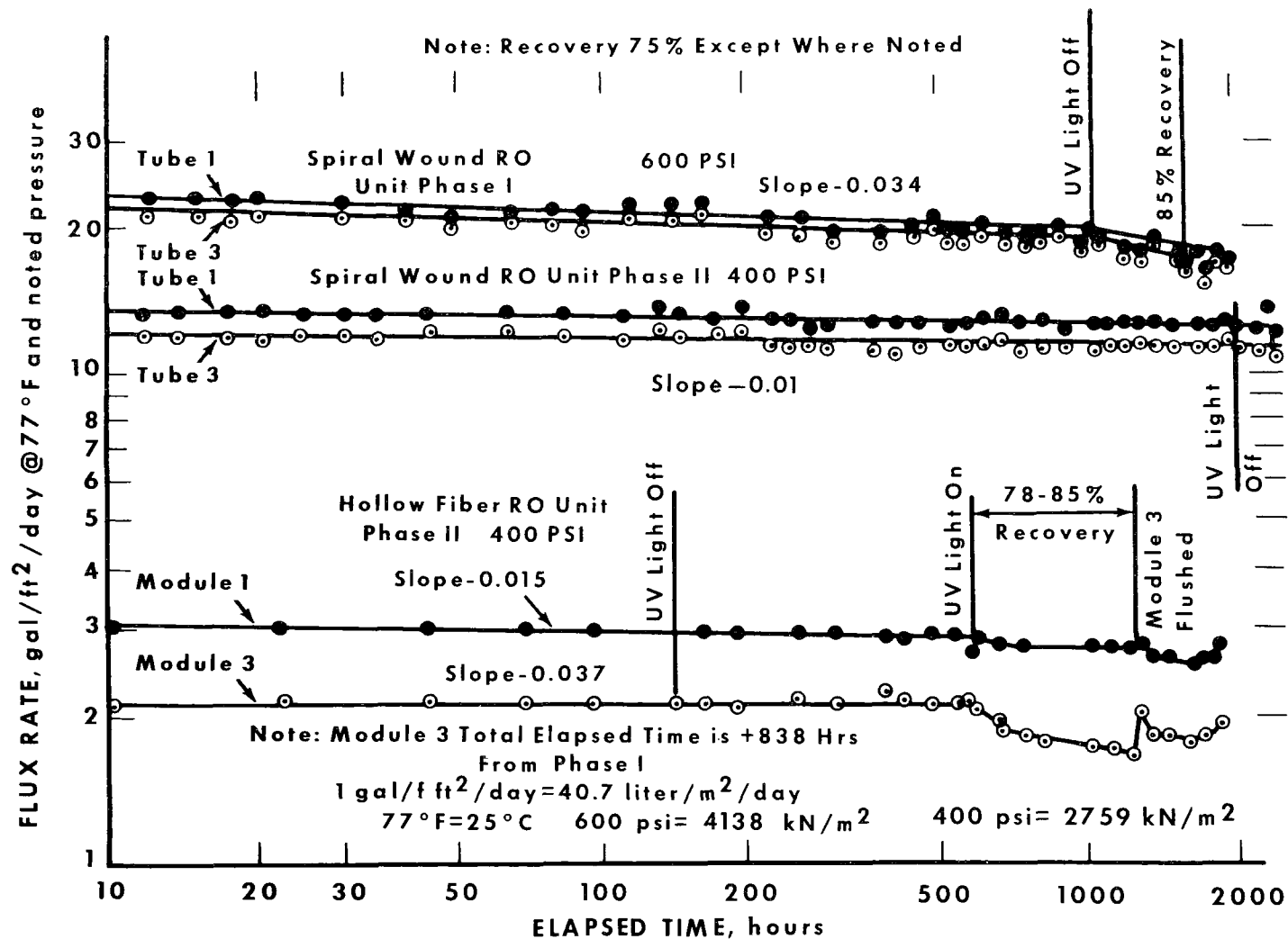


Figure 23

A summary of reverse osmosis flux trends at Mocanaqua, Pa.

was detected in the routine chemical analyses as noted in Table 35. At 75 percent recovery and the UV off, it was felt that bacterial-propagated iron precipitation was causing the flux decline.

Operating parameters for the spiral-wound unit during the 84 percent recovery run are given in Table 34.

Chemical analyses for the 75 percent recovery operation (Table 35) indicate a 99+ percent rejection on all multivalent ions. Product waters would still require treatment for iron and manganese and pH adjustment before potable water quality criteria could be met.

### Spiral-Wound Phase II Studies

The manufacturer suggested that increasing the b/p flow ratio would decrease the log-log slope observed during Phase I. One way of accomplishing a b/p increase was to lower the operating pressure and thereby reduce product flow. Lowering input pressure to  $2758 \text{ kN/m}^2$  (400 psi) would also serve to lessen membrane compaction which contributes to flux losses. During Phase I, the maximum b/p ratio per module was 12:1 and the minimum was 5:1 (from Table 33). During Phase II, the maximum b/p ratio was 22:1 and the minimum 10:1 (Table 36) which amounted to about a 200 percent increase over Phase I.

As the earlier oxidation tests had shown pH control to be an effective oxidation inhibitor and as the lower pH would also inhibit precipitation of the ferric iron already present, sulfuric acid was injected into the feed water to lower the blended feed pH to 2.9. The UV light was also used during the majority of this Phase II study.

Table 36 presents the operating parameters for this 2,454 hr Phase II study at 75 percent recovery.

Early in the study, leaks were observed in tubes 1 and 2. By probing each module and measuring the conductivity of product water at various points along the inside of the modules' product tubes,

Table 34. OPERATING PARAMETERS FOR SPIRAL-WOUND PHASE I STUDY AT 84 PERCENT RECOVERY AT MOCANAQUA, PENNSYLVANIA

Parameter	Value
Raw water feed flow, gpm	4.92
Product water flow, gpm	4.13
Brine water discharged, gpm	0.79
Brine water recycled, gpm	5.50
Minimum brine/product flow ratio (Tubes 1 & 2), ratio/module	8:1
Maximum brine/product flow ratio (Tube 3), ratio/module	12:1
Water recovery, percent	83.9
Recovery of blended feed, percent	39.6
Feed pressure, psig	600.0
Feed water temperature, °F	66.6
Tube one flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77°F	17.03
Tube two flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77°F	17.06
Tube three flux, gal/ft <sup>2</sup> /day @ 600 psi net and 77°F	16.25
Length of run, hours	70
Date of run	July 13 - July 17, 1971

All values are means from four data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77°F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25°F, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 35. CHEMICAL ANALYSES FOR SPIRAL-WOUND STUDIES AT MOCANAQUA, PENNSYLVANIA

Sample Designation	pH	Cond.	Acidity	Calcium	Magnesium	Total iron	Ferrous iron	Aluminum	Sulfate	Manganese	Dissolved oxygen
<u>Spiral-wound Phase I @ 75 Percent Recovery</u>											
Raw feed	3.4	1080	240	130	88	77	64	12	750	-	<1.0
Blended feed	3.1	2070	460	260	170	180	130	24	1340	-	<1.0
Brine	2.9	3540	810	490	310	330	250	44	2300	-	<1.0
Product	4.4	17	38	0.4	0.3	0.4	0.3	0.2	0.9		
Rejections (a)		99.2%	91.7%	99.8%	99.8%	99.8%	99.8%	99.2%	99.9%		
<u>Spiral-wound Phase I @ 85 Percent Recovery</u>											
Raw feed	3.4	1010	210	180	130	140	78	15	850		
Blended feed	3.0	2800	700	400	380	310	250	55	1420		
Brine(b)			(1260)	(1080)	(780)	(840)	(470)	(90)	(5100)		
Brine	2.9	4800	1290	760	710	540	440	100	2840		
Product	4.4	23	10	0.7	0.8	0.5	0.35	0.5	1.0		
<u>Spiral-wound Phase II @ 75 Percent Recovery</u>											
Raw feed	3.4	1110	220	140	110	100	73	14	930	17	
Acidified feed	2.9	1520	420	140	110	100	77	14	980	17	
Blended feed	2.8	2830	610	330	260	250	190	33	2110	43	
Brine	2.7	4150	880	520	380	370	280	54	3130	68	
Total product	3.8	67	33	1.3	4.0	2.4	2.0	0.8	19	0.5	
Overall rejections(a)		97.6%	94.6%	99.6%	98.5%	99.0%	98.9%	97.6%	99.1%	98.8%	
Tube 1		86	-	1.6	3.1	3.3	-	1.1	30	0.6	
Rejections(a)		97.0%		99.5%	98.8%	98.7%	-	96.7%	98.6%	98.6%	
Tube 3		37		0.55	0.75	0.68	-	0.75	5.8	0.21	
Rejections(a)		98.7%		99.8%	99.7%	99.7%		97.7%	99.7%	99.5%	

(a) Rejections = (blended feed - product)/blended feed X 100.

(b) Brine values in parenthesis were calculated based on the recovery of the reverse osmosis unit and assuming the raw feed values were correct. At 83.4 percent recovery, the concentration factor is 6.02. This calculation was necessary since massive precipitation occurred in the brine sample before analysis could be made at Norton.

Note: All units are mg/l except pH and specific conductance (micromhos/cm).



Table 36. OPERATING PARAMETERS FOR SPIRAL-WOUND PHASE II STUDY AT 75 PERCENT RECOVERY AT MOCANAQUA, PENNSYLVANIA

Parameter	Value
Raw water feed flow, gpm	5.18
Product water flow, gpm	3.86
Brine water discharged, gpm	1.32
Brine water recycled, gpm	6.32
Minimum brine/product flow ratio (Tubes 1 & 2), ratio/module	10:1
Maximum brine/product flow ratio (Tube 3), ratio/module	22:1
Water recovery, percent	74.5
Recovery of blended feed, percent	33.6
Feed pressure, psig	399
Feed water temperature, °F	66.6
Tube one flux, gal/ft <sup>2</sup> /day @ 400 psi net and 77°F	12.81
Tube two flux, gal/ft <sup>2</sup> /day @ 400 psi net and 77°F	12.55
Tube three flux, gal/ft <sup>2</sup> /day @ 400 psi net and 77°F	11.58
Length of run, hours	2,454
Date of run	July 27 - November 9, 1971

All values are means from 100 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

all leaks were found to be near the ends of the modules where glue connected the membrane to the perforated product tube (see Figure 1). The modules weren't replaced because considerable operating time would be lost and since modules in tube 3 had no leaks, their product quality would be representative of normal modules. Also, as the leaks in tube 1 and 2 were very small, they would have no effect on flux studies. Therefore, chemistry data in Table 35 are given for product water from tubes 1 and 3 as well as for the entire unit.

Although unit rejections were lower for Phase II than for Phase I because of the leaks, tube 3 rejections were comparable to Phase I results.

A log-log plot of Phase II flux is given in Figure 23. Log-log slopes of  $-0.012$  for tube 1 and  $-0.009$  for tube 3 were obtained during the 2,454 hr of operation at 75 percent recovery. These values were improvements over the  $-0.034$  slopes from Phase I. The combination of acid injection to inhibit precipitation of ferric hydroxide and the higher b/p ratios and brine flow rates were believed responsible for the flux stabilization. Discontinuing use of the ultraviolet light at 2,002.5 hr elapsed time had no apparent effect on flux stability.

Possibly the higher b/p ratio and correspondingly higher brine flow rates--or acid injection alone--may have been solely responsible for flux improvement, but unfortunately, no tests were made to prove or disprove this conjecture.

A phosphoric acid flush at the end of the 2,454 hr study did not improve flux.

Approximately 60 ml of sulfuric acid (98 percent, technical grade) was required to treat each 1,000 gal of water entering the RO unit in order to lower blended feed pH to 2.9. This amounted to 27 mg of concentrated acid per liter of water treated.

### Hollow-Fiber Phase I Studies

Phase I<sup>16</sup> hollow-fiber testing began with a single permeator operating at 75 percent recovery at 2758 kN/m<sup>2</sup> (400 psi) and continued for a total of 838 hr. Operating parameters are given in Table 37 and chemical data are presented in Table 40.

Rejections of all multivalent ions were in the range of 99 percent based on raw feed. These rejections, though slightly less than the spiral-wound, were still excellent. As with the spiral unit, the product water would require treatment for pH, iron, and manganese before potable standards could be met.

The flux trend for the single hollow-fiber permeator is shown linearly in Figure 24 and on a log-log basis in Figure 25. The log-log flux decline slope was 0.037 during the 838 hr study. This flux decline slope was comparable to Phase I spiral-wound results. A small increase in pressure drop across the permeator was observed which probably indicated minor iron fouling.

### Phase II Hollow-Fiber Studies

For Phase II studies, two additional permeators were added to the Phase I system to form a 2-1 array as shown in Figure 17. The Phase I permeator, which had accumulated 838 hr of operation, was used as the last permeator in the array. The permeators were operated in this 2-1 array to allow high recovery experiments and confine the expected calcium sulfate fouling to a single permeator. Generally, hollow-fiber units are not used in staged arrays but are arrayed for parallel operation since brine flow requirements for hollow-fiber systems are not as critical as for tubular and spiral-wound systems.

