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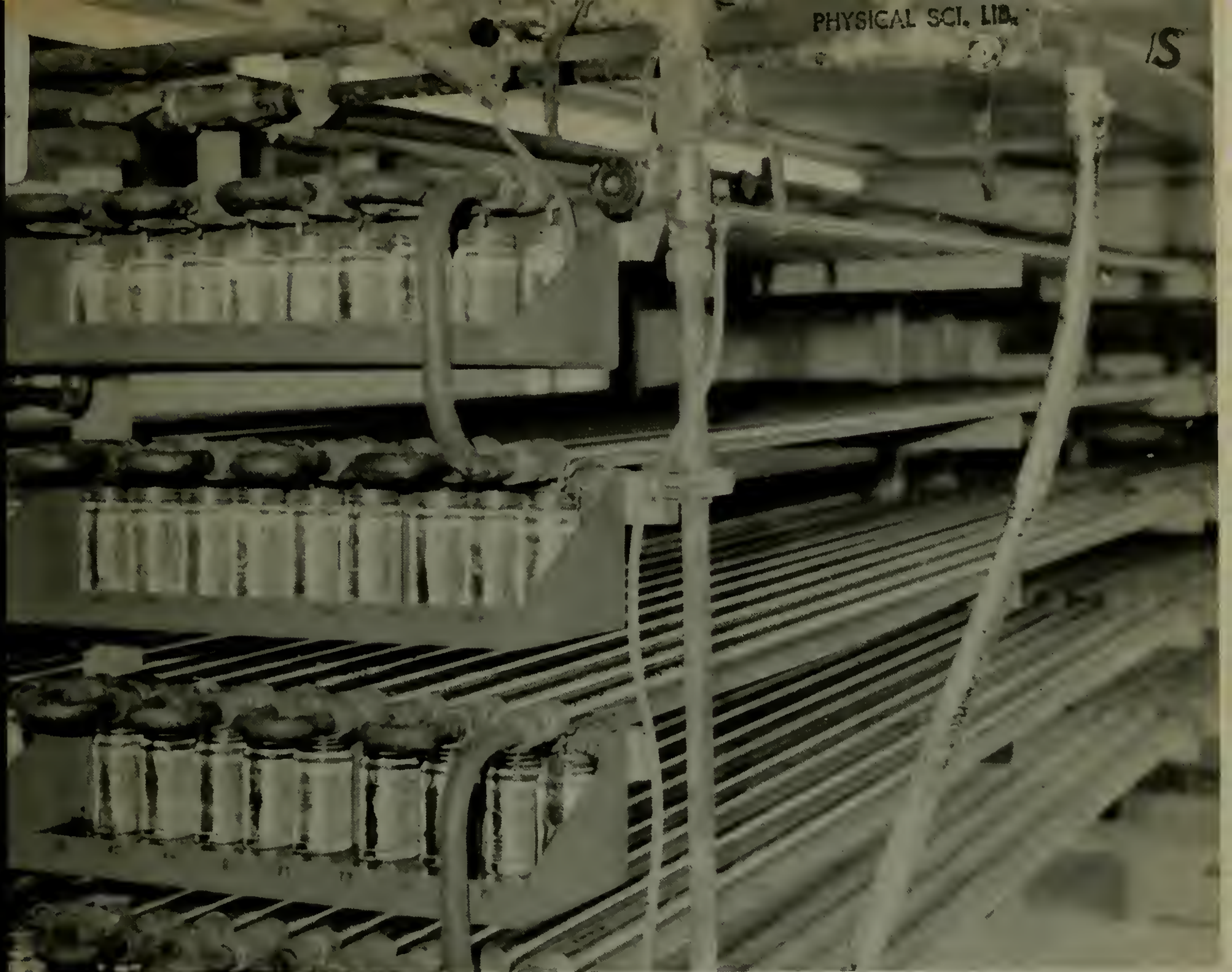

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PHOTO ON THE COVER — The 180-tube reverse osmosis unit, supplied by the University of California at Los Angeles, in operation at the Department of Water Resources Waste Water Treatment Evaluation Facility in Firebaugh, California. The sample bottles (foreground) collect product water from each tube to enable evaluation of the performance of the reverse osmosis membrane.

Department of
Water Resources

Bulletin 196-76

Agricultural Waste Water Desalination by Reverse Osmosis

Technical Aspects

October 1976

Claire T. Dedrick
Secretary of Resources

Edmund G. Brown Jr.
Governor

Ronald B. Robie
Director

The Resources
Agency

State of
California

Department of
Water Resources

FOREWORD

Bulletin No. 196-76, "Agricultural Waste Water Desalination by Reverse Osmosis, Technical Aspects", reviews the study completed by the Department of Water Resources in 1974. The study was conducted by the Department's San Joaquin Division at the Waste Water Treatment Evaluation Facility near Firebaugh, California.

The first part of the study focused on an experimental reverse osmosis unit developed by the University of California, Los Angeles, which fabricated the equipment and provided the technical guidance for its operation. The second part involved a cooperative test program sponsored by the Department of Water Resources and the U. S. Department of the Interior's Office of Water Research and Technology. This portion of the study consisted of an evaluation of three types of reverse osmosis plants -- all used to desalt agricultural waste water.

Several significant breakthroughs in the reverse osmosis process were made as a result of this study. First, it was successfully demonstrated that three types of reverse osmosis units could be operated for a sustained period using agricultural waste water. Next, in a cooperative venture with the University of California, Berkeley, various investigations of slime control methods proved that control practices can prevent membrane deterioration caused by bacterial action. Finally, and probably the most important development in this study, was the demonstration that the reverse osmosis unit can recover 90 percent of the agricultural waste water.

The Department is continuing its studies at Firebaugh with emphasis on economic aspects of the process. The results will be reported in subsequent bulletins in the 196 Series.

Ronald B. Robie

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CHAPTER I. SUMMARY AND CONCLUSIONS, AND FUTURE STUDIES

Summary and Conclusions

Desalination studies using three reverse osmosis test models were completed at the Waste Water Treatment Evaluation Facility at Firebaugh in December 1974. The purpose of the studies was to investigate the feasibility of desalting agricultural tile drainage water by the reverse osmosis process and to establish the relative desalting capabilities of several designs of reverse osmosis equipment.

Three reverse osmosis pilot plants were operated for approximately 18 months on a continuous basis using feedwater from a subsurface tile drainage system. This feedwater had a salinity that varied seasonally from 2,000 parts per million (ppm) (2,000 milligrams per litre [mg/l]*) to more than 6,000 ppm (mg/l). It was chemically pretreated to prevent biological fouling and deterioration of the semipermeable membrane, and to inhibit calcium sulfate scaling. During the last 12 months of the study, the feedwater was softened by an ion-exchange process.

The following conclusions summarize the results of tests conducted with the tubular, spiral-wound, and hollow-fine-fiber reverse osmosis systems.

1. The reverse osmosis process effectively desalted agricultural tile drainage water and provided a high-quality recovery product. Adequate desalting capability was demonstrated by all three reverse osmosis systems with respect to membrane and plant performance.