During Phase II, several variations in operating parameters were made. In order to evaluate the effect of the ultraviolet light on system operation, the light was turned off from 140 hr elapsed time (e.t.) through 595 hr e.t. This time interval represented 978-1433 hr e.t. on permeator number 3 (last stage permeator). As seen in

Table 37. OPERATING PARAMETERS FOR HOLLOW-FIBER PHASE I STUDY AT 75 PERCENT RECOVERY AT MOCANAQUA, PENNSYLVANIA

Parameter	Value
Raw water feed flow, gpm	2.08
Product water flow, gpm	1.55
Brine water discharged, gpm	0.53
Water recovery, percent	74.4
Feed pressure, psig	400.0
Feed water temperature, °F	53.3
Unit flux, gal/ft <sup>2</sup> /day @ 77°F and 400 psi net	2.32
Length of run, hours	838

All values are means from 78 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

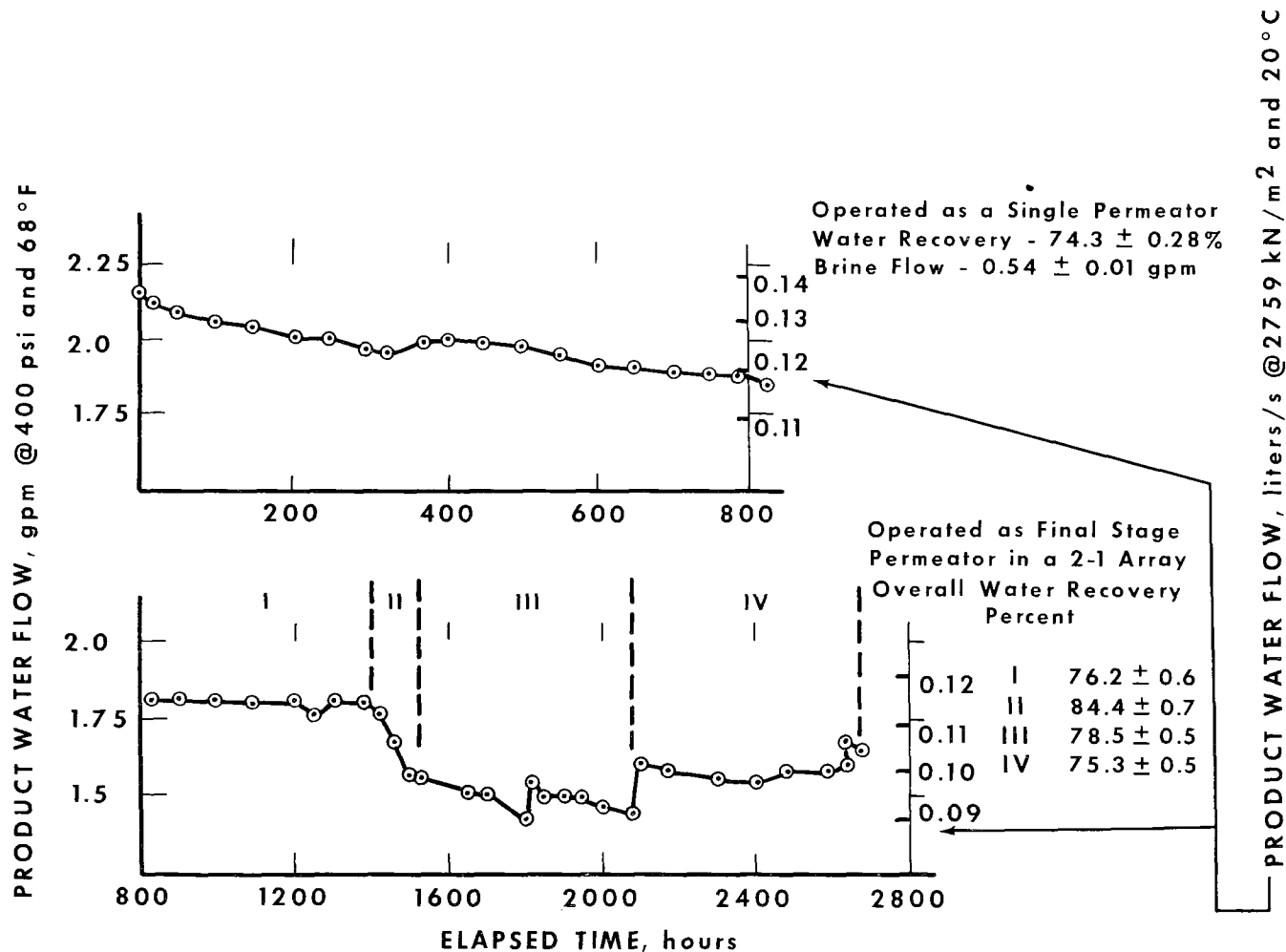


Figure 24  
Operational history of hollow-fiber permeator #691<sup>(15,16)</sup>  
during the Mocanaqua study

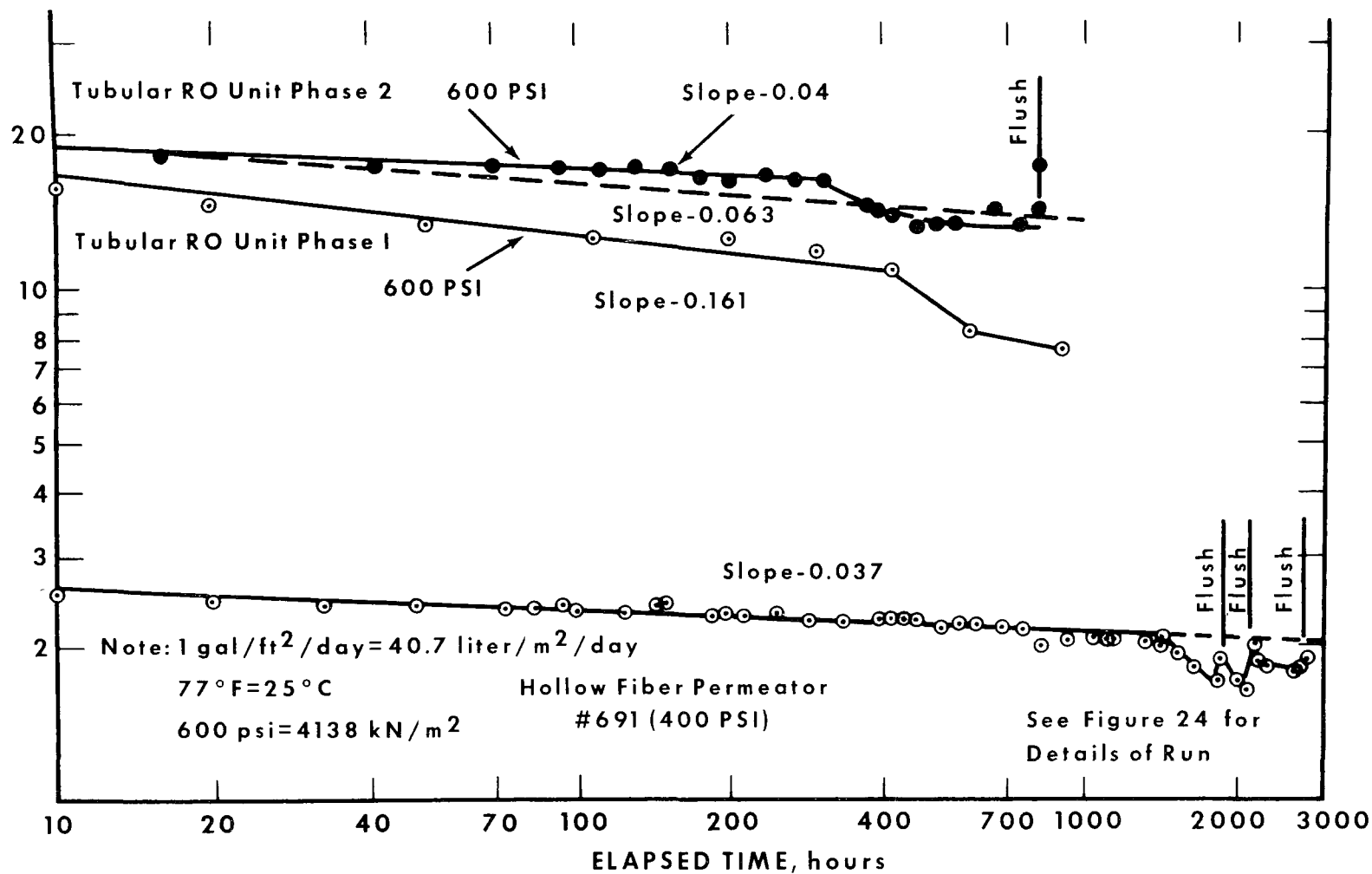


Figure 25  
Tubular and hollow-fiber reverse osmosis unit flux  
trends during the Mocanaqua study.

Figure 23, no apparent flux trend change occurred as a result of no UV. This was opposite to the dramatic slope change which occurred on spiral-wound when the UV was turned off.

At 390 hr through 426 hr, e.t., the system recovery was increased to 85 percent. This increase in system recovery had very little effect on the recoveries of permeators 1 and 2 whose recoveries were still below 65 percent. Thus, very little change in flux occurred in the first two permeators during this high system recovery operation. Permeator 3, however, which was subject to the most severe pollutant concentrations, suffered a drastic flux loss. Upon lowering recovery again to 75 percent, permeator 3's flux again stabilized (Figure 23).

At 596 hr elapsed time (1,434 for permeator 3), the UV light was turned on again but system recovery was increased to 85 percent. These operating conditions were maintained for 111 hr, including operating at 80 percent recovery for 38 hr, before system recovery was lowered (707 hr e.t., 1,545 e.t. for permeator number 3).

Again, severe flux losses occurred in permeator 3 (log-log slope =  $-1.77$ ). Although the flux in permeator 3 stabilized, it was now following a significantly steeper flux decline slope (log-log slope =  $-0.36$  at 78-80 percent recovery). A subsequent flush with disinfectant failed to improve flux. Sodium hydrosulfide was used to flush permeator 3 at 2,081 hr (on permeator 3) and successfully restored flux to the original flux decline slope of  $-0.037$  at 78 percent recovery. Flux immediately dropped again, however, but stabilized at lower values until the end of the run at 2,670 hr e.t. (permeator 3).

Permeators 1 and 2 appeared to suffer a flux slope change near 600 hr elapsed time after following an initial slope of  $-0.015$  until that time. Following the 85 percent recovery test which ended at 707 hr elapsed time, first stage permeator flux stabilized following a log-log slope of  $-0.03$  for approximately 540 hours until 1,243 hr e.t. During the last 590 hr of operation, all three permeators lost

and then regained flux prior to a final sodium hydrosulfide flush. This flush virtually restored first stage permeator flux to the original -0.015 slope values. Since the test was terminated at this point, it was not possible to determine if the -0.015 slope could be maintained following the flush. Although the flush improved permeator 3's flux, it did not return the flux to the original slope values.

A post mortem analysis of permeator number 3 by the manufacturer revealed that the fouling was largely due, as expected, to calcium sulfate precipitation.

In the case of the two first stage permeators whose flux had been restored by the final flush, an additional  $214 \text{ kN/m}^2$  (31 psi) pressure drop had been acquired during the study which was not removed. Since neither of these first stage permeators had ever operated above 66 percent recovery, it must be assumed that iron fouling caused the flux losses and pressure drop increase as it is unlikely that calcium sulfate would precipitate at that recovery level on the Mocanaqua water.

Operating parameters for Phase II hollow fiber at 75 and 85 percent recovery are given in Tables 38 and 39 respectively. Chemical data from 75 percent recovery operations are reported in Table 40.

Rejections during Phase II were comparable to Phase I results, i.e., in the range of 99 percent based on raw feed.

A complete log-log flux plot for the initial permeator, which was used both in Phase I and Phase II, is given in Figure 25. This permeator operated for 2,670 hr (838 during Phase I and 1,832 during Phase II).

Significant variations were noted in the log-log flux curve of the hollow-fiber unit. The slope appeared to increase as brine flow decreased and a possible relationship may exist in the form of a b/p flow limit although insufficient data were available to substantiate this relationship. As brine flow rates decreased, recovery and risk of precipitation increased and this may have caused



Table 38. OPERATING PARAMETERS FOR HOLLOW-FIBER PHASE II STUDY AT  
75 PERCENT RECOVERY AT MOCANAQUA, PENNSYLVANIA

Parameter	Value
Raw water feed flow, gpm	6.18
Total product flow, gpm	4.72
Brine water discharged, gpm	1.46
Unit water recovery, percent	76.4
Feed pressure, psig	400
Feed temperature, °F	54.3
Permeator No. 1 product flow, gpm	1.86
Recovery, permeator No. 1, percent	59.9
Flux, permeator No. 1, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	2.78
Permeator No. 2 product flow, gpm	1.83
Recovery, permeator No. 2, percent	59.5
Flux, permeator No. 2, gal/ft <sup>2</sup> /day @ 400 psi & 77°F	2.74
Permeator No. 3 product flow, gpm	1.03
Recovery, permeator No. 3, percent	41.4
Flux, permeator No. 3, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	1.92
Length of run, hours	1667
Date of run	June 10 - August 28, 1971

All values are means from 83 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 39. OPERATING PARAMETERS FOR HOLLOW-FIBER PHASE II STUDY AT 85 PERCENT RECOVERY AT MOCANAQUA, PENNSYLVANIA

Parameter	Value
Raw water feed flow, gpm	5.73
Total product flow, gpm	4.86
Brine water discharged, gpm	0.87
Unit water recovery, percent	84.8
Feed pressure, psig	400
Feed temperature, °F	54.0
Permeator No. 1 product flow, gpm	1.89
Recovery, permeator No. 1, percent	65.5
Flux, permeator No. 1, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	2.84
Permeator No. 2 product flow, gpm	1.85
Recovery, permeator No. 2, percent	65.0
Flux, permeator No. 2, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	2.78
Permeator No. 3 product flow, gpm	1.12
Recovery, permeator No. 3, percent	56.3
Flux, permeator No. 3, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	2.10
Total operating time @ 85 percent recovery, hours	147
Longest run, hours	111
Date of run	6/26-6/28/71, 7/5-7/9/71

All values are means for 11 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 40. CHEMISTRY ANALYSES FOR HOLLOW-FIBER STUDIES AT MOCANAQUA, PENNSYLVANIA

Sample Designation	pH	Cond.	Acidity	Calcium	Magnesium	Total iron	Ferrous iron	Aluminum	Sulfate	TDS	Manganese	DO	Silica
Phase I @ 75 Percent Recovery (15,16)													
Raw feed <sup>(a)</sup>	3.4	-	-	110	80	65	59	8.0	740	1250	14	-	10
Brine <sup>(a)</sup>	2.9	-	-	420	310	260	230	31	2700	4900	53	-	43
Product <sup>(a)</sup>	4.5	-	-	0.55	0.59	0.54	0.52	0.18	2.2	28.	0.08	-	0.49
Rejections <sup>(b)</sup>		-	-	99.5%	99.3%	99.2%	99.1%	97.8%	99.7%	97.8%	99.4%	-	95.1%
Phase II @ 75 Percent Recovery													
Raw feed	3.4	1020	210	150	115	110	71	15	940	1320 <sup>(a)</sup>	14 <sup>(a)</sup>	<1.0 <sup>(a)</sup>	11 <sup>(a)</sup>
Brine	3.0	3400	720	590	410	440	300	58	3000	5810 <sup>(a)</sup>	57 <sup>(a)</sup>	<1.0 <sup>(a)</sup>	49 <sup>(a)</sup>
Product	4.3	32	32	1.2	1.4	1.2	0.76	0.80	4.6	2.5 <sup>(a)</sup>	0.12 <sup>(a)</sup>	<1.0 <sup>(a)</sup>	0.83 <sup>(a)</sup>
Rejections <sup>(b)</sup>		96.9%	84.8%	99.2%	98.8%	98.9%	98.9%	94.7%	99.5%	98.1%	99.1%		92.5%

All units are mg/l except for pH and specific conductance (micromhos/cm).

(a) Analyses by Rex Chainbelt. All other analyses by EPA.

(b) Rejections =  $\frac{\text{Raw feed concentration} - \text{product concentration}}{\text{Raw feed concentration}} \times 100.$

the observed slope changes. Whatever the reason, flux slopes were minimized when the brine flow rate was in excess of 3.785 l/min (1 gal/min).

#### Tubular Unit<sup>15,16</sup> Phase I Studies

The tubular RO system was also operated in two separate phases during this study. Phase I utilized 60 Type 310 modules in a 6-4-2 array with five modules in each series in each row. The last two modules in bank 2 and the last 3 modules in bank 3 contained volume displacement rods (VDR) that increased the brine velocity. The normal inside diameter in the tubular system is  $\frac{1}{2}$  in (1.27 cm) which corresponds to a linear brine velocity of 1.64 ft/sec per gpm of brine flow (0.132 m/sec per liter/min). The volume displacement rods effectively increased this velocity to 2.5 ft/sec per gpm (0.2 m/sec per liter/min) of brine flow. When utilizing VDR's, headloss through the module increased significantly. In a module without VDR's, the headloss at one gpm (3.785 l/min) brine flow was five psi (34.5 kN/m<sup>2</sup>) per module, while with VDR's this increased to 22 psi (151.7 kN/m<sup>2</sup>) per module.

Initial Phase I operation was at 600 psi (4138 kN/m<sup>2</sup>) and 75 percent recovery. During Phase I, the product water flux decreased steadily from 13 gal/ft<sup>2</sup>/day to 8.5 gal/ft<sup>2</sup>/day (345 l/m<sup>2</sup>/day) in only 480 hours. It was originally assumed that the system had been contaminated with iron oxidizing bacteria because of trouble experienced with the UV light. At 160 hr, the system was disinfected with a quaternary ammonium compound (L-11-X), and a slight increase in flux was noted. However, membrane relaxation probably occurred during this time since the unit operated at low pressure. Relaxation generally results in a flux increase for a short period of time. Immediately after the disinfection, the flux continued to decline rapidly. At this point, it was felt that the brine velocities might possibly be too low and that concentration polarization effects were causing the rapid fouling. Minimum brine velocities were increased from 1.2 - 1.4 ft/sec to 2.0 - 2.2 ft/sec (0.37 m/s - 0.67 m/s).

Phase I chemical data are presented in Table 41.

### Tubular Unit Phase II Studies

At the end of Phase I, it was noted that the flux declines experienced with the tubular system were not experienced with the hollow-fiber system or the spiral-wound system also operating alongside. It was also noted that both the spiral-wound system and the hollow-fiber system had considerably lower salt passage (higher rejection) as compared to the tubular system. The high salt passage of the tubular 310 membrane may have had some influence on the flux declines experienced. To test this, five high-flux--low-salt-passage modules (type E610) were installed and put into operation for Phase II. During Phase II, recovery was limited to less than 50 percent at  $4138 \text{ kN/m}^2$  (600 psi) due to the use of only five modules. Operating parameters for this 807 hr study are given in Table 42 and chemical data are presented in Table 41. Rejections were higher for Phase II (type E610) membranes than for Phase I membranes (type 310). Figure 25 presents the flux history for these modules. An extremely high initial compaction was experienced during the first few hours of operation. The flux then stabilized on a -0.040 log-log slope for the first 300 hr. A gradual decline then occurred through about 440 hr, at which time the flux stabilized at  $13.7 \text{ gal/ft}^2/\text{day}$  ( $557 \text{ l/m}^2/\text{day}$ ) for the remainder of the study. The change in the flux decline slope experienced from near 300 hours e.t. was also noticed to a lesser degree on the hollow-fiber unit and was believed caused by a higher-than-normal iron (III) content in the AMD. The decline was probably entirely due to iron fouling since operation at 40-45 percent recovery was well below the  $\text{CaSO}_4$  fouling range. The modules were flushed with a sodium hydrosulfite solution (4 wt percent) for 1 hr. This resulted in a dramatic increase in flux as shown in Figure 25. Since additional operating time was not available, it is not known how much of this flux increase was due to cleaning and how much was due to membrane relaxation. It is felt that a substantial gain was accomplished since membrane relaxation

Table 41. CHEMISTRY ANALYSES FOR TUBULAR STUDIES<sup>(15,16)</sup> AT MOCANAQUA, PENNSYLVANIA

Sample Designation	pH	Cond.	Acid-ity	Cal-cium	Magne-sium	Total iron	Ferrous iron	Alum-inum	Sul-fate	TDS	Manga-nese	DO	Sil-ica
<u>Phase I @ 75 Percent Recovery</u>													
Raw feed	3.4	1050	250	125	92	78	61	12	660	1320 <sup>(a)</sup>	14 <sup>(a)</sup>	-	11
Brine	3.1	2400	560	330	240	230	150	30	1650	3520 <sup>(a)</sup>	39 <sup>(a)</sup>	-	16
Product	4.2	46	46	2.2	1.4	0.9	1.0	1.0	4.4	53 <sup>(a)</sup>	0.31 <sup>(a)</sup>	-	7.2
Rejections		95.6%	81.6%	98.2%	98.5%	98.8%	98.4%	91.7%	99.3%	96.0%	97.8%	-	34.5%
<u>Phase II @ 42.5 Percent Recovery</u>													
Raw feed <sup>(a)</sup>	3.4	-	-	110	83	70	63	8.3	800	1320	14	-	12
Brine <sup>(a)</sup>	3.1	-	-	200	150	130	160	15	1450	2300	25	-	21
Product <sup>(a)</sup>	4.3	-	-	0.6	0.45	0.4	0.62	0.15	2.0	25	0.08	-	1.0
Rejections	-	-	-	99.5%	99.5%	99.4%	99.0%	98.2%	99.8%	99.6%	99.4%	-	91.7%

<sup>(a)</sup>Analyses by Rex Chainbelt.

All other analyses by EPA.

All units are mg/l except for pH and specific conductance (micromhos/cm).

Rejections =  $\frac{\text{Raw feed concentration} - \text{product concentration}}{\text{Raw feed concentration}} \times 100.$

Table 42. OPERATING PARAMETERS FOR TUBULAR PHASE II STUDY AT 43 PERCENT RECOVERY(15,16) AT MOCANAQUA, PENNSYLVANIA

Parameter	Value
Raw water feed flow, gpm	1.48
Product water flow, gpm	0.63
Brine water discharged, gpm	0.85
Water recovery, percent	42.5
Feed pressure, psig	617.0
Feed water temperature, °F	55.0
Unit flux, gal/ft <sup>2</sup> /day @ 77°F & 600 psi net	15.60
Length of run, hours	807

All values are means from 34 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 600 psi and 77°F) to liters/m<sup>2</sup>/day @ 4138 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

alone would not account for an increase in flux of about 33 percent.

The salt passage properties for both the types 310 and 610 tubular modules are shown in Table 43. The salt passage was calculated based on average brine concentration experienced on the membrane, i.e., the average of feed and brine concentrations. This procedure allows comparison of salt passages while operating the RO system at different product water recoveries.

Generally, salt passage for the type 310 modules ranged from 1 to 1.5 percent for Ca, Mn, Fe, Al, and  $\text{SO}_4$ . Silica passage was extremely high at an average percent of 54. The type 610 modules had significantly lower salt passage; i.e., 0.4 to 0.5 percent for Ca, Mg, Mn, Fe, Al, and  $\text{SO}_4$ . Silica passage was also considerably lower than the 310 modules at an average percent of 6.2 percent passage. No apparent changes occurred in the salt passage throughout the operational period.

The mechanical operation of the tubular system was excellent. No module failures were experienced over the entire 2,800 hr operation. This reflected the improvements made in tube construction since the 1969 study.<sup>4</sup>

In summary, a number of points can be made regarding tubular system operation. The use of volume displacement rods is definitely not recommended. The price paid in headloss far exceeds the benefits obtained. If higher velocities are required, it appears recirculation of brine would be the preferred alternative. With regard to required velocities, it appears that a minimum velocity of about 1.5 ft/sec (0.46 m/s) is desirable, since operation at this velocity with the higher-flux--low-salt-passage modules was satisfactory. It should be noted, however, that the recoveries during Phase II were quite low (45-70 percent), and that operation at higher recoveries may require higher velocities to offset the concentration polarization effects due to higher brine concentrations. Additional study at higher recoveries is necessary to answer this question.



Table 43. SALT PASSAGE FOR TUBULAR STUDIES<sup>(15,16)</sup> AT MOCANAQUA, PENNSYLVANIA

Parameter	Salt Passage - Percent	
	Type 310 Membrane Phase I	Type 610 Membrane Phase II
Calcium	1.45	0.43
Magnesium	1.11	0.36
Manganese	1.21	0.45
Total iron	1.19	0.45
Aluminum	1.40	0.39
Silica	53.6	5.88
TDS	2.34	0.87
Ferrous iron	1.15	0.51
Sulfate	1.27	0.20

Analyses by Rex Chainbelt.

Note: Salt passage is related to salt rejection. Whereas rejection measures a membrane's impermeability to passage of ions, salt passage is a measure of the relative permeability to passage of ions. Therefore, salt rejection plus salt passage equals 100 percent if both are measured in respect to the same initial concentration.

It is not known if the high initial flux loss experienced during Phase I with the type 310 modules was specific for the modules utilized or a result of the higher salt passage. In any event, low-salt-passage modules are definitely recommended for both flux and product water quality considerations.

Comparing the flux history of Phase I 310 modules to the flux history from the 1969 field testing,<sup>1</sup> significantly lower flux declines were noted in the present study. For example, greater than 80 percent of the original flux was lost in 400 hr in the previous study compared to about 45 percent of the original flux in the present study. This would indicate that the pretreatment system did have some effect on the tubular system operation.

A more in-depth report of the hollow-fiber and tubular studies at Mocanaqua is available<sup>16</sup>, and a complete discussion of system comparisons made from the results of this Mocanaqua study is presented in the "Discussion" section of this report.

#### Calcium Sulfate Fouling at Mocanaqua

Very little or no calcium sulfate fouling occurred at 75 percent recovery since both the spiral-wound and hollow-fiber log-log flux plots had shallow slopes and were linear. In contrast, the severe fouling observed at 85 percent recovery was due to calcium sulfate precipitation. Therefore, at some point between 75 and 85 percent recovery, the solubility of calcium sulfate was exceeded and precipitation occurred.

At 75 percent recovery, the brine was concentrated four times in relation to the raw feed; at 85 percent, the brine concentration was 6.67 times that of the raw feed. Typical calcium and sulfate values were used to generate Table 44.

Table 44. CALCIUM SULFATE MOLAR SOLUBILITY PRODUCTS

Recovery	Concentration factor	Raw Feed		Brine		Molar solubility product
		calcium mg/l	sulfate mg/l	calcium mg/l	sulfate mg/l	
75%	4.	120	800	480	1920	$24 \times 10^{-5}$
80%	5.	120	800	600	3000	$47 \times 10^{-5}$
85%	6.67	120	800	800	5340	$111 \times 10^{-5}$

As the recovery was increased from 75 to 85 percent, the product of molar concentrations<sup>3</sup> of calcium and sulfate in the brine increased from  $24 \times 10^{-5}$  to  $111 \times 10^{-5}$ . Since no  $\text{CaSO}_4$  precipitation occurred at 75 percent recovery, the limiting concentration was in excess of  $24 \times 10^{-5}$ ; if the point of precipitation were midway between 75 and 85 percent recovery, this would correspond to a solubility product near  $50 \times 10^{-5}$ . It is felt that precipitation occurred in the solubility product range of 35 and  $50 \times 10^{-5}$ .

#### NORTON FERRIC IRON STUDIES COMPARING HOLLOW-FIBER AND SPIRAL-WOUND UNITS

Following termination of the RO study at Mocanaqua, EPA returned two of the three hollow-fiber modules to Norton. These were permeators 1 and 2 of the Mocanaqua 2-1 array which had operated for 1,832 hr at Mocanaqua at recoveries ranging from 58 to 66 percent. Also returned to Norton was the 4 K spiral-wound unit which had accumulated 2,454 hours of 75 percent recovery operation at Mocanaqua.

At Norton, the hollow-fiber studies were conducted in two phases. Phase I consisted of the two first stage permeators from Mocanaqua which were operated in parallel. During Phase II, three new permeators were operated in a 2-1 array similar to the Mocanaqua Phase II study.

#### Hollow-Fiber Studies - Phase I

In the parallel array, recoveries of the individual permeators could be independently varied. This allowed direct comparison of

fouling trends as related to brine concentration. Since minimum brine flows were not a problem with hollow-fiber systems, recycling brine to maintain a minimum flow was not felt necessary by the manufacturer.

Differential pressure (the pressure loss across a module) is an indicator of fouling in a permeator. Although the normal differential pressure ( $\Delta P$ ) for a hollow-fiber permeator is 10 psi ( $69 \text{ kN/m}^2$ ), the  $\Delta P$  of the two permeators at the beginning of the Norton study was 49 psi ( $338 \text{ kN/m}^2$ ). Apparently the fouling observed at Mocanaqua had not been completely removed before the Norton study began.

Operation of the modules on Grassy Run water began at approximately 75 percent recovery and 400 psi ( $2758 \text{ kN/m}^2$ ). These conditions were maintained for the first 500 hr (2,325 total hours) of operation. During this period,  $\Delta P$  increased from 50 to 90 psi ( $345$  to  $621 \text{ kN/m}^2$ ) in each permeator, flux declined rapidly, and two sodium hydrosulfide flushes were needed to maintain performance (Figures 26 and 27). Typical operating parameters for the permeators during this period are given in Table 45. The log-log flux decline slope for the first 315 hr of the 500 hr period was  $-.035$ . In the remaining 185 hr, the slope significantly increased to  $-0.45$  in permeator number 2. During the next 750 hr of operation the  $\Delta P$  and flux decline continued to increase even though the recovery had been lowered to 50 percent. The rate of decline was significantly greater in permeator 2 than in permeator 1.

A sodium hydrosulfide--BIZ combination flush dramatically reduced the  $\Delta P$ . Fouling continued, however, despite the 50 percent recovery rate. Salt rejections decreased with each sodium hydrosulfide flush.