2. The desalination process was governed primarily by conditions imposed by the feedwater. These conditions included (a) seasonal variations in the level of feedwater total dissolved solids (TDS), (b) high calcium sulfate content and the limitations caused by the low solubility of this mineral, and (c) presence of bacterial organisms capable of attacking the membrane or creating a buildup of surface fouling.

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*The numerical value for dissolved solids concentration is identical in the metric system and hereafter will not be given.

3. Successful desalination was contingent upon adequate feedwater pretreatment and module maintenance. The measures employed differed with the type of membrane or modular configuration but included pH adjustment, bacterial and scale control, particulate matter filtration, and mechanical or chemical cleaning of the membrane to remove surface fouling.

4. The productivity of the reverse osmosis process was limited by the scaling characteristics of the tile drainage water. The use of chemical additives to inhibit calcium sulfate scaling resulted in increased desalted water production. An optimum recovery level of 70 percent was attained by the three pilot plants when they used feedwater supplied at a TDS of 2,000 ppm (mg/l) and treated with a scale inhibitor. This recovery level was reduced to 50 percent when desalting feedwater at 6,000 ppm (mg/l).

5. The removal of hardness constituents (Ca^{++} and Mg^{++} ions) from the tile drainage water by the ion-exchange process was successfully demonstrated. The three reverse osmosis pilot plants attained recovery levels as high as 90 percent when using softened feedwater at a TDS of more than 6,000 ppm (mg/l).

To evaluate the desalting capability of different designs of reverse osmosis equipment, three test models were selected on the basis of different configurations and types of semipermeable membrane material. The tubular model, which uses the cellulose acetate membrane, consists of 180 tubular assemblies joined in an end-to-end series arrangement. The spiral-wound model has a four-stage, 2-1-1-1 parallel-series array of five desalting modules. Each module contains three spirally wrapped desalting cartridges that use the cellulose acetate membrane. The hollow-fine-fiber model has a two-stage, 2-1 parallel-series array of three permeators, each containing a bundle of the aromatic polyamide fiber membranes.

Performance of the pilot plants was limited not only by equipment capability but also by the prevailing salinity of the feedwater, and especially its scaling tendency due to a high calcium sulfate content. Since the salinity varies seasonally, plant performance also varied as optimum levels of recovery were adjusted to match the limitations imposed by the feedwater TDS. Recoveries were improved by the addition of 5 ppm (mg/l) of sodium hexametaphosphate as a scale inhibitor. When softened feedwater was provided, the recovery rates were substantially increased since the risk of scaling was minimized.

Under a stable and continuous operating condition that safely precluded any calcium sulfate scaling, the three test plants maintained a 70-percent recovery level when desalting feedwater supplied at a TDS of 2,000 ppm (mg/l). When this feedwater was at a TDS of 6,000 ppm (mg/l), a 50-percent recovery was safely and continuously maintained. Special maximum recovery tests were conducted with the tubular model resulting in a recovery rate of 87 percent when feedwater with a TDS of 2,000 ppm (mg/l) was used. This level of recovery, however, was established as the point at which incipient calcium sulfate scaling occurred. Such a level was unstable since the calcium sulfate concentration had exceeded the solubility limit at which the mineral precipitates.

None of the test models exhibited a superior desalting capability as a result of its particular design configuration or type of membrane used, although there were wide variations in the desalination rates when measured in terms of product flux. The tubular plant was capable of producing 20 gallons per square foot, day (gfd) (82 millilitres per square centimetre, day [ml/cm^2, day]) of product flux when operating at a 70-percent recovery rate. The spiral-wound plant produced 10 gfd (41 ml/cm^2, day), and the hollow-fine-fiber plant produced 2.0 gfd (8.2 ml/cm^2, day) of flux at the same recovery rate. These flux values, however, are regarded as normal for each plant. They represent differences in membrane permeation characteristics, rather than equipment desalting efficiency.

During the approximate 18 months of operation, data on the three test plants indicated no time-related deterioration of the semipermeable membrane from chemical or biological activity. This demonstrated that the feedwater treatment and membrane cleaning procedures provided for the desalting operation were successful in maintaining membrane life and performance. Operating problems attributable to membrane malfunction or failure were generally caused by factors other than the application of feedwater treatment or membrane cleaning methods.

The three pilot plants, however, differed in their ability to respond to the cleaning procedures adopted to keep the membranes free of surface foulant. Mechanical (sponge-ball) and chemical (citric acid) cleaning methods as well as flushing with feedwater at low pressure were successfully used with the tubular plant. The spiral-wound plant was effectively cleaned with the citric acid treatment and feedwater flushing procedure. The hollow-fine-fiber plant responded to the citric acid treatment, but not to the flushing procedure.

An ion-exchange unit added to the feedwater pretreatment operation made softened feedwater available to the reverse osmosis plants after December 1973. The exchange process used a synthetic zeolite resin to remove the hardness constituents (Ca^{++} and Mg^{++} ions) from the feedwater; saturated sodium chloride brine was used for resin regeneration.

The ion-exchange system removed more than 95 percent of the Ca^{++} ions from the feedwater, thereby greatly reducing the scaling potential of this water in the desalination process. As a result, 90-percent recovery levels were readily attained by all three reverse osmosis plants, even during periods when the feedwater TDS was consistently more than 6,000 ppm (mg/l). Attempts were made to attain a product recovery of 95 percent with the tubular plant, but this level could not be consistently held because the low flow rate through the tubes resulted in unstable plant operation.

The spiral-wound and hollow-fine-fiber plants were newly manufactured proprietary products with hardware of good quality and design that provided excellent service in processing the highly saline tile drainage water. Multistage centrifugal pumps supplied the system pressure, and throttling valves on the feedwater supply and reject brine lines were used for pressure and flow control. While this method of regulation was adequate, it was limited somewhat by the interdependence of pressure and flow, attributable to centrifugal pump performance characteristics.

Two important features of the spiral-wound design were ease of removal of the desalting cartridges for inspection and the provision of sampling taps to monitor the five modules for product water quality. This monitoring capability allowed timely detection of leakage through the brine-side seals, which cause fouling of the desalting cartridges with precipitated calcium sulfate. One cartridge was damaged beyond use and required replacement because of this seal leakage. The time taken to replace the cartridge was the only significant outage incurred by this plant. Subsequent brine-side seal failures were averted through periodic inspection and replacement, and no other desalting cartridges were damaged. The citric acid treatment was successfully used for module cleaning, and the plant also responded well to the feedwater flushing operation. This was demonstrated when the desalting cartridges, fouled with regenerant brine from the softener, were restored to normal service by flushing with product water under low pressure.

The hollow-fine-fiber plant demonstrated excellent desalting performance and would have incurred only nominal outage time if 111 days were not used waiting for replacement permeators. The original permeators were damaged when regenerant brine from the softener was accidentally discharged into the feedwater stream. This resulted in the replacement of one set of permeators during the test operation, a factor in the high level of performance of this plant. Since the hollow-fine-fiber module did not respond to the flushing procedure normally used to clear calcium sulfate deposits, such fouling should not be risked, since the only recourse would be replacement of the permeators. A conservative approach with a relatively lower productivity level would therefore be expected in the operation of this plant.