In attempts to control the fouling, several variables were investigated to determine their relationship to the problem. Bacteriological effects were studied by UV disinfection of the raw feed

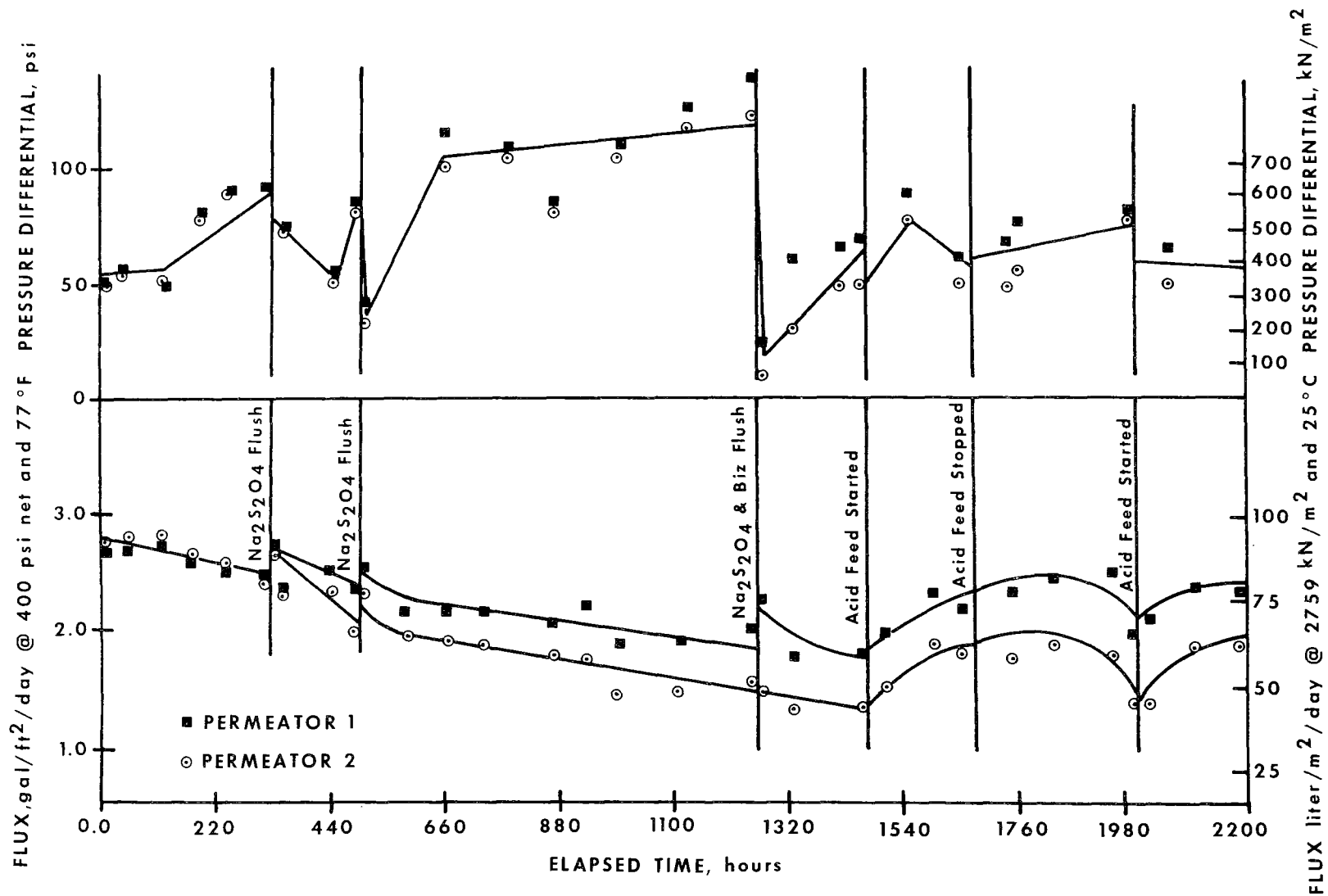
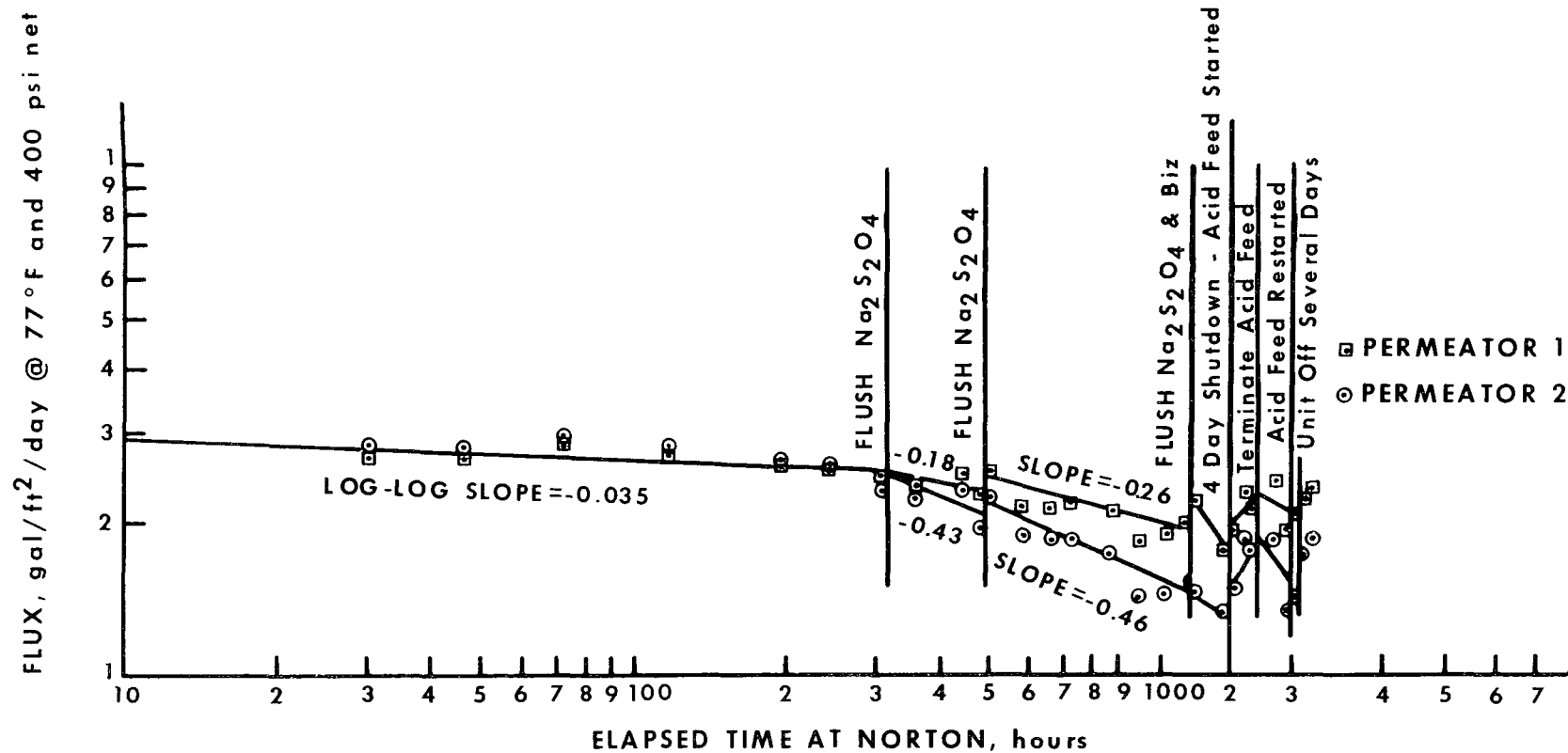


Figure 26

Flux and  $\Delta P$  history for the hollow-fiber phase I study at Norton



NOTE: 1 gal/ft<sup>2</sup>/day = 40.7 liter/m<sup>2</sup>/day

400 psi = 2759 kN/m<sup>2</sup>

77 °F = 25 °C

Figure 27

Flux trends during the two permeator hollow-fiber phase I study at Norton

Table 45. OPERATING PARAMETERS FOR NORTON TWO PERMEATOR HOLLOW-FIBER STUDY AT 72 PERCENT RECOVERY

Parameter	Value	
	No. 1	No. 2
Raw water feed flow, gpm	2.435	2.415
Product water flow, gpm	1.763	1.750
Brine water discharged, gpm	.672	.665
Brine water recycled, gpm	0	0
Water recovery, percent	72.4	72.5
Feed pressure, psig	407.8	
Feed temperature, °F	60.2	
Tube one flux, gal/ft <sup>2</sup> /day @ 400 psi & 77°F	2.601	
Tube two flux, gal/ft <sup>2</sup> /day @ 400 psi & 77°F	2.576	
Length of run, hours	Data thru 500 hours	
Date of run	September 23 - October 14, 1971	

All values are means from 23 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

water, and calcium sulfate concentration and in-module turbulence were studied by lowering the recovery and thus increasing the brine flow rate. None of these factors were successful in flux stabilization, however. Acid injection to lower the feed pH from 2.8 to 2.5 was attempted at 1,500 hr (3,332 hr total on membrane) elapsed time to study the possibility of iron precipitation. As illustrated in Figures 26 and 27, acid injection was relatively successful in flux stabilization, thus confirming the probability of iron fouling. However, acid was so high that the supply of acid at Norton was exhausted in 2 weeks. It required 0.0001 gal of acid per gallon of water treated to lower the influent pH from 2.8 to 2.5 (0.12 ml/l treated).

Since spiral-wound units had performed successfully on the Norton water in the past, it was difficult to understand the inability of the hollow-fiber system to cope with the ferric water. To ensure that some unknown condition in the water would not also affect the spiral system, the relatively dilapidated 10 K spiral unit, which had not operated since June 1970, was restarted using the same modules as were used in 1970. The 10 K unit operated alongside the hollow-fiber unit from September through December 1971 for a total period of 1,094 hr. During this period, the 10 K operated at 400 psi ( $2758 \text{ kN/m}^2$ ) and approximately 65 percent recovery and gained flux in each of the five tubes. At the same time, the hollow-fiber unit was fouling severely.

At the end of the 10 K test, a sodium hydrosulfide flush of the spiral system failed to significantly improve flux. The increase in flux observed over the 1,094 hr period was attributed to gradual removal of fouling that had occurred during the 1970 neutrolosis tests (the last time it was operating).

After approximately 2,200 hr of operation at Norton (4,000 total hr), tests on the two hollow-fiber permeators were discontinued when a satisfactory pressure differential and flux could not be maintained even at low recoveries. The difference in flux stability of the permeators between the Mocanaqua site and Norton is readily apparent in



Figure 28 which is a log-log plot including both sites. The single significant factor in the hollow-fiber test was that acid injection to control influent pH at 2.5 was absolutely necessary to maintain any operation of hollow-fiber permeators on the Norton water (pH 2.8).

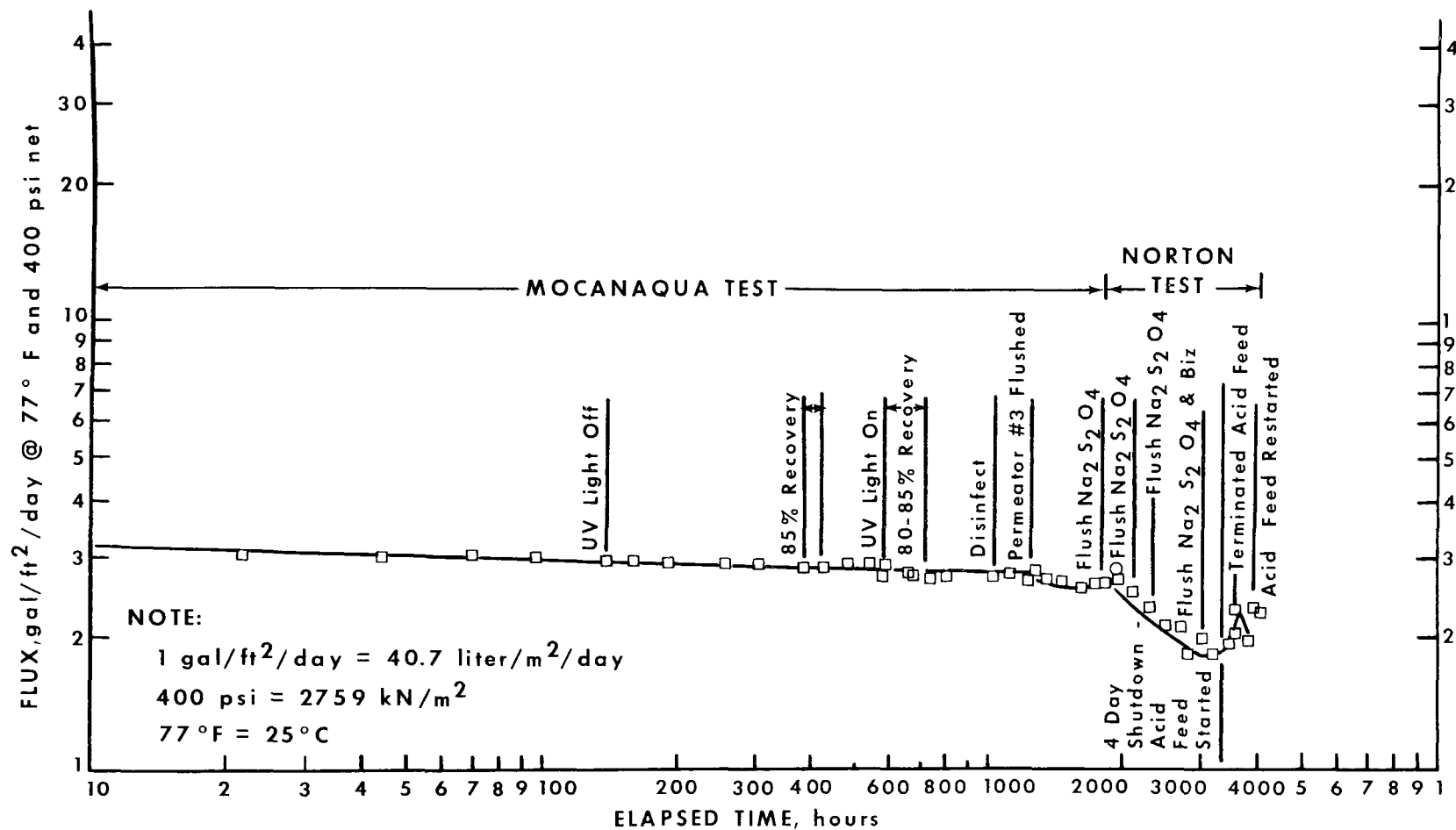
The manufacturer requested one of the permeators to determine cause of fouling. In return, they supplied three new permeators to be installed in a 2-1 array as was used in Mocanaqua.

#### Hollow-Fiber Studies Phase II

Testing on the 2-1 array began January 31, 1972, and continued with relatively stable fluxes as long as  $H_2SO_4$  was injected to maintain a feed pH of 2.5. After 231.1 hr of operation, the pH probe line fouled and stopped flow through the probe. The influent pH rose from 2.5 to 2.8 and  $\Delta P$  across permeators 1 and 2 increased from 13 psi to 110 psi in approximately 8 hr. Flux, when corrected for pressure losses, dropped roughly 10 percent in the same 8 hr period. Permeator 3 was not affected by the influent pH as, even without acid adjustment, the pH into permeator 3 was below pH 2.5 since it received brine from permeators 1 and 2.

A log-log plot of the flux of each of the three permeators is given in Figure 29.