The tubular plant was an experimental design, employing a positive displacement pump with a variable speed drive (varidrive) and a gas-pressurized regulating valve for operating control. This separate control of flow and system pressure permitted a more varied mode of operation. The equipment for this plant, however, had several years of prior test service before this evaluation study, and the plant experienced equipment maintenance and repair problems related to extended usage.

This plant had several features that allowed operation at high levels of productivity, making it an efficient design for desalting agricultural tile drainage water. Its tubular assembly could be readily fabricated and simply and quickly installed. Low-cost replacement could be made of damaged tubes or those showing poor desalting characteristics. Desalting performance could be improved through the substitution of tubes with membranes with properties better adapted to a particular feedwater salinity or equipment operating level.

Future Studies

As a result of the first-phase studies, desalting studies have begun in the second phase to:

1. Establish the economic feasibility of desalting by the reverse osmosis process. This phase will provide design information from which desalting costs can be estimated for comparison of reverse osmosis desalting with alternative methods of agricultural waste water disposal (such as disposal into the San Francisco Bay system) and to determine the feasibility of integrating the reverse osmosis process into an overall agricultural waste water utilization project.

2. Use a desalination plant of advanced design with a capacity of 20,000 to 30,000 gallons per day (gpd) (75.71 to 113.60 cubic metres per day [m^3/day]). Plant selection is to be based on results of the first-phase study with consideration given to the specific requirements of desalting agricultural waste water.

3. Use a feedwater treatment system specifically tailored to the needs of the selected design to provide membrane protection against chemical and biological deterioration and surface fouling.

4. Make cost studies of the effectiveness of scale-inhibiting chemical additives and various ion-exchange processes for improving reverse osmosis productivity.

5. Develop a computerized monitoring system to predict reverse osmosis performance and thereby maintain an efficient level of production and minimize operating problems. This system could be patterned after the present University of California, Los Angeles, computer program written to predict reverse osmosis plant performance for desalting Alamitos tile drainage water.

CHAPTER II. INTRODUCTION

This bulletin reviews the investigations made by the Department of Water Resources (DWR) on the desalination of subsurface tile drainage water by the reverse osmosis process. These investigations were carried out at the Waste Water Treatment Evaluation Facility (WWTEF) located near Firebaugh, California, during the years 1971 through 1974.

DWR has been involved in these investigations because of its responsibility in matters related to the reclamation and disposal of agricultural waste water in the San Joaquin Valley. Various studies to reclaim or improve the quality of agricultural waste water were made by DWR at the WWTEF as early as 1967. These early studies investigated various biological-chemical processes required to condition the waste water for disposal into a drainage system or estuarial waters.

The first DWR investigations into the desalination process were made in 1971 with the test operation of an experimental reverse osmosis (RO) plant developed by the University of California, Los Angeles (UCLA). Several configurations of this RO plant were subsequently operated at the WWTEF serving to establish the technical feasibility of desalting subsurface tile drainage water by the RO process.

Following the UCLA investigations, DWR arranged with the U. S. Department of Interior's Office of Water Research and Technology (OWRT) (formerly the Office of Saline Water) to jointly sponsor a test program to evaluate three comparable designs of RO equipment to desalt subsurface tile drainage water. The program began in May 1973 and was conducted for 18 months using three prototype RO plants that possessed different design configurations and types of desalting modules. The RO plants were tested simultaneously under similar operating conditions, utilizing a single source of feedwater to provide a common basis for evaluation.

In conjunction with the desalting studies on RO equipment, DWR contracted with the University of California, Berkeley (UCB), for a study into the effects of bacterial activity on the life and performance of the RO membrane. This bacteriological study was made concurrently with the RO studies, using the facilities and personnel at the WWTEF, and laboratory work at Berkeley by UCB investigators. In this study, bacterial organisms responsible for membrane deterioration and surface fouling were identified, and several feedwater pretreatment chemicals were evaluated regarding their effectiveness as bactericides.

Background

Water conveyance facilities such as the California Aqueduct make large quantities of new water available to the west side of the central and southern regions of the San Joaquin Valley. The importation of this water will cause additional land to be put to agricultural use, and the use of this water for surface irrigation will allow more intensive farm production.

These regions of the Valley, however, are normally arid and lack adequate rainfall for agriculture (1). Much of the land has shallow layers of impermeable subsoil with a high content of precipitated minerals. Surface irrigation of these soils results in slow permeation and creation of local high ground water conditions, requiring installation of a subsurface drainage system to avoid loss of farm productivity. Plant evapotranspiration also adds salts to the soil by allowing pure water to transpire from the plant leaves. The saline drainage water is therefore a result of water leaching minerals already present in the soil and of salts that plants leave behind after the evapotranspiration process.

The need to provide subsurface drainage for irrigated lands, and a means of disposal for the drainage water, has been recognized for some time. DWR, in cooperation with federal agencies, has conducted extensive investigations of waste water salinity and disposal problems in the San Joaquin Valley (2). As a result of these investigations, a plan was proposed for the development of a drainage facility to collect and transport agricultural waste water for disposal into the Sacramento-San Joaquin Delta. To provide an outlet for the farm waste water for its San Luis service area, the U. S. Bureau of Reclamation (USBR) is presently constructing the San Luis Drain. This drainage system will provide export of waste water for impoundage at the Kesterson Reservoir (3).

In 1967 DWR joined an interagency study group (USBR and the predecessor to the Environmental Protection Agency) to establish the waste water treatment center (originally designated the Interagency Agricultural Wastewater Treatment Center) near Firebaugh for the purpose of investigating various approaches to agricultural waste water treatment for reclamation or proper disposal (4). The Firebaugh location was chosen because of the year-round availability of tile drainage water from the Alamitos sump. The sump serves as a year-round source of drainage for the WWTEF.

The interagency study group primarily investigated methods of removing nitrate-nitrogen from tile drainage water. These investigations were prompted by concern over the algal bloom that might be caused by disposing nitrogen-rich water into the San Joaquin Delta and the subsequent adverse effect on the receiving water. Biological-chemical processes such as algae stripping and bacterial denitrification were investigated in these nitrogen removal studies.

DWR then initiated studies into the desalination process using a tubular membrane RO plant developed at the engineering laboratory of UCLA (5). This plant was obtained for test purposes under a cooperative arrangement whereby UCLA was reimbursed for providing the equipment and technical direction for its operation. DWR supplied the personnel and facilities at the WWTEF for operation of the RO plant.

RO studies with the UCLA-designed equipment began in July 1971 and continued through 1972, during which time several design configurations were test-operated (6). Studies were carried out to establish the feasibility of desalting tile drainage water by RO and to develop appropriate operating techniques and equipment.

The first UCLA-designed equipment to be test-operated was a unit made up of 24 tubular assemblies. This unit was a pilot installation that provided operating experience for the test personnel and an opportunity to observe the effects of tile drainage water on the properties of the cellulose acetate (CA) semipermeable membrane.

The second unit installed was comprised of 180 tubes and was intended to allow study of RO plant and membrane performance and to establish optimum levels of desalted water production for a one-year period of operation. After four months, however, plant operation was suspended because of severe membrane deterioration and calcium sulfate ($CaSO_4$) precipitation problems.

The next unit installed was specifically designed and operated to investigate the problems adversely affecting the 180-tube unit performance. This third unit had 60 tubes divided into five parallel sections, with each section equipped to receive chemical additives. The purpose of this operation was to investigate the effects of feedwater treatment chemicals on the CA membrane and its backing material, and to test the effectiveness of antiprecipitant chemicals in preventing $CaSO_4$ scaling.

Preliminary studies with the UCLA RO plants developed useful information on membrane performance, equipment operation, and feedwater pretreatment criteria for desalting tile drainage water (6). Typical problems dealt with included CA membrane biological and chemical deterioration, surface fouling, and $CaSO_4$ scaling. Feedwater pretreatment procedures developed included the use of sulfuric acid to control pH, low-level chlorination, dechlorination with carbon filtration, and the use of sodium hexametaphosphate (SHMP) as a scale inhibitor.

In June 1972, DWR and OWRT agreed to jointly sponsor the evaluation study included in this bulletin (Task Agreement No. 3 to OWRT Agreement No. 14-30-2587). The agreement provided for the test operation of three prototype RO desalting plants to establish their technical capability to desalt tile drainage water. The test program was also to develop preliminary information for the selection of a larger-capacity RO plant to be operated for design data and cost determination purposes.

The task agreement initially provided for an 18-month test to evaluate three designs of desalting plants but was later amended with provisions for a 12-month extension and completion in December 1974. The selected plants were to each have a desalting capacity of 2,000 to 5,000 gpd (7.57 to 18.93 m^3/day) and employ desalting modules of differing design. OWRT supplied two types -- a hollow-fine-fiber and a spiral-wound design -- and DWR provided a tubular-membrane design obtained from UCLA. DWR made the facilities at the WWTEF available for the program and agreed to construct a shelter to house the RO units, install the necessary support equipment, provide test personnel to operate the units, and supply tile drainage water for testing purposes. Funding for the joint program was shared by DWR and OWRT.

In April 1973, DWR contracted with UCB for a study on the bacteriological aspects of membrane decomposition and surface fouling in an RO system. The study was carried out during 1973 and 1974 and involved two phases. In the initial phase, identification was made of specific types of microorganisms found in RO water that affected the life and performance of the CA membrane. The final phase investigated the effect of various feedwater pretreatment procedures in controlling bacteriological deterioration of the membrane in an RO test unit. A complete review of this study is presented in the appendix of this bulletin.

The initial phase of study involved collecting and culturing the various kinds of bacterial organisms found in Firebaugh RO water for identification. Those organisms considered to be active in surface fouling or membrane decomposition were isolated to determine their roles in this respect.

DWR provided the services for collecting various water samples from its RO operation at Firebaugh. It also devised a single-tube RO unit that simulated the large-scale RO unit operation but which desalted raw feedwater rather than the pretreated feedwater supplied to the large unit. Its purpose was to provide bacterial growth specimens under typical RO operating conditions but unaffected by feedwater treatment chemicals.

Water samples for bacteria culturing were collected monthly from April through August of 1973. The samples were taken to Berkeley where the investigative work was carried out at UCB's laboratory facilities. CA membranes, in various conditions of usage, were also collected from the two RO units. Following completion of the investigations on the initial phase of study, the report, "Bacterial Aspects of Slime Formation and Membrane Failure in Reverse Osmosis Systems", was issued in September 1974.

The report concluded that several types of bacteria grow inside the RO tubes and appear to biodegrade the CA membrane, causing membrane failure. These bacteria originate in the soil and find the particular combination of cellulose acetate material and inorganic constituents of tile drainage water suitable for growth.

The final phase of study had two objectives, and to achieve them, an experimental RO system made up of four parallel lines with three tubes in each line was installed and operated at the WWTEF. The first objective was to determine the effect of various feedwater chemical pretreatment operations upon surface fouling and membrane biodeterioration. The second was to correlate the various components of cellulose acetate material with membrane biodegradation.

The experimental system was a 12-tube special-purpose RO unit designed and fabricated by UCLA. The 12-tube RO unit was installed at the WWTEF in February 1974 and operated for test purposes from March 1974 to February 1975. DWR personnel operated the unit and monitored its performance. UCB personnel collected various RO water samples, spongeball cleaning residue, and membrane specimens for the investigative work at Berkeley.

Following completion of this phase of study, the final report, "Prevention of Biodeterioration and Slime Formation in Reverse Osmosis Units Operated at Firebaugh, California", was issued in June 1975. This report is included as the appendix of this bulletin.

The report concluded that feedwater pretreatment by acidification, oxygen removal, or chlorination must be performed to protect the membrane from biodeterioration. Oxygen removal appears to be the single best method in preventing membrane biodeterioration without causing the surface fouling and chemical handling problems associated with acidification or chlorination.

The study also found that individual CA membrane compositions can affect the susceptibility of the membrane to biological attack. This susceptibility was found to be less for membranes prepared from cellulose acetate having a high acetyl content and high viscosity. Susceptibility, however, was greater for membranes prepared at the higher cure temperatures.

CHAPTER III. DESALINATION BY REVERSE OSMOSIS

Osmosis and Reverse Osmosis

Normal osmosis is a process in which water in a dilute aqueous solution will pass through a semipermeable membrane into a more concentrated solution, leaving much of the solute behind. This process continues until the concentrated solution acquires an osmotic pressure differential sufficient to stop further passage of water through the membrane. When pressure greater than the osmotic pressure difference is applied to the concentrated solution, the water flow reverses. This phenomenon is known as reverse osmosis.

For a given aqueous solution, the osmotic pressure is a function of the concentration and ionic characteristics of the solute and is directly proportional to the solute concentration. The following equation defines the relationship (5):

Equation 1 $\quad p_o = \bar{a}C = 0.0117C$

where p_o = osmotic pressure in pounds per square inch (psi) (kilopascal [kPa])

C = solute concentration in ppm (mg/l)

$\bar{a}$ = an empirically determined proportionality constant in psi/ppm (kPa/mg/l)

The value of $\bar{a}$ for a dilute aqueous solution of sodium chloride has been experimentally determined to be 0.0117 psi/ppm (0.0807 kPa/mg/l) and may be used for approximating the osmotic pressure of agricultural waste (brackish) water.

With the application of sufficient pressure to induce reverse osmosis across the semipermeable membrane, the rate of water and solute passage through the membrane is determined approximately by the following equations (7):

Equation 2 $\quad Qw = A(dP-dp_o)$

Equation 3 $\quad Qs = B(C_1-C_2) \simeq BC_1$

where Qw = product water flux through the membrane
A = membrane water permeation coefficient
dP = applied pressure differential
dp_o = osmotic pressure differential
Qs = solute flux through the membrane
B = membrane salt permeation coefficient
C_1 = salt concentration in brine water
C_2 = salt concentration in product water

For most reverse osmosis applications, salt permeation is low enough so that C_2 is small compared to C_1, and therefore Equation 3 may be written as $Q_s \simeq BC_1$. The two independent equations govern the design and performance of an RO system.

Semipermeable Membrane

Two types of semipermeable membranes were used in this evaluation study. A CA membrane was used in the tubular and spiral-wound modules and prepared by a process developed and patented by UCLA (8). An aromatic polyamide membrane was used in the hollow-fine-fiber module and is a product of the E. I. Du Pont de Nemours & Company (9).