A sodium hydrosulfide flush of permeators 1 and 2 was moderately effective on permeator 1, but a failure occurred in permeator 2. The feed distribution tube, made of polyethylene, collapsed during the flush and allowed the "O" ring seals to fail. Raw water went directly from the feed into the brine line bypassing the membrane altogether. The manufacturer repaired the permeator on-site, flushed it, and restarted the run but a high pressure loss again recurred across permeators 1 and 2. The manufacturer took both permeators back to further investigate the failure and fouling and supplied two new ones to continue the test. Operating parameters for the study are given in Table 46. Typical chemical analyses are



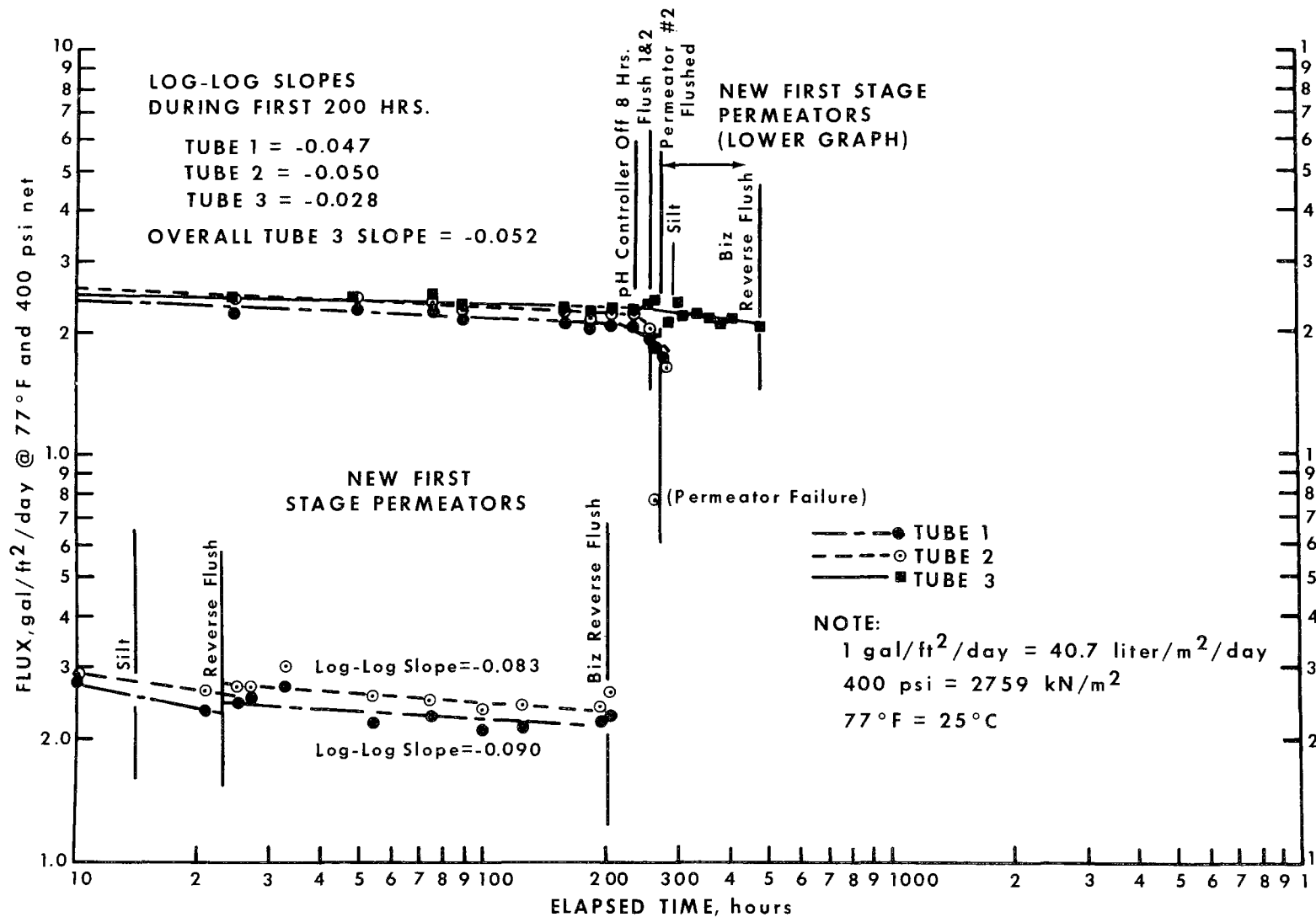


Figure 29  
 Flux trends for 6K hollow-fiber phase II study @ 69.7 percent recovery

Table 46. OPERATING PARAMETERS FOR NORTON HOLLOW-FIBER 3-PERMEATOR PHASE II STUDY AT 70 PERCENT RECOVERY

Parameter	Value
Raw water feed flow, gpm	5.509
Total product flow, gpm	3.869
Product flow, permeator #1, gpm	1.303
Product flow, permeator #2, gpm	1.387
Product flow, permeator #3, gpm	1.179
Brine water flow through 1&2 (each), gpm	1.409
Brine water discharged (#3), gpm	1.640
Recovery - permeator #1, percent	48.0
Recovery - permeator #2, percent	49.6
Recovery - permeator #3, percent	41.8
Total unit recovery, percent	70.2
Feed pressure - unit, psig	400.0
Feed temperature - unit, °F	44.6
Permeator one flux, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	2.195
Permeator two flux, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	2.337
Permeator three flux, gal/ft <sup>2</sup> /day @ 400 psi net & 77°F	2.356
Length of run, hours	279.1
Date of run	January 31-February 15, 1972

All values are means from 9 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

given in Table 47. The high hollow-fiber rejections are significant. The manufacturer reported that manufacturing defects were responsible for the module failure following the sodium hydrosulfide flush.

The two new permeators were installed at 279 hr elapsed time on the unit. Careful modifications of the pH control system were made to insure that the pH probe would not foul as before and operation of the hollow-fiber system was resumed.

Within 20 hr, a severe rain washed sediment from a new mine road into Grassy Run. An immediate flux loss occurred in the two first stage permeators. Correspondingly, the  $\Delta P$  increased from 5 psi to 62 psi (34.5 to 428 kN/m<sup>2</sup>). The third permeator was unaffected. The spiral-wound 4 K unit, operating alongside, suffered no flux loss nor  $\Delta P$  increase during the period.

A reverse flush was partially successful in restoring flux and reducing  $\Delta P$  (from 62 down to 35 psi) (428 to 241 kN/m<sup>2</sup>). After a few additional hours of operation,  $\Delta P$  lowered to a normal value of 9 psi and flux again increased (though still not back to normal). After a few more hours of operation, however, the trend reversed and  $\Delta P$  increased to near 70 psi and flux continued to drop. At 472.6 hr elapsed time (193.1 hr on permeators 1 and 2), testing was terminated as very little improvement in  $\Delta P$  or flux had occurred in permeators 1 and 2. However, permeator 3 was still performing well. A one-hour reverse flow BIZ flush was unsuccessful in reducing  $\Delta P$  or increasing flux in any of the permeators. The flux performance of these permeators is included in Figure 29.

In all the hollow-fiber studies at Norton, flux and  $\Delta P$  stability of the first stage permeators were unsatisfactory. However, the second stage permeator performance was significantly superior to the first stage performance even though the second stage was receiving water with much higher pollutant concentrations.

Since the Phase I Norton tests indicated acid injection was necessary to stabilize flux, it was deduced that iron precipitation

Table 47. CHEMISTRY ANALYSES FOR NORTON STUDY (1972)

	pH	Cond.	Acidity	Calcium	Magnesium	Iron	Aluminum	Manganese	Sulfate
<u>Hollow Fiber 6K Unit - Phase II</u>									
Acidified raw feed	2.6	1570	800	96	29	110	36	4.0	1100
Brine (from 1&2)									
(Feed to #3)	2.3	2950	1520	200	56	220	70	7.7	2300
Final Brine	2.1	5600	2790	330	100	400	120	13	2920
Product #1	3.8	27	55	<.1	<.1	0.2	<.1	0.2	<1.0
Product #2	3.8	48	20	<.1	<.1	0.2	<.1	0.2	7.0
Product #3	3.7	64	14	<.1	<.1	0.2	<.1	0.2	7.7
Rejections #1		98.3%	93.1%	99.9%	99.7%	99.8%	99.7%	95.0%	99.9%
Rejections #3		97.8%	99.1%	99.9%	99.8%	99.9%	99.9%	97.4%	99.7%
<u>Spiral Wound</u>									
Raw Feed	2.7	1800	630	110	30	140	43	3.3	810
Blended Feed	2.5	3200	1370	220	68	290	90	8.1	1820
Brine	2.4	4400	2050	320	96	420	140	14	2800
Total Product	3.6	55	10	0.4	0.1	0.24	0.50	<.01	3.5
Product #1	3.9	60	8	0.1	0.1	0.30	0.58	<.01	3.5
Product #2	3.9	55	7	0.2	0.1	0.25	0.56	<.01	2.7
Product #3	4.0	48	10	0.1	0.1	0.12	0.25	<.01	2.7
Total Rejections		98.3%	99.3%	99.8%	99.9%	99.9%	99.4%	99.9%	99.8%

All units in mg/l except for conductivity (micromhos/cm) and pH.

was causing the observed fouling. This deduction was further reinforced in the first stage of Phase II tests when the pH probe fouled and an immediate flux loss occurred. However, when the siltation problem during the latter part of Phase II caused an immediate  $\Delta P$  increase, some additional insight to the nature of the fouling was gained. Since 10 micron filtration preceded the RO unit, the fouling particles were less than 10 microns in size and probably were colloidal in nature. Possibly, the fouling seen earlier during Phase I was largely colloidal deposition reinforced by iron precipitation.

A first-stage permeator was opened and visually inspected at the end of the Phase II tests. The outside of the fiber bundle, where brine concentrations were the greatest, showed absolutely no fouling as the fibers were extremely clean. Upon dissecting the bundle, the fibers grew darker toward the central distributor tube through which the raw water enters. The fibers immediately surrounding the central distributor were coated with a brown film resembling mud. Samples taken throughout the bundle were sent to West Virginia University for X-ray analyses. Significant quantities of allophane-like (poorly crystalline) material composed of alumina and silica were present on the membrane.<sup>17</sup> The alumina/silica ratios suggested the existence of significant quantities of clays. This result confirmed the diagnosis of colloidal fouling. Also present on the membranes were large amounts of metallic iron particles which were attributed to the carbon steel connecting rod of the Moyno high-pressure pump. The connecting rod sheared at the end of the hollow-fiber test. Dr. Smith of West Virginia University also investigated the use of a combination ultrasonic and Calgon cleaning technique for removal of the residue on the membrane. Calgon served as an effective wetting agent and the ultrasonic treatment completely removed the coating from the membrane surface. However, it is not known whether this technique would be applicable in a module which had not been dissected.

The difference in hollow-fiber flux stability at Mocanaqua and the instability at Norton is attributed to the fact that Grassy Run

at Norton is a surface stream subject to siltation and sewage loads not seen in the underground mine discharge at Mocanaqua. Even though ferric iron was observed to be more difficult to treat than ferrous, it is felt that acid injection to approximately pH 2.5 will control iron precipitation.

The inability of the hollow-fiber system to tolerate colloidal or particulate matter less than 10 microns in size must be deemed a major disadvantage and would significantly limit the application of hollow-fiber systems on acid mine streams unless the problem can be overcome.

### Spiral-Wound Studies

Although the 4 K spiral system was returned to Norton in November 1971, logistical problems delayed resumption of testing until January 30, 1972. This 2 mo down time allowed considerable relaxation to occur in the membrane which had operated for 2454 hr at Mocanaqua. Consequently, when testing began at Norton, the flux rates were in the range of 12 gal/ft<sup>2</sup>/day (490 l/m<sup>2</sup>) (higher than at the end of the Mocanaqua study). In addition to membrane relaxation, corrections for temperature and osmotic pressure at the new site may have resulted in slightly higher flux values.

The osmotic pressure-conductivity relationship for the Norton water is shown in Figure 30.

Operation of the 4 K spiral system at Norton was at 400 psig (2758 kN/m<sup>2</sup>), 70 percent recovery, and better than 10:1 b/p flow ratio. The unit accumulated an additional 1946 hr of operating time to bring the total membrane time to 4400 hr.

Flux performance is shown two ways in Figure 31: in the top plot, the complete flux history for tubes 1 and 3 is shown; in the lower plot, operating time at Norton is presented independently. A least squares regression analysis provided a log-log line of best fit for the Norton operation with a slope of -0.036 for tube 1 and -0.016 for tube 3. Tube one's slope, though very reasonable, was significantly