The CA membrane is prepared from a solution composed of cellulose acetate, formamide, and acetone in a typical ratio of 25:30:45 percent by weight. The resulting membrane is cast into a tubular-shaped film; it is composed mainly of cellulose diacetate and has a dense surface layer formed during casting and a relatively porous sublayer. The total film thickness is about 100 micrometres (µm), and the dense layer has a thickness of about 0.2 µm. The thin, dense layer is formed on the side exposed to the air during casting and is recognized as the primary barrier to salt passage. This surface must be in contact with the brine to gain full membrane performance.

As a final step in fabrication, the membrane is cured by contact with hot water at about 25-psi pressure. The curing process gives the membrane its salt-rejecting capability; an uncured membrane offers virtually no resistance to salt passage. Cure temperatures range from 169° Fahrenheit (F) (76° Celsius [C]) to 201° F (94° C), with permeability to both flux and salt decreasing with increasing cure temperature. Thus, a membrane cured at 169° F (76° C) has a high permeability and is referred to as a "loose" membrane, while one cured at 201° F (94° C) has a low permeability and is considered a "tight" membrane.

The polyamide base membrane is used in the form of a thin, hollow fiber about the size of a human hair. The fiber is actually a uniform-shaped, thick-walled cylinder with an outside diameter of 84 µm and an inside diameter of 42 µm. Like the CA membrane, the wall of the cylinder is asymmetric, having a dense outer layer of about 0.1 µm and a relatively porous substrate. Unlike the CA membrane, however, it does not undergo a curing process that provides a range of permeability.

The hollow fiber shape has several features not found in other membrane designs. The fibers are able to withstand high pressures without collapsing, are self-supporting, and are less susceptible to mechanical damage. Most important, the small fibers allow effective packing of a large surface area in a small space resulting in high productivity per unit volume. This feature is offset somewhat by the relatively low permeability -- 2.0 gfd (8.2 ml/cm^2, day) compared with the 20 gfd (82 ml/cm^2, day) permeability of the CA membrane.

Operating Parameters

As previously mentioned, product water flux and salt passage through the semipermeable membrane are described by Equations 2 and 3. Equation 2 shows that the product flux is proportional to the applied pressure when the osmotic pressure difference is held constant. The coefficient A indicates that product flux is dependent upon other factors besides pressure, such as brine flow rate, brine quality, and water temperature. Operating pressure and brine flow rate are the more important parameters because they directly affect water and salt permeation and can be readily manipulated in an RO operation. Three conditions dependent on the primary factors of pressure and flow rate also affect membrane permeability; they are compaction, concentration polarization, and osmotic pressure.

Pressure

The primary influence of operating pressure in the RO process is its effect on the product water flux and quality. In general, an increase in applied pressure causes an increase in product flux and a decrease in product salinity. Pressure also causes structural changes within the membrane, a condition described as compaction.

Equation 3 shows that water quality depends only on the solute concentration difference across the membrane film. The effect of applied pressure on water quality is therefore indirect -- while the salt flows through the membrane at a constant rate (depending upon brine salinity), higher pressures result in greater desalted water flow, thus producing a more dilute or better quality product. Therefore, poorer water quality can be expected at low operating pressure (200 psi [1,380 kPa]) and is the reason why operation at higher pressures (600 to 800 psi [4,140 to 5,520 kPa]) is preferred for the RO process (10).

Brine Flow

The brine flow over the membrane surface is important to both product flux and quality because of its effect on boundary layer conditions. Equation 3 shows the dependence of product quality on the salt concentration at the brine-membrane interface. The barrier imposed by the membrane to salt passage results in a buildup of salinity at the interface, a condition known as concentration polarization. Since this effect is most pronounced at low brine velocities, it is important that brine flow rates be maintained sufficiently high to decrease boundary layer thickness and increase convective mixing with turbulent flow. This minimizes the effects of concentration polarization which not only causes poor product water quality but also increases the probability of precipitation of sparingly soluble salts.

Temperature

Water temperature is important because of its direct effect on membrane permeability (constant A of Equation 2). For the CA membrane, an increase in water temperature of 1° F (0.6° C) causes a 1.5-percent increase in product water flux (7). Operation at temperatures greater than 100° F (38° C) for any length of time will cause the membrane to undergo permanent changes which will reduce product flux. Temperature effects on osmotic pressure and solubility limits of precipitating salts are not considered significant.

The temperature of the feedwater supplied to the WWTEF varies seasonally from 55° F (13° C) to 78° F (26° C). Since this temperature change occurs over a long period of time, its effect on the CA membrane is masked by other time-dependent changes in membrane permeability. Consequently, it is difficult to establish a valid relationship between changes in water temperature and membrane permeation rates.

Concentration Polarization

Due to the passage of desalted water through the membrane and the rejection of salts by the membrane, there is an accumulation of salts at the brine-membrane interface (7, 8). The excess salt concentration at the membrane surface is termed concentration polarization, and the brine film next to the membrane containing the high salt concentration is called the boundary layer. Concentration polarization depends greatly on brine flow rate and membrane permeation rate, and its effect on desalination is especially pronounced at low brine velocities and high permeation rates.

Boundary layer effects (concentration polarization) manifest themselves in several ways, and past investigations have shown that these effects can be as important in the RO process as intrinsic membrane properties. The excess salt concentration results in a greater effective osmotic pressure which decreases the net driving force and water flux. The increased concentration also results in a higher salt flux through the membrane and the likelihood of salt precipitation on the membrane surface. Membrane deterioration may also be more rapid at higher brine concentrations.

Compaction

Changes in membrane structure taking place over a period of use affect permeability characteristics and therefore membrane constant A of Equation 2. This physical change in the membrane is referred to as compaction and is associated with changes in the water content and density of the membrane (8). It has been determined that water content decreased and compaction increased with increased pressure or increased time of service.

The effects of compaction are gradual, resulting in a deterioration of flux or salt rejection. Compaction proceeds at a faster rate at higher pressures. Differences in this effect may be related to the temperature of cure of the CA membrane. The effects of compaction, however, cannot be readily differentiated from other time-related factors affecting membrane life and performance.

Ion Rejection

Several ion-rejecting properties of the CA membrane are important to RO desalting. Most importantly, the CA membrane can be tailored to a specific degree of ion rejection by manipulating the cure temperature during membrane manufacture to produce a "tight" membrane with high salt rejection and relatively low flux or a "loose" membrane with high flux and a low salt rejection (8).

One characteristic common to all RO membranes is the preferential ion rejection of the multivalent ion species. The rejection of divalent ions such as Ca^{++}, Mg^{++}, and $SO_4^{=}$ is much greater than for monovalent ions such as Na^{+} and Cl^{-}. This characteristic is more evident in CA membranes of high temperature cure than of low temperature cure.

CA membranes have poor boron-rejecting characteristics, an important factor in desalting agricultural waste water containing boron because of the low tolerance of many farm crops to this element. The best rejection of boron achieved with the high cure membrane was about 60 percent (8). Membranes of lower temperature cure showed correspondingly lower boron rejection, and rejection decreased with decreasing feed pH. In this respect, the polyamide base membrane is not as sensitive to pH and therefore retains a relatively better boron-rejecting characteristic at lower feed pH.

Brine Quality and Pretreatment

Brine quality is usually defined in terms of a TDS value, although its pH and ionic composition are also important in the RO process. When the ions of a sparingly soluble mineral are concentrated beyond the saturation point, the mineral will precipitate and deposit on the membrane surface, impeding further permeation. Therefore, the solubility of these precipitating minerals will effectively set the limit of concentration and product recovery attainable for the RO process. The effect of $CaSO_4$ precipitate on the membrane surface is considered temporary since no permanent change takes place in the membrane and original performance can be restored by removal of the precipitate and a return to normal operating conditions (7).

Product recovery can be increased by maintaining adequate flow turbulence to reduce concentration polarization effects or pretreating the feedwater with a chemical additive to suppress precipitation. A constituent of the precipitating mineral can also be removed from the feedwater by an ion-exchange process to reduce the scaling potential of the mineral.

The ions of certain minerals combine to produce deposits of iron, aluminum, and calcium compounds on the membrane surface, resulting in a gradual loss of permeability but not drastically reducing product flux. Since the precipitation of these minerals is promoted at alkaline pH, treatment of the feedwater with sufficient acid to lower pH levels of 5.5 to 6.5 will effectively prevent fouling from these mineral deposits. Since CA membranes tend to hydrolyze under highly alkaline pH conditions, acidification to pH levels of 5.5 to 6.5 will also reduce the rate of membrane hydrolysis (8).

UCLA investigators used their tube-type RO unit in a study to predict the scaling threshold limit of $CaSO_4$ in tile drainage water. The study was based on a computer program developed at the Holifield National Laboratory that predicts the concentration factors at which water with a given ionic strength will precipitate the various forms of $CaSO_4$ (anhydrite, hemihydrate, dihydrate) (11, 12). Studies at UCLA and field data from the WWTEF have shown good correlation with the theoretical results of the computer program, and this program is now being used to predict the brine concentrations at which calcium sulfate dihydrate (gypsum) will precipitate.

Membrane Fouling

Semipermeable membranes reject particulate matter, bacteria, colloids, and other substances of large molecular size. Unless these substances are removed from the feedwater through prefiltering or pretreatment before the RO process, desalination will result in the fouling of the semipermeable membrane (13). Prefiltering the feedwater removes most suspended solids and is best accomplished by using an in-line cartridge filter of 5- to 25-µm size (14).

Particulate filters, however, cannot prevent fouling caused by precipitated minerals or bacterial growth on the membrane surface. Although bacteria are found in the feedwater in only minute quantities, they can multiply rapidly on the membrane surface where deposited materials provide a ready source of nutrients (15). Bacteria not only promote surface fouling but also can attack cellulose acetate, causing deterioration of the membrane and loss of rejecting capacity.

After an extended period of operation, the RO membrane will require surface cleaning to remove a buildup of fouling material resulting from the deposition of particulate matter, bacterial growth, or precipitated minerals. The simplest method of cleaning the membrane surface is to pass a continuous flow of feedwater (preferably desalted water) through the desalting module to remove loose particles or dissolve the minerals. The tubular-membrane module can be readily cleaned by passing a spongeball through the tube under low feedwater pressure. Most mineral precipitates occurring during desalination (calcium carbonate, oxides of iron or aluminum) are soluble under acidic conditions (pH of 4) and may be removed by circulating an aqueous solution of citric acid through the desalting module.

Surface treatment of the membrane with a spongeball or citric acid solution generally results in a significant increase in product flux, especially following the cleaning operation. Cleaning with citric acid removes material imbedded in the membrane surface, and the resulting increased porosity may also result in increased salinity of the product water. This increase in product flux and salinity after cleaning is more evident with an old or used membrane than with a new one. Cleaning effects are also more apparent in the low-temperature-cured, "loose" membrane than in the high-temperature-cured, "tight" membrane.

Differences in the properties of the CA and polyamide base membranes result in different feedwater pretreatment and equipment operating and maintenance requirements. The polyamide base (nylon) material is regarded as more resistant to chemical and bacterial attack, and especially to the effects of hydrolysis. Therefore, it can be used with feedwater pH levels up to 8.0, while the CA membrane is limited to pH of 5.5 to 6.5. The polyamide material, however, is much less tolerant to chlorine -- safe exposure is limited to 0.05 ppm (mg/l) on a long-term basis and 0.5 ppm (mg/l) over a short period of time (16). The CA membrane can be exposed to 0.3 ppm (mg/l) of chlorine on a continuous basis without harmful effects.

The early UCLA studies with the tube-type RO unit have shown the susceptibility of cellulose acetate to bacterial attack when exposed to untreated tile drainage water for a prolonged period. These studies showed that a bactericidal chemical such as chlorine at a 1.0-ppm (mg/l) level prevented this deterioration (17). Chlorination at this level, however, raised the possibility that the chemical itself would damage the CA membrane. The long-term effect of chlorine on membrane performance, however, could not be easily evaluated or differentiated from other time-dependent effects such as membrane hydrolysis or compaction.

To avoid chlorine damage to the semipermeable membrane, a low-level chlorination procedure was adopted for feedwater pretreatment at the WWTEF. This procedure consisted of initial pretreatment of the feedwater with 0.2 ppm (mg/l) of chlorine residual and detention of the feedwater in a holding tank for about 40 minutes to allow the chlorination to take effect, followed by dechlorination of the feedwater with an activated carbon filter.

CHAPTER IV. REVERSE OSMOSIS FEASIBILITY STUDY

In July 1971, DWR began a study in RO desalting to determine its feasibility as a method for reclaiming subsurface tile drainage water. The study was made at the WWTEF where facilities and a supply of tile drainage water from the Alamitos sump was available for test purposes, and investigations were carried out with a tubular-membrane RO plant furnished by UCLA under a contractual arrangement.

WWTEF -- Location and Facilities

The WWTEF is located along the Delta-Mendota Canal about 3 miles (5 kilometres) west of Firebaugh, California (shown on Figure 1). The test site occupies about 2 acres (0.8 hectare) of land and has several structures and facilities installed during its use by the interagency study group for nitrogen removal studies. The present desalination activities use only the water supply system of the original installation and occupy a test shelter and adjoining outdoor concreted area (shown on Figure 2). The shelter is an 18-foot-by-80-foot (5.5-metre-by-24-metre) wood frame structure containing a small office space and equipment test area. The outdoor canopied space is occupied by the feedwater treatment and other accessory equipment.

Feedwater Supply

Water for the WWTEF is obtained from the Alamitos tile drainage system, which collects subsurface water from 400 acres (162 hectares) of farmland adjoining the site. This water is pumped to an 820,000-gallon (3,100-cubic metre [m^3]) elevated storage pond where it is drawn upon for use at the WWTEF. The farmland is planted with field crops typically grown in this locality.

The flow from the tile drainage system varies throughout the year, with low flows during the winter months and high flows during the summer growing season when intensive surface irrigation is carried out on the adjoining farmland. The salinity of this water varies from 2,000 ppm (mg/l) to more than 6,000 ppm (mg/l), also depending upon seasonal factors and irrigational practices. The water drawn from the storage pond has essentially no turbidity, a pH of about 7.1, and a temperature varying seasonally from 55° F (13° C) to 78° F (26° C).