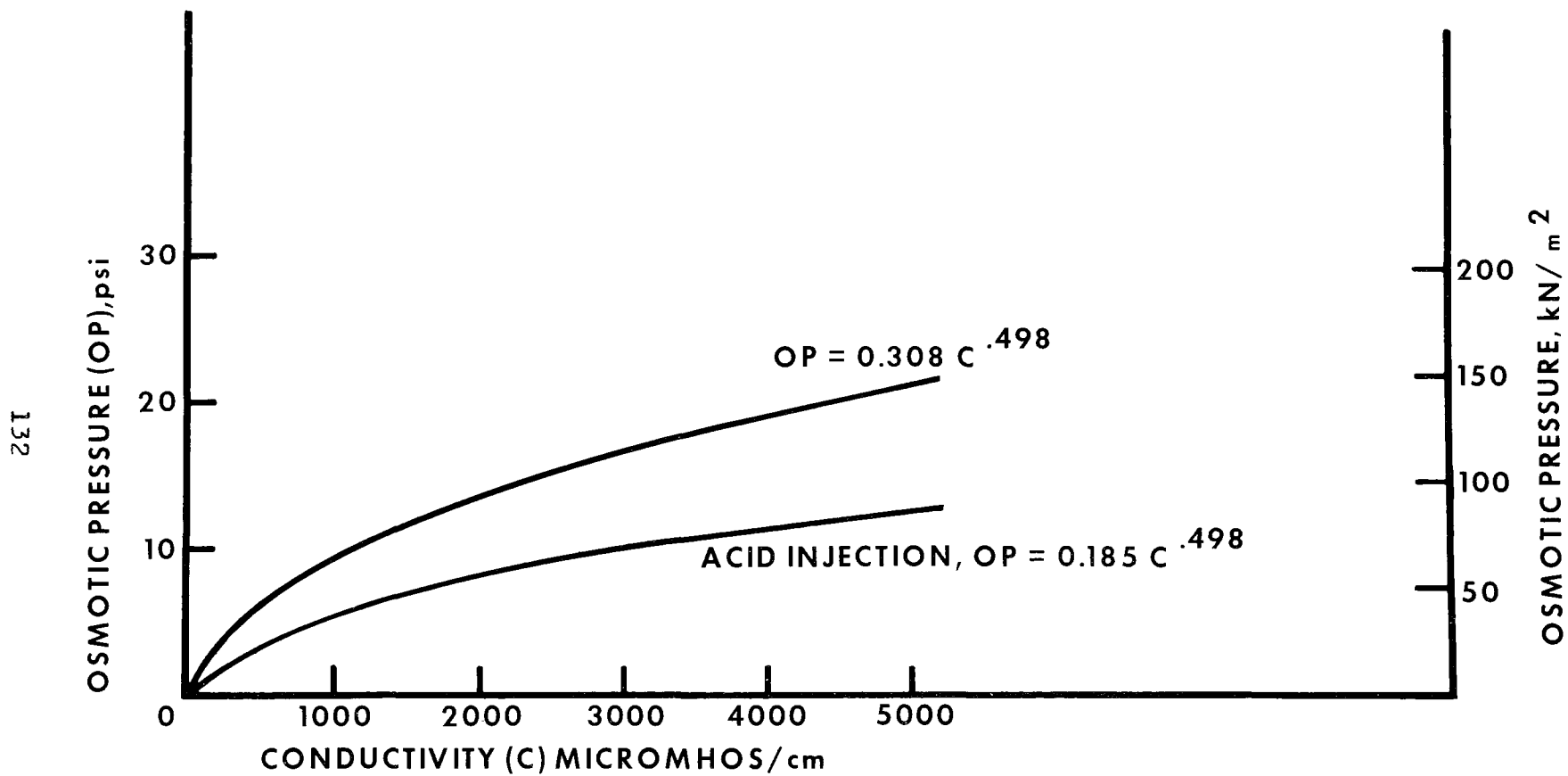


Figure 30

Osmotic pressure - conductivity relationship of Grassy Run at Norton

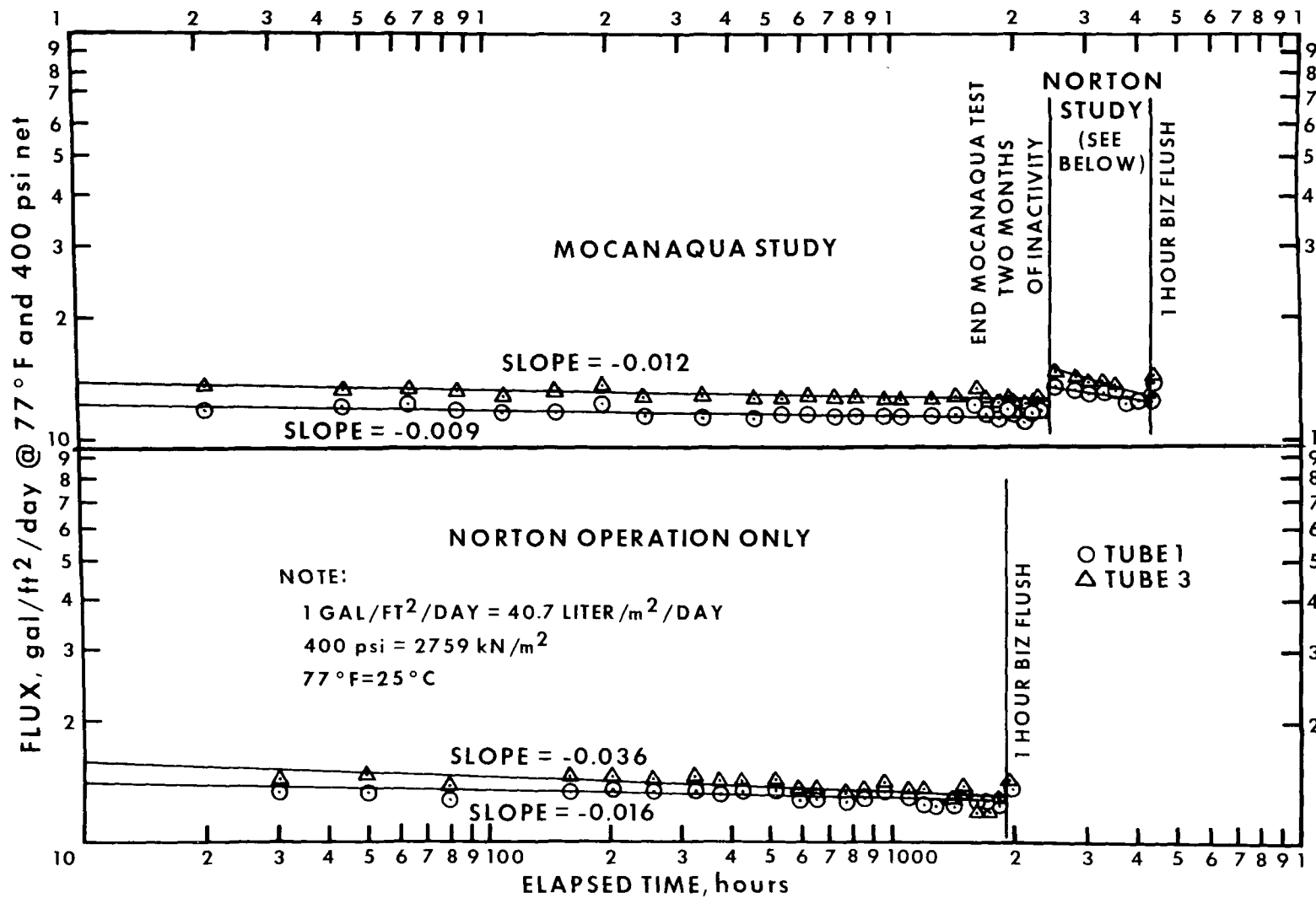


Figure 31  
Total 4K spiral unit operating history

greater than the  $-0.010$  slope observed on the same modules at Mocanaqua. It is felt that the increase in slope was directly related to the fact that Grassy Run is a surface stream subject to colloidal loads far higher than the deep mine discharge at Mocanaqua. This contrast was sharply evident in the previously mentioned hollow-fiber studies.

Near 1600 hr elapsed time at Norton, it was apparent from the log-log plot that some fouling was beginning to appear. At 1933 hr, the unit was flushed for 1 hr, with a 2 percent by weight BIZ solution, which had been neutralized to pH 7 by citric acid. As shown in Figure 31, the flush restored flux significantly. In fact, flux values after the flush corresponded to values that would have been obtained if a  $-0.01$  log-log slope had been followed during the Norton study.

While the unit was operating at Mocanaqua, small leaks were present in tubes 1 and 2 which slightly degraded product quality. Similarly, at the beginning of Norton testing, the leaks were still present. Gradually, as the Norton run progressed, the leaks significantly diminished and product quality from tubes 1 and 2 approached that of tube 3. This increase in rejection was attributed to a small buildup of fouling which, in essence, plugged the leaks.

A summary of operating parameters for the 4 K unit is given in Table 48 and chemical analyses are presented in Table 47.

#### Discussion of Norton Ferric Iron Comparison Studies

Surface streams such as Grassy Run appear to be considerably more difficult to treat using reverse osmosis due to colloidal and organic loads not experienced in deep mine discharges. This conclusion was dramatically demonstrated by the hollow-fiber unit that had operated quite satisfactorily on the Mocanaqua deep mine discharge but suffered severe fouling on the Norton surface stream. It is felt that the ionic state of the iron (whether ferrous or ferric), though important in pretreatment planning, was not an insurmountable problem as evidenced by the satisfactory operation of

Table 48. OPERATING PARAMETERS FOR NORTON SPIRAL-WOUND 4K STUDY  
AT 69.6 PERCENT RECOVERY

Parameter	Value
Raw water feed flow, gpm	5.076
Product water flow, gpm	3.531
Brine water discharged, gpm	1.545
Brine water recycled, gpm	6.577
Minimum brine/product flow ratio, ratio/module	10.6:1
Maximum brine/product flow ratio, ratio/module	21.6:1
Water recovery, percent	69.6
Recovery of blended feed, percent	30.3
Feed pressure, psig	400.1
Feed temperature, °F	59.2
Tube one flux, gal/ft <sup>2</sup> /day @ 77°F & 400 psi net	13.68
Tube two flux, gal/ft <sup>2</sup> /day @ 77°F & 400 psi net	13.32
Tube three flux, gal/ft <sup>2</sup> /day @ 77°F & 400 psi net	13.04
Length of run, hours	1946 (4400 total hours on membrane)
Date of run	January 30, 1972 - May 17, 1972

All values are means from 53 data sets.

Note: To convert flux (gal/ft<sup>2</sup>/day @ 400 psi and 77°F) to liters/m<sup>2</sup>/day @ 2758 kN/m<sup>2</sup> and 25°C, multiply by 40.67; to convert gallons per minute to liters/second, multiply by 0.063; and to convert psi to kN/m<sup>2</sup>, divide by 0.145.

spiral system under both ferrous (Mocanaqua) and ferric (Norton) conditions. The spiral system was significantly more tolerant to colloidal loads than the hollow-fiber system as shown by the satisfactory spiral system operation on the Norton water. However, the increase in the spiral system's rate of flux decline at Norton as compared to Mocanaqua was directly attributed to colloidal fouling. Importantly, the rate of spiral flux decline was still very acceptable and could be controlled quite easily through periodic flushing.

No decrease in salt rejection capability was noted on the spiral unit during the entire 4400 hr of operation.

Operation of the spiral system at high b/p flow ratios (10:1) and lower pressure (400 psi -  $2758 \text{ kN/m}^2$ ) produced significant improvements in flux stability compared to the 1970-71 3013 hr Norton 4 K study where approximately 25 percent of the flux was lost in the first 500 hr.

#### POST TREATMENT OF PRODUCT WATER

In an effort to produce a product of potable quality, product samples from the early part of the spiral testing and from the hollow-fiber Phase II study were neutralized to pH 7.5 and analyzed. The three critical parameters were pH, iron, and manganese. As shown in Table 49, neutralization effectively increased pH and removed iron but manganese levels remained unchanged and in excess of the 0.05 mg/l limit. Neutralization to pH 9-10 would have been required for manganese removal.<sup>19</sup> In that case, reacidification would have been necessary to reduce pH to acceptable limits of pH 6.0 to 8.5. A quick neutralization to pH 10 confirmed removal of manganese to potable standards. A more complete discussion of this problem is presented in the Discussion, Section VI, of this report under the subsection Significances of Rejection.

Table 49. EFFECT OF NEUTRALIZATION ON RO PRODUCT QUALITY

	Spiral-Wound		Hollow-Fiber	
	Product	Neutralized Product	Product	Neutralized Product
pH	3.8	7.5	3.9	7.5
Conductivity	100	60	65	55
Acidity	58	0	56	0
Alkalinity	0	10	0	5
Calcium	0.5	5.6	0.2	3.2
Magnesium	0.2	0.2	0.1	0.1
Iron	0.38	0.07	0.07	0.005
Aluminum	0.10	0.08	< 0.1	< 0.1
Sulfate	7.0	7.7	5.7	8.3
Manganese	0.3	0.3	0.2	0.2

Data 2/8/72 - Norton Study

	Spiral-Wound	
	Product	Neutralized Product
pH	4.0	10.0
Manganese	0.06	0.001

Data 3/20/72 - Norton Study

All units in mg/l except for conductivity (micromhos/cm) and pH.

## SECTION VI

### DISCUSSION

#### CALCIUM SULFATE PRECIPITATION - MAXIMUM RECOVERY PREDICTION

In each of the spiral-wound studies made at the various AMD sites, one result was significant--the limiting factor in high recovery reverse osmosis operation was calcium sulfate precipitation.

Gulf Environmental Systems presented a discussion of the  $\text{CaSO}_4$  problem<sup>3</sup> and suggested the following method to predict precipitation:

$$\sqrt{\frac{\text{Pmc}}{\text{Ksp}}} = 3.0 \text{ to } 4.0 \text{ when fouling occurs, where}$$

Pmc = Product of molar concentration of calcium  
and sulfate in the brine.

$$\text{Pmc} = (\text{Mg/l calcium} \div 40.08) \times (\text{Mg/l SO}_4 \div 96.06) \times 10^{-6}$$

Ksp = Solubility Product of Calcium Sulfate in distilled  
water where solubility  $\approx$  2000 mg/l and  $\text{Ksp} = 2.16 \times 10^{-4}$

Unfortunately, a broad range of 3.0 to 4.0 was not adequate in predicting RO recovery with any degree of accuracy.

Using Gulf's approach, data from each site mentioned in this report were evaluated and a judgmental estimate was made of the maximum sustainable recovery level at each site. This engineering estimate was based solely upon experience and was thus empirical in nature and subject to error and disagreement.

Since the brine samples from each test were supersaturated in calcium sulfate, precipitation occurred prior to analysis. It was felt that using raw feed values and calculating brine concentrations based on recovery would give more reliable values for calcium and sulfate concentrations. For example, if the RO unit were operated at 75 percent recovery, the brine values would be concentrated four times in relation to raw feed values. Calculations of the brine concentration were then made based on the assumed maximum recovery.

The major argument against Gulf's method is that Ksp is a value for calcium sulfate solubility in distilled water. A Ksp for highly polluted brine with all involved ionic competitions would be a significantly different value than that for distilled water.

Earlier work at Gulf included formulations by Marshall, Slusher, and Jones<sup>18</sup> for correcting Ksp of  $\text{CaSO}_4$  for ionic strength. Although the work was at higher temperatures and sodium chloride solutions, Gulf felt the relationships were generally valid for RO applications.

The ionic strength (I) of a solution is defined as:

$$I = (\frac{1}{2}) \sum M_i Z_i^2$$

$M_i$  = molar concentrations of individual ions

$Z_i$  = ionic charges

Marshall, Slusher, and Jones related ionic strength (I) to Ksp for calcium sulfate as follows:

$$K_{sp} = 1.8 \times 10^{-3} (I)^{0.75}$$

Therefore, a second approach was used where  $\sqrt{P_{mc}/K_{sp}}$  was calculated using Ksp corrected for ionic strength.

Table 50 presents a summary of all tests along with estimates of maximum sustainable recoveries at those sites and corresponding values of  $\sqrt{P_{mc}/(2.16 \times 10^{-4})}$  and  $\sqrt{P_{mc}/K_{sp} \text{ (corrected)}}$ .

Table 51 presents a summary of chemistry analyses at all sites. The  $\sqrt{P_{mc}/K_{sp}}$  corrected for ionic strength was calculated from these values.

It was felt that the results of Table 50 provided rough limits for the calcium sulfate threshold of  $\sqrt{P_{mc}/(2.16 \times 10^{-4})} = 2.0$  and  $\sqrt{P_{mc}/K_{sp}} = 1.2$  (where Ksp was corrected for ionic strength).

Computer programs were then written to calculate the maximum predicted recovery based on analyses of the raw feed water. The program incremented recovery, calculated brine concentrations, and solved  $\sqrt{P_{mc}/K_{sp}}$  until limits of 2.0 ( $K_{sp} = 2.16 \times 10^{-4}$ ) or 1.2 (Ksp corrected for ionic strength) were reached.