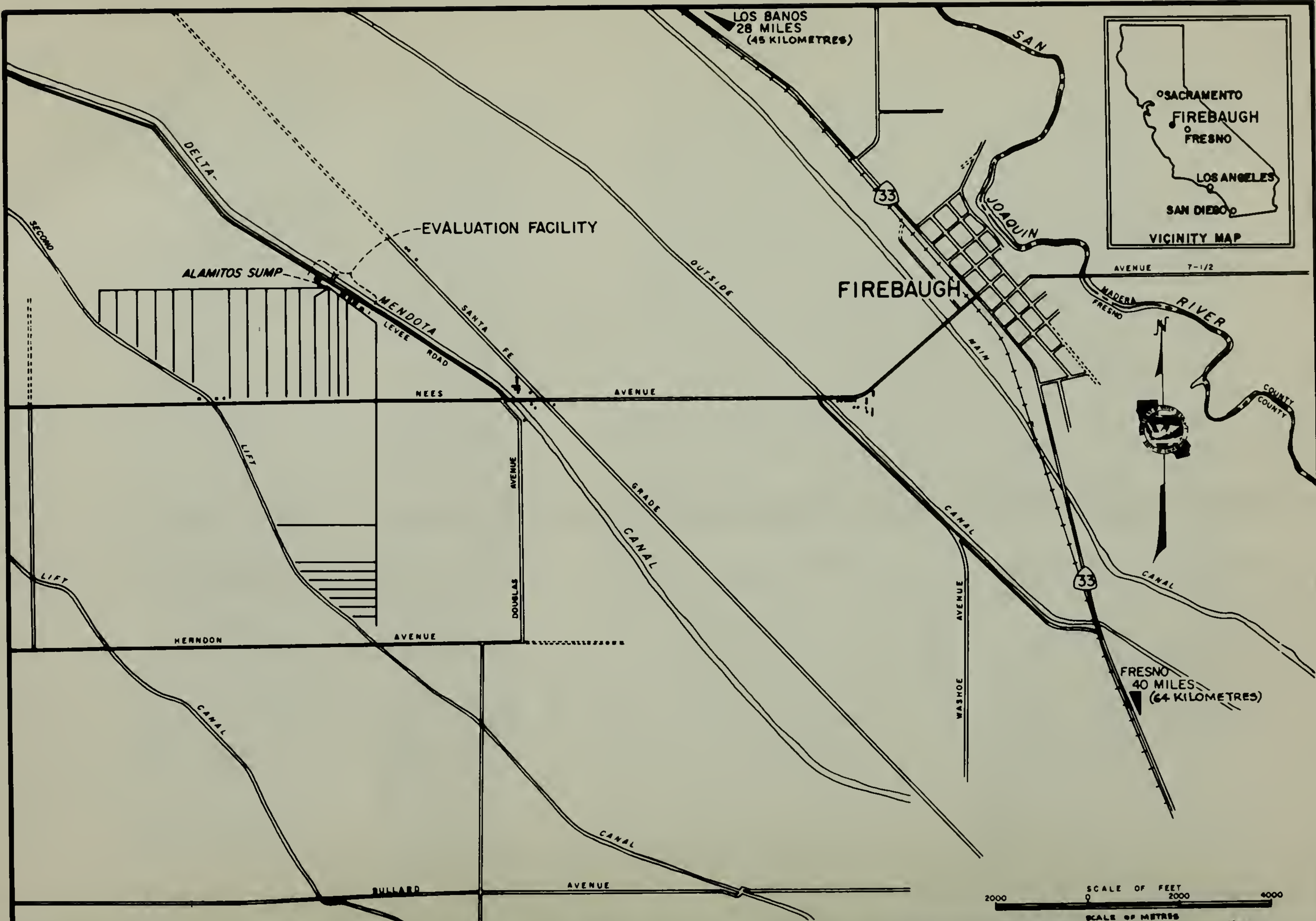

FIGURE 1- LOCATION OF WASTE WATER TREATMENT EVALUATION FACILITY

Front View

Canopied Equipment Area

FIGURE 2. THE WASTE WATER TREATMENT EVALUATION FACILITY

The water supplied by the Alamitos tile drainage system has an unusually high concentration of calcium sulfate dihydrate (gypsum), a natural mineral abundant in the Firebaugh area, leached out by the drainage water during percolation through the soil.

Tubular Membrane Reverse Osmosis Pilot Plant

The tubular membrane RO pilot plant used in the RO feasibility study was designed and fabricated at UCLA and provided in several configurations for testing at the WWTEF. These different configurations were made possible because the design of the plants allowed flexibility in the number of tubes installed for desalting purposes without altering the basic operating equipment. A description of the construction and operation of the pilot plants is given under the section, "Tubular Reverse Osmosis Unit" in Chapter V.

Three configurations of this pilot plant were test-operated for the feasibility study during 1971 and 1972. The first unit operated was a 24-tube configuration that served as a pilot installation. It was followed by a second unit consisting of 180 tubes and a third unit of 60 tubes, which was used for special investigations. The RO plants were operated and maintained by DWR personnel, while UCLA provided the technical guidance in operating the equipment and in conducting the various studies.

24-tube RO Unit Operation

This unit served as a pilot installation to develop information on equipment operation and semipermeable membrane performance to be applied to desalting tile drainage water and to provide test personnel with experience required for the operation of the 180-tube unit. Specifically, the unit was used to determine (a) the performance of differently cured membranes at several operating pressures and flows, (b) the effect of subsurface tile drainage water upon the life and performance of the semipermeable membrane, and (c) the extent of chemical treatment required for the feedwater to inhibit membrane deterioration due to hydrolysis or bacterial activity.

The 24-tube RO unit was started up on July 22, 1971, and completed 98 days of operation without any major interruption. Figure 3 provides a chronological summary of the performance data and important occurrences regarding the operation of the unit. Feedwater flow and pressure were maintained at 6.0 gallons per minute (gpm) (0.38 litres per second [l/s]) and 600 psi (4,140 kPa), respectively, except when they were manipulated for the pressure-flow variation tests. Temporary