Table 50. REVERSE OSMOSIS RECOVERY LIMITATIONS DUE TO CALCIUM SULFATE FOULING

Site	Actual Values					Calculated Values		
	Actual recovery	Raw feed Ca	SO <sub>4</sub>	$\sqrt{\frac{P_{mc}}{2.16}}$	$\sqrt{\frac{P_{mc}}{K_{sp}}}$ (corrected)	Estimated maximum recovery (a)	$\sqrt{\frac{P_{mc}}{2.16}}$	$\sqrt{\frac{P_{mc}}{K_{sp}}}$ (corrected)
Norton 10K - Test #1	91.2%	110	810	3.72	1.74	85%	2.18	1.25
Norton 10K - Test #2	84.8%	110	850	2.21	1.29	85%	2.24	1.30
Norton Neutrololosis-Test 4 (b)	55.6% (b)	470 (b)	4700 (b)	3.67	1.66	30% (b)	2.33	1.25
Norton Neutrololosis-Test 5 (b)	54.6% (b)	460 (b)	3000 (b)	2.84	1.59	40% (b)	2.15	1.33
Morgantown	50.0%	530	10900	5.27	1.87	<1%	2.66	1.22 (c)
Ebensburg #1	83.6%	190	1640	3.73	1.89	75%	2.45	1.45
Ebensburg #4	53.2%	160	1300	1.07	0.85	75%	2.00	1.26
Norton 4K - 3000 hr	72.8%	120	1100	1.47	0.94	80%	1.99	1.14
Norton 4K - Neutralized brine	50.0%	400	3100	2.44	1.55	20%	1.53	1.16
4K Mocanaqua #1	74.8%	130	750	1.36	0.99	80%	1.71	1.14
4K Mocanaqua #1	83.9%	130	800	2.20	1.33	80%	1.77	1.16
4K Mocanaqua #2	74.5%	140	930	1.55	1.05	80%	1.98	1.22
4K Norton (1972)	75.0%	96	1060	1.40	0.93	85%	2.33	1.28
						Mean	2.10	1.24

(a) Maximum sustainable recovery (estimated).

(b) Blended feed values.

(c) Excessive at any recovery.

Table 51. SUMMARY OF RAW FEED CHEMISTRY ANALYSES

Site	Actual recovery	Cond.	Acidity	Ca	Mg	Total iron	Ferrous iron	Al	Sulfate
Norton 10K-Test 1	91.2%	1100	630	110	33	110	3	35	810
Norton 10K-Test 2	84.8%	1200	540	110	37	80	3	31	850
Norton Neutrolosis Test #4(a)	55.6%	5200	2700	470	270	520	10	190	4700
Norton Neutrolosis Test #5(a)	54.6%	3000	1150	460	120	210	10	91	3000
Morgantown	50.0%	7000	5200	530	420	2300	1300	320	10900
Ebensburg #1	83.6%	1500	380	190	54	135	100	32	1640
Ebensburg #4	53.2%	1180	390	160	51	130	96	30	1300
4K Norton - 3000-hr	72.8%	970	440	120	39	130	3	63	1100
4K Norton	50.0%	3200	66	400	170	1.3	0.1	4.5	3100
4K Mocanaqua #1	74.8%	1080	240	130	88	77	64	12	750
4K Mocanaqua #1	83.9%	1100	230	130	90	80	70	13	800
4K Mocanaqua #2	74.5%	1110	220	140	110	100	73	14	930
4K Norton (1972)	75.0%	960	620	96	29	115	3	36	1060

(a) Blended feed values.

All units are mg/l except for pH and conductivity (micromhos/cm).

In Table 52, results of computer predictions can be compared with the estimated maximum recovery for each site. Maximum recovery predictions by both methods agree very well with each other and with the original estimate of maximum recovery.

Since agreement between both methods was close, use of  $\sqrt{P_{mc}(2.16 \times 10^{-4})} = 2.0$  is recommended since only calcium and sulfate determinations are needed to compute maximum recovery. Using 2.0 as the limit, the following formula was derived to enable prediction of maximum recovery:

$$R = 100 - 0.055 \sqrt{(Ca) \times (SO_4)}$$

where R = maximum recovery (percentage)

Ca = AMD feed calcium concentration (mg/l)

SO<sub>4</sub> = AMD feed sulfate concentration (mg/l)

This method of predicting maximum recovery is felt to be accurate to  $\pm 5$  percent recovery on acid mine drainage.

#### COMPARISON OF SPIRAL-WOUND, HOLLOW-FIBER, AND TUBULAR SYSTEMS

In order to compare RO systems, it was vital that all comparisons be made on the same basis, i.e., under the same operating conditions. For this reason, water flux, when corrected for osmotic pressure (which corrects for water quality and recovery) and temperature, served as an effective unit for comparing of membrane performance. Water flux, however, did not compensate for efficient packaging of the membranes in the RO system, and therefore was a poor basis for comparing system performance.

For this report, system performance was evaluated on the basis of product output per cubic foot of vessel volume per unit of time. To arrive at this factor, water flux was divided by pressure vessel volume.

Table 53 presents a summary of observed flux and productivity data from the Mocanaqua studies where spiral-wound, hollow-fiber, and tubular systems operated on a side-by-side basis. Tubular and Phase I spiral-wound data--although actual operation was at

Table 52. COMPARISON OF PREDICTED MAXIMUM RECOVERY WITH EMPIRICAL ESTIMATES OF MAXIMUM RECOVERY

	Estimated maximum recovery (table 50)	Predicted maximum recovery using calcium sulfate limit of	
		$\sqrt{\frac{P_{mc}}{2.16 \times 10^{-4}}} = 2.0$	$\sqrt{\frac{P_{mc}}{K_{sp}}} = 1.2$ (Corrected)
Norton 10K - Test 1	85%	84%	85%
Norton 10K - Test 2	85%	84%	83%
Norton Neutrolosis - Test 4 <sup>(a)</sup>	30% <sup>(a)</sup>	19% <sup>(a)</sup>	26% <sup>(a)</sup>
Norton Neutrolosis - Test 5 <sup>(a)</sup>	40% <sup>(a)</sup>	36% <sup>(a)</sup>	30% <sup>(a)</sup>
Morgantown	1%	1%	2%
Ebensburg #1	75%	70%	67%
Ebensburg #4	75%	75%	73%
Norton 4K - 3000 hour	80%	81%	82%
Norton 4K - neutralized brine	20%	39%	25%
4K Mocanaqua #1	80%	83%	82%
4K Mocanaqua #1	80%	83%	81%
4K Mocanaqua #2	80%	81%	80%
4K Norton (1972)	85%	83%	84%

<sup>(a)</sup> Recovery of blended feed.

Table 53. COMPARISON OF WATER PRODUCTION CAPABILITIES OBSERVED DURING MOCANAQUA STUDIES

	Pressure vessel volume ft <sup>3</sup>	Enclosed membrane area ft <sup>2</sup>	Membrane packing density ft <sup>2</sup> /ft <sup>3</sup>	Avg. flux gal/ft <sup>2</sup> / day <sup>(a)</sup>	Total vessel flux/day gal/day <sup>(a)</sup>	Output per cubic foot of vessel volume	
						per day <sup>(a)</sup>	per min. <sup>(a)</sup>
Spiral-wound (Phase I)	1.13	150	133	(19.28 @ 600) 12.86	(2892 @ 600) 1929	(2559 @ 600) 1707	(1.78 @ 600) 1.19
Spiral-wound (Phase II)	1.13	186	165	12.31	2290	2026	1.41
Hollow-fiber (Phase II)	0.65	1500	2308	2.48	3720	5723	3.97
Tubular (Phase II)	0.63	16.9	26.8	(15.60 @ 600) 10.40	(264 @ 600) 176	(418 @ 600) 280	(0.29 @ 600) 0.19

(a) At 77°F (50°C) and 400 psi net pressure.

Note: To convert ft<sup>3</sup> to m<sup>3</sup>, multiply by 0.028; to convert ft<sup>2</sup> to m<sup>2</sup>, multiply by 0.093; to convert flux values (gal/ft<sup>2</sup>/day @ 77°F and 400 psi) to l/m<sup>2</sup>/day @ 25°C and 2758 kN/m<sup>2</sup>, multiply by 40.67.

4138 kN/m<sup>2</sup> (600 psi)--were also normalized to 2758 kN/m<sup>2</sup> (400 psi) to enable direct comparison with the hollow-fiber unit.

In terms of average flux, spiral-wound membranes were clearly superior with 2758 kN/m<sup>2</sup> (400 psi) fluxes of 12.3 gal/ft<sup>2</sup>/day for spiral versus 10.40 for tubular and only 2.48 for hollow-fiber (500 l/m<sup>2</sup>/day vs. 423 vs. 100.8).

Because hollow-fiber permeators packed from 8-10 times as much membrane in the same volume as the spiral system and 88 times as much as the tubular system (see Packing Density, Table 53), the low specific flux of the hollow-fiber was made up for by greater membrane area. Although the hollow-fiber flux rate ranged from only 12 percent to 20 percent that of the spiral system, depending on the spiral's operating pressure, the hollow-fiber product output per cubic foot of vessel volume was from 2.2 to 3.3 times spiral output and from 14 to 21 times tubular output, again depending upon operating pressures.

The tubular system ranked lowest in both flux and output per cubic foot of vessel volume.

In Table 54 are the relative costs for each system. Since a detailed cost analysis was beyond the scope of this report, initial costs for purchase of one pressure vessel complete with membrane were used. Dividing the initial cost by the observed output (gallons per day of product) yielded the initial cost-per-unit-output figures shown in the table. Although prices and relationships observed were valid for the Mocanaqua study, extrapolation of these figures for large units would result in large errors. Other factors such as hardware requirements would vary with each application and manufacturer and were not included in pressure-vessel--membrane-package--cost figures.

A third basis for comparison was product quality. Rejections were calculated by comparing the product concentration with concen-

Table 54. RELATIVE COST COMPARISONS FROM MOCANAQUA STUDY

System	Cost for one pressure vessel and membrane	Observed output (gal. per vessel per day @ 77° F & indicated net pressure)	Initial cost per unit output (gal/day)
Spiral-wound Phase I	\$ 850. (20)	2892 @ 600	\$0.29
Spiral-wound Phase II	\$ 850. (20)	2290 @ 400	\$0.37
Hollow-fiber Phase II	\$1000. (21)	3720 @ 400	\$0.27
Tubular Phase II	\$ 265. (22)	264 @ 600	\$1.00

Note: To convert gal/day to l/day, multiply by 3.785 and to convert \$/gal/day to \$/l/day, divide by 3.785.

trations entering the RO unit. A summation of system rejections is presented in Table 55. Spiral-wound membranes held a slight edge in rejecting ability.

The previously mentioned leaks during spiral-wound Phase II studies were apparent in unit rejections (Table 55), but tube 3 rejections were of the same level as those from Phase I spiral studies.

Under Mocanaqua conditions, the rejection advantage of spiral membranes would be of little significance as product water from all three units would require additional treatment for pH, manganese, and iron before drinking water standards could be met.

The final basis for comparison was the decrease of productivity with time as evaluated by log-log flux decline slopes. In Table 56 are examples of log-log slopes (derived from Figures 23 and 25 and Table 53) chosen to simulate comparable recovery conditions. In all these examples, recoveries in the respective tubes or units were near or below 60 percent.

Phase II spiral-wound system again had a slight advantage in flux decline slope over the hollow-fiber systems; however, the hollow-fiber slope was superior to Phase I spiral performance. The tubular system's slope, calculated from the line of best fit of the tubular log-log flux plot, was considerably steeper than either the spiral or hollow-fiber slope.

Extrapolation of the flux curve to predict flux values at 3 and 5 years was necessarily based on the assumption that the log-log flux decline slope remained constant. Validity of that assumption is certainly open to debate and only sustained operation over that period of time would prove or disprove it. If the assumption were valid, the flux levels at 3 and 5 years of elapsed time are given in Table 56.



Table 55. COMPARISON OF MEMBRANE PERFORMANCE AT MOCANAQUA

System	Flux, gal/ft <sup>2</sup> /day @ 77° F & indicated pressure	Rejections(a), Percent									
		Conduc-tivity	Acid-ity	Cal-cium	Magne-sium	Total iron	Ferrous iron	Alum-inum	Sul-fate	Manga-nese	Sili-con
Spiral-wound Phase I	19.28 @ 600 psi	99.2	91.7	99.8	99.8	99.8	99.8	99.2	98.8	-	
Spiral-wound Phase II	12.31 @ 400 psi	97.6	94.6	99.6	98.5	99.0	98.9	97.6	99.1	99.8	
Spiral-wound Tube 3, Phase II	11.58 @ 400 psi	98.7	-	99.8	99.7	99.7	-	97.7	99.7	99.5	
Hollow-fiber Phase I	2.32 @ 400 psi	-	-	99.5	99.3	99.2	99.1	97.8	99.7	99.4	95.1
Hollow-fiber Phase II	2.48 @ 400 psi	96.9	84.8	99.2	98.8	98.9	98.9	94.7	99.5	-	-
Tubular Phase I		95.6	81.6	98.2	98.5	98.8	98.4	91.7	99.3	-	
Tubular Phase II	15.6 @ 600 psi	96.2	-	99.5	99.5	99.4	99.0	98.2	96.9	99.4	90.0

(a) Rejection = (Influent concentration-product concentration)  $\times$  100  $\div$  Influent concentration.

Note: To convert flux gal/ft<sup>2</sup>/day to l/m<sup>2</sup>/day, multiply by 40.67; to convert psi to kN/m<sup>2</sup>, divide by 0.145.

Table 56. PROJECTED MEMBRANE PERFORMANCE<sup>(a)</sup> - MOCANAQUA STUDIES

Unit	Flux @ <sup>(b)</sup> 100 hrs. gal/ft <sup>2</sup> /day	Log-log flux de- cline slope	Predicted flux after 3 years	Predicted flux after 5 years
Spiral-wound Phase I Tube 1	21.5	-0.034	17.8	17.5
Spiral-wound Phase II Tube 1	13.0	-0.012	12.2	12.1
Hollow-fiber Phase II Tube 1	2.9	-0.015	2.7	2.6
Tubular Phase II	17.2	-0.063	12.1	11.7

(a) Assumptions:

1. Log-log flux decline slope remains constant.
2. Salt rejection is assumed to remain constant.

(b) Taken from log-log graph of flux versus time.

Note: To convert gal/ft<sup>2</sup>/day to l/m<sup>2</sup>/day, multiply by 40.67.

## SIGNIFICANCE OF REJECTIONS

Most important of the several factors that determine reverse osmosis product quality are raw water quality, recovery level, and membrane rejection capability.

If water of potable quality is required without posttreatment of the product, then significant restrictions are placed upon the mode of operation and characteristics of the RO unit.

Iron and manganese concentrations in potable water are restricted by the U. S. Public Health Service to 0.3 and 0.05 mg/l, respectively. Of all commonly appearing AMD constituents, iron and manganese are the most critical for treatment to potable standards.

Since the membrane rejection ratio is constant, product quality is directly dependent on concentrations on the brine (concentrated) side of the membrane. Increasing recovery serves to increase brine-side concentrations and in turn degrades product quality. Therefore, for every raw feed concentration, it is possible to calculate the maximum recovery that can be obtained without the product concentration exceeding the U. S. Public Health Service limit. A family of operating curves has been developed for iron and manganese and may be used to approximate this maximum recovery (Figures 32 and 33). For example, if an influent water contained 50 mg/l of iron and 5 mg/l of manganese, the maximum recovery to meet potable standards would be 30 percent for the iron criteria when using 99.5 percent rejecting membranes. The same conditions allow a 66 percent recovery before manganese limits are exceeded.

It is not necessary for the RO unit to reduce the iron and manganese to this low level since the product water must receive post-treatment in the form of neutralization to increase the pH to an acceptable level. RO-treated water normally has a pH less than 5. Neutralizing to pH 7 and filtering will remove residual iron, and thus, the iron concentrations can be kept in acceptable limits. If the iron is in the ferrous state, it will rapidly oxidize at pH 7,

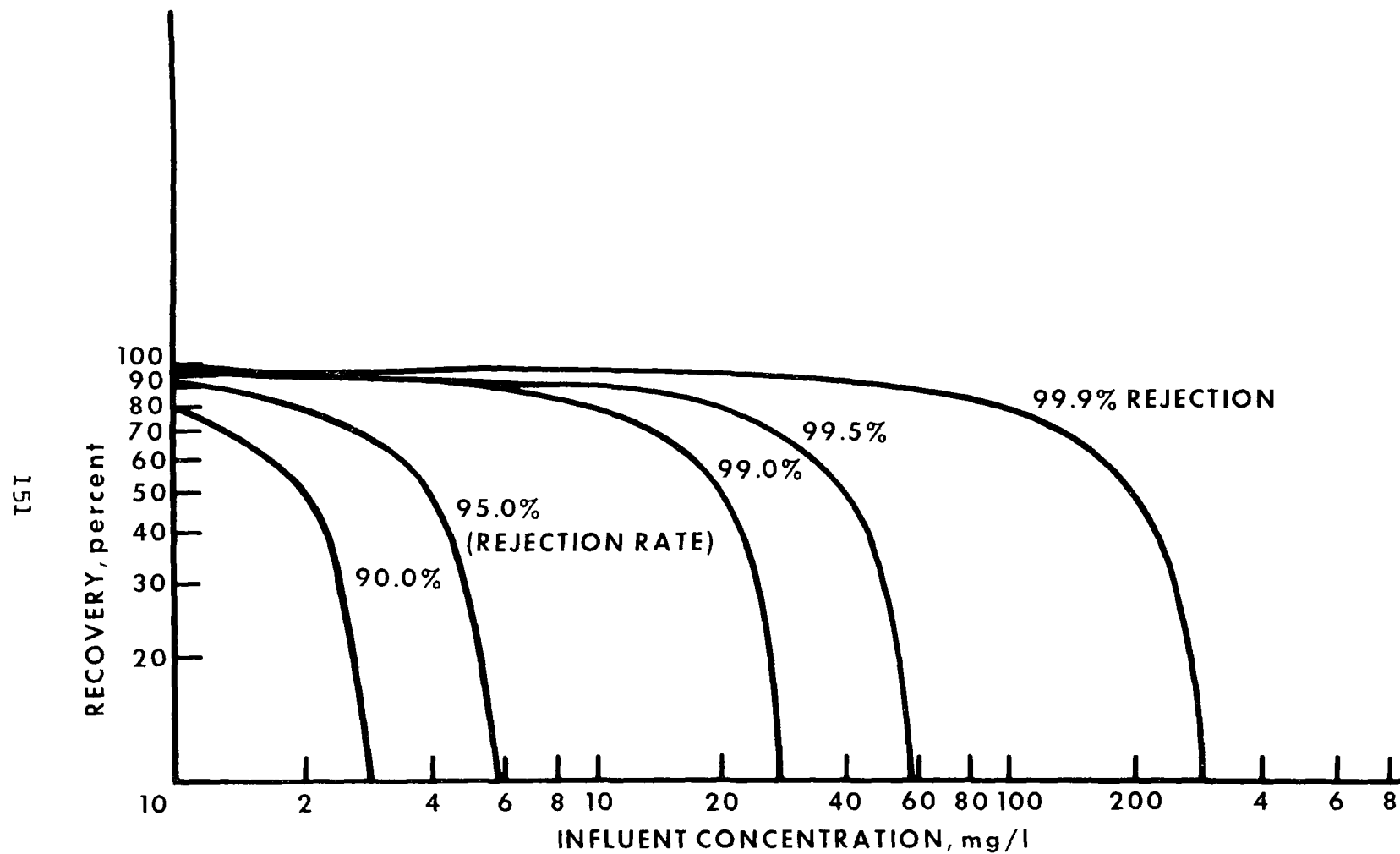


Figure 32

Maximum operating conditions to obtain potable product  
for iron limits of 0.30 mg/l

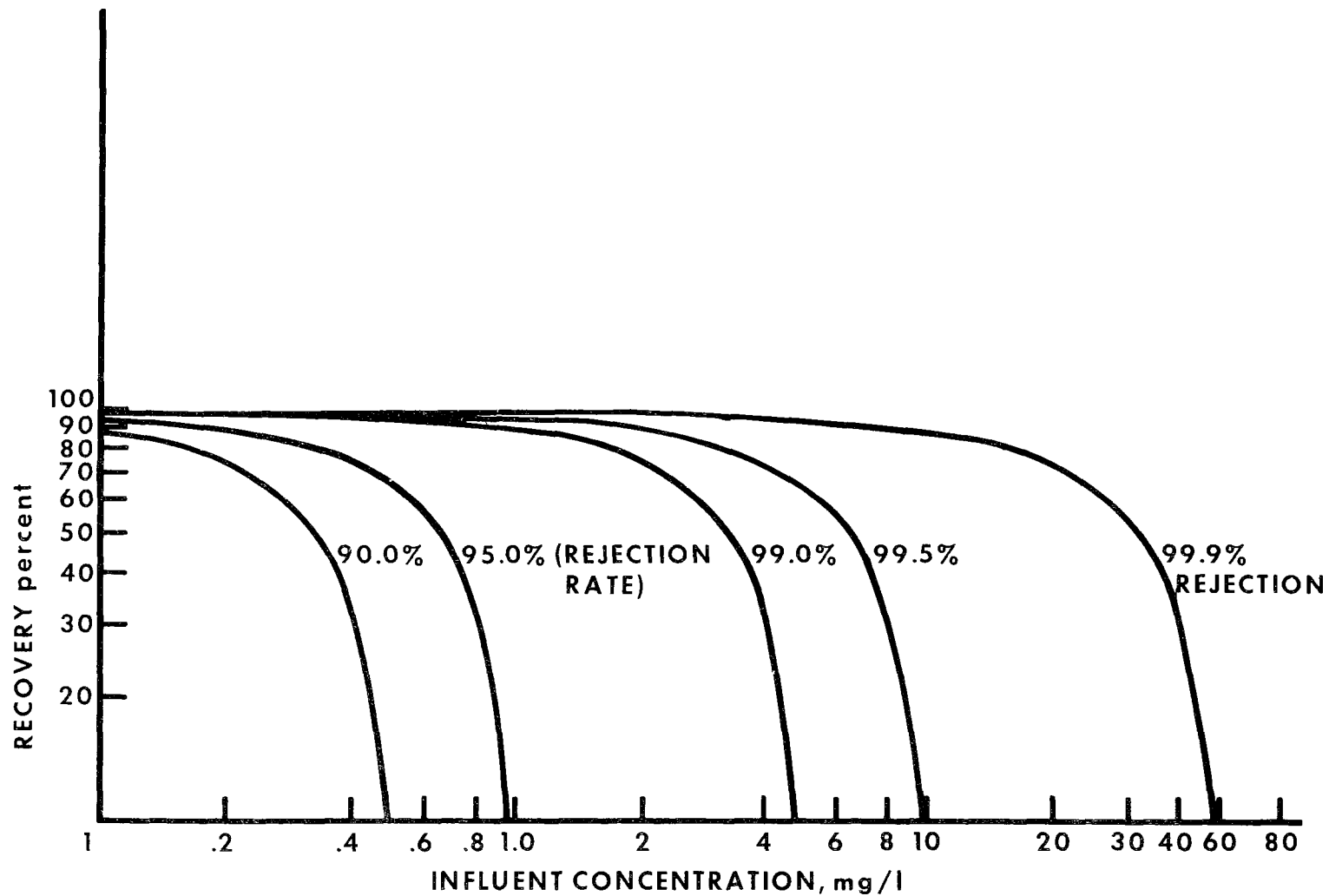


Figure 33  
Maximum operating conditions to obtain potable product  
for manganese limits of 0.05 mg/l

and then it can be removed by filtering. To remove residual manganese by neutralization, Hill<sup>19</sup> states that neutralization to pH 9-10 is required. This neutralization in itself would exceed normally acceptable pH limits and acidification of the water would be needed following manganese removal.

In conclusion, assuming potable quality product water is required from the RO unit, membrane rejection is generally not significant for iron removal since post neutralization is required anyway. However, for AMD waters containing significant amounts of manganese, the rejection capability is of vast importance in achieving potable quality at minimum cost. Membranes with rejections below 95 percent would not appear desirable for AMD potable applications.

If the RO system can be operated in a mode where the iron and manganese can be reduced to an acceptable level by the addition of a posttreatment step, then the unit can be operated at a high recovery.

## SECTION VII

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SECTION VIII  
LIST OF INVENTIONS AND PUBLICATIONS

INVENTION

A patent application (No. 213117) has been filed for the neutrolosis process. The title is "Reverse Osmosis - Neutralization Process for Treating Contaminated Waters" by Ronald D. Hill, Roger C. Wilmoth, and Robert B. Scott. As of this report, the patent is pending.

PUBLICATIONS

The following list of presentations and publications resulted from portions of the work included in this report:

"Neutrolosis Treatment of Acid Mine Drainage" by Ronald D. Hill, Roger C. Wilmoth, and Robert B. Scott, a paper presented at the Purdue Industrial Waste Conference, Lafayette, Indiana, in May 1971;

"Treatment of Ferrous Iron Acid Mine Drainage by Reverse Osmosis" by Roger C. Wilmoth, Donald G. Mason, and Mahendra Gupta, a paper presented at the Fourth Symposium in April 1972;

"Mine Drainage Pollution Control by Reverse Osmosis" by Roger C. Wilmoth and Ronald D. Hill, a paper presented at the AIME Fall Meeting, Birmingham, Alabama, in October 1972;

and "Mine Drainage Pollution Control Via Reverse Osmosis", Mining Engineering, March 1973, page 45-47, by Roger C. Wilmoth and Ronald D. Hill.

## SECTION IX

### GLOSSARY

Flux - A measure of productivity or permeability; the rate of product flow through the membrane, usually expressed as gallons per day per square foot of membrane area under specified conditions of temperature and pressure.

Log-Log Flux Decline Slope - Even in pure water (nonfouling) systems, reverse osmosis membranes lose flux with time. This flux loss is linear when plotted on log-log paper. Log-log flux slopes of test runs are indicative of the fouling that may be occurring, its severity, and its rate as compared with normal pure water values.

Pressure Drop ( $\Delta P$ ) - The pressure loss across a module or tube in an RO unit due to hydraulic restriction in the brine channel and piping. Increases in  $\Delta P$  are rough indicators of fouling.

Recovery - The percentage of the raw water fed to the reverse osmosis unit that results as product.

Reverse Osmosis - Flow through a semipermeable membrane where the direction of flow is from the concentrated solution to the dilute solution. Such a flow is induced by pressure applied to the concentrated solution.

Salt Rejection - A measure of a membrane's ability to selectively allow pure water to pass through but reject the passage of impurities; a measure of a membrane's impermeability with respect to salts; usually expressed as a percentage:

$$\frac{(\text{Influent Quality} - \text{Product Quality})}{(\text{Influent Quality})} \times 100$$

Salt Passage - The percentage of salts passing through the membrane as compared to the initial pollutant concentration. Equal to 100 minus salt rejection.

<b>BIBLIOGRAPHIC DATA SHEET</b>		1. Report No. EPA-670/2-73-100	2.	3. Recipient's Accession No.
4. Title and Subtitle Application of Reverse Osmosis to Acid Mine Drainage Treatment			5. Report Date December, 1973	
			6.	
7. Author(s) Roger C. Wilmoth			8. Performing Organization Rept. No.	
9. Performing Organization Name and Address  U.S. Environmental Protection Agency Crown Mine Drainage Control Field Site, Box 555 Rivesville, W. Va. 26588			10. Project/Task/Work Unit No. 1BB040/21AFY/31	
			11. Contract/Grant No.	
12. Sponsoring Organization Name and Address U.S. Environmental Protection Agency National Environmental Research Center Cincinnati, OH 45268			13. Type of Report & Period Covered Final Report	
			14.	
15. Supplementary Notes Environmental Protection Agency report number, EPA-670/2-73-100, December 1973.				
16. Abstracts Spiral-wound reverse osmosis systems were tested on four different acid mine drainage discharges in West Virginia and Pennsylvania. Comparison studies were made of the hollow-fiber, tubular, and spiral-wound systems at a ferrous iron acid discharge; and of hollow-fiber and spiral-wound systems at a ferric iron acid discharge. At all sites, the limiting factor in high recovery operation was calcium sulfate insolubility. An empirical formula was developed for predicting maximum recovery. Application of reverse osmosis was demonstrated to be technically feasible for a large percentage of acid mine drainage discharges. A process called "neutrolosis" was developed in which the reverse osmosis brine is neutralized and clarified, and the supernatant recycled to the influent to the reverse osmosis unit. In this manner, the neutrolosis process discharges only a high quality product water and a neutralized sludge. Neutrolosis recoveries as high as 98.8 percent were achieved at a ferric iron acid discharge site.				
17. Key Words and Document Analysis. 17a. Descriptors Acid Mine Drainage* Reverse Osmosis* Calcium Sulfate* Coal Mines Brine Disposal Water Pollution Control Iron Manganese  17b. Identifiers/Open-Ended Terms West Virginia* Pennsylvania* Neutrolosis* Water Recovery  17c. COSATI Field/Group				
18. Availability Statement			19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages
			20. Security Class (This Page) UNCLASSIFIED	22. Price