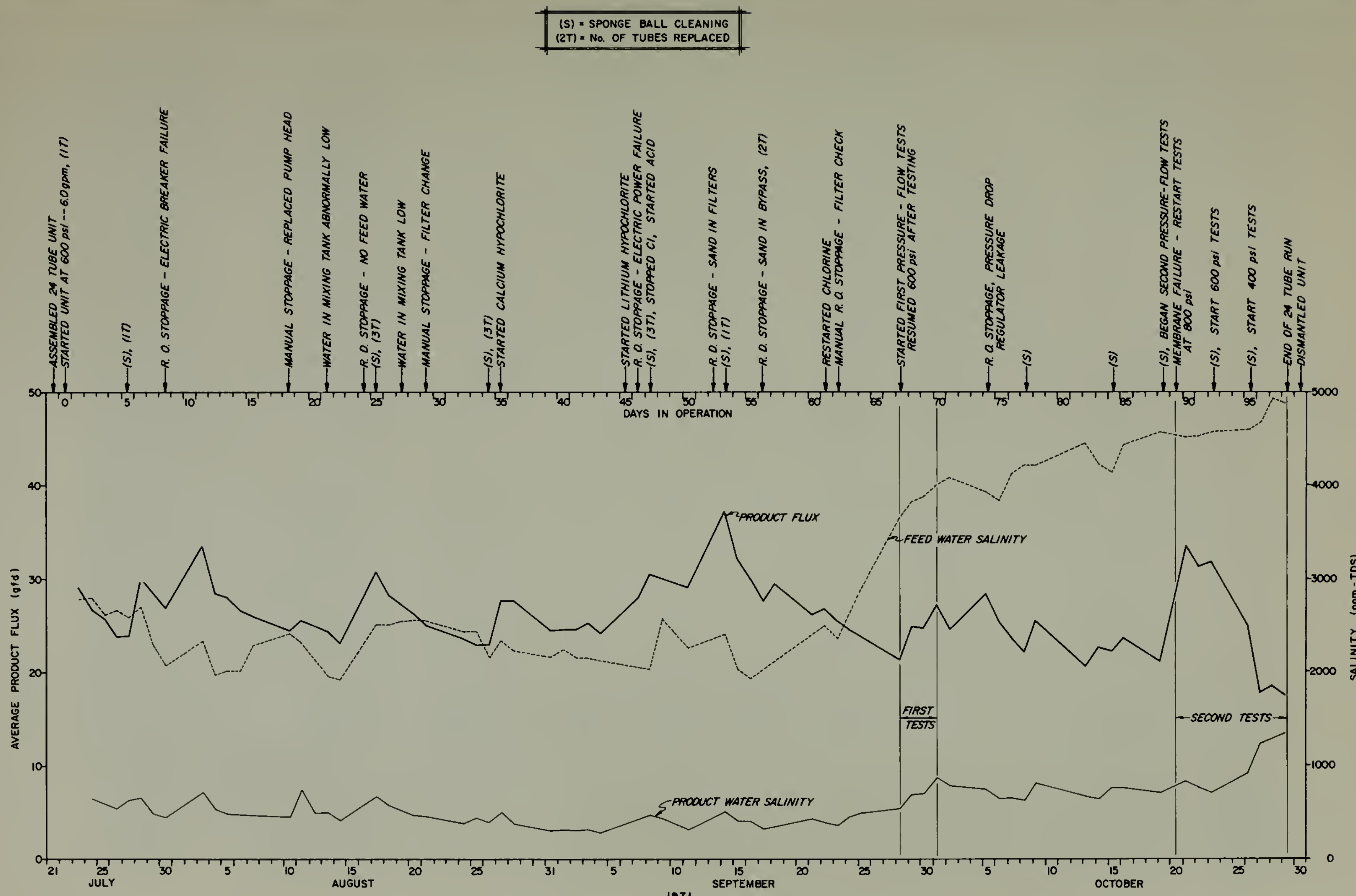

FIGURE 3-24-TUBE (UCLA) REVERSE OSMOSIS UNIT-SUMMARY OF OPERATIONS shutdowns of the unit were caused by electrical failures, clogged filter, pump and pressure regulator repairs, and membrane failures.

Unit performance was monitored by regular sampling of feed, product, and brine water. Quantity samples were taken weekly from individual tubes and daily for total production. Water quality was determined on the same basis by measurement of TDS. A typical mineral analysis for water samples taken on September 1, 1971, is shown in Table 1.

TABLE 1

MINERAL ANALYSIS OF WATER SAMPLE
FOR 24-TUBE REVERSE OSMOSIS UNIT
September 1, 1971

Constituent	Concentration (ppm or mg/l)		
	Feed	Product	Brine
Calcium	166	8.4	191
Magnesium	72	4.9	85
Sodium	525	84	595
Potassium	3.0	0.3	3.4
Sulfate	1,130	43	1,300
Bicarbonate	454	77	516
Chloride	173	52	192
Nitrate	99	55	105
Boron	5.2	3.9	5.5
TH as $CaCO_3$*	709	41	827
TDS	2,480	307	2,850
pH	8.3	7.4	8.3

*TH = total hardness,
$CaCO_3$ = calcium carbonate

The membranes were periodically fouled by the accumulation of bacterial matter and inorganic precipitates along the wall. These substances were substantially removed by passing a spongeball through the tube assembly at a booster pump pressure of 45 psi (310 kPa). Immediately after the tubes were cleaned, there was an increase in product flow and product salinity.

Treatment of the feedwater consisted of chlorination and acidification which extended the life of the CA membrane. Chlorine was added at a concentration of 1.0 ppm (mg/l) for bacterial control, and sulfuric acid (H_2SO_4) was added to maintain a feedwater pH at levels between 4.0 and 6.0, which inhibits membrane hydrolysis. Chlorination (lithium hypochlorite salt) was started on the 35th day and was continued throughout the operation except during a 15-day period when only H_2SO_4 was added for pH control. Chlorination was purposely delayed in order to determine the effects of the feedwater upon the membrane before and after treatment. Residual matter obtained from the tube cleaning throughout this period showed a marked clearing after chlorination began, an indication that this treatment was beneficial in reducing bacterial accumulation.

During the first five days of operation, the 24-tube unit produced an average of 1,400 gpd (5.3 m^3/day) with a feedwater input of 9,000 gpd (34 m^3/day) or about 16-percent recovery. The product water salinity averaged about 600 ppm (mg/l) compared to a feedwater salinity of 2,700 ppm (mg/l). Five days prior to the beginning of the pressure-flow tests, the feedwater salinity had increased to about 4,000 ppm (mg/l). The production had decreased to 1,250 gpd (4.73 m^3/day) and the product salinity increased slightly to 640 ppm (mg/l). By the end of the investigation (during the pressure-flow tests at 600 psi [4,140 kPa] and 6.0 gpm [0.38 l/s]), the product salinity had increased to about 1,000 ppm (mg/l).

Minor fluctuations in the flux and product quality were caused by feedwater salinity changes, occasional periods of spongeball cleaning, and other stoppages. Abrupt increases in flux were observed whenever the unit was shut down for cleaning or other maintenance, or by automatic stoppages. The higher flux rates were usually accompanied by increases in the product salinity, which was attributed to removal of the extraneous materials causing membrane fouling and the relaxation of the membranes following a period of compaction.

Membrane deterioration was found to be the most frequent cause of tube failure. This was first observed in three tubes that failed during cleaning on August 16, 1971. Subsequently, all the tubes removed for replacement and most of the tubes examined at the end of the study showed evidence of deterioration. In some cases, the CA membrane toward the end of the tube had dissolved and a light brown, slimy substance coated the deteriorated areas. The delay in chlorination and consequent lack of adequate bacterial control could have been responsible for this deterioration. Figure 4 illustrates the variability of damage to the tube membranes.

Two sets of pressure-flow variation tests were conducted to evaluate the permeability characteristics of the differently cured membranes. The first tests required three days to complete and were based on hourly pressure changes at selected flows. The second tests required 14 days and were based on 72-hour periods at selected pressures and flows, the results of which are presented on Figure 5.

End Deterioration --
1/8 to 1/4 Inch

Membrane Brittleness
at Flared End

End Deterioration --
2 to 3 Inches

Complete End Deterioration
for More than 5 Inches

FIGURE 4. ADVANCED STAGES OF BIOLOGICAL
MEMBRANE DETERIORATION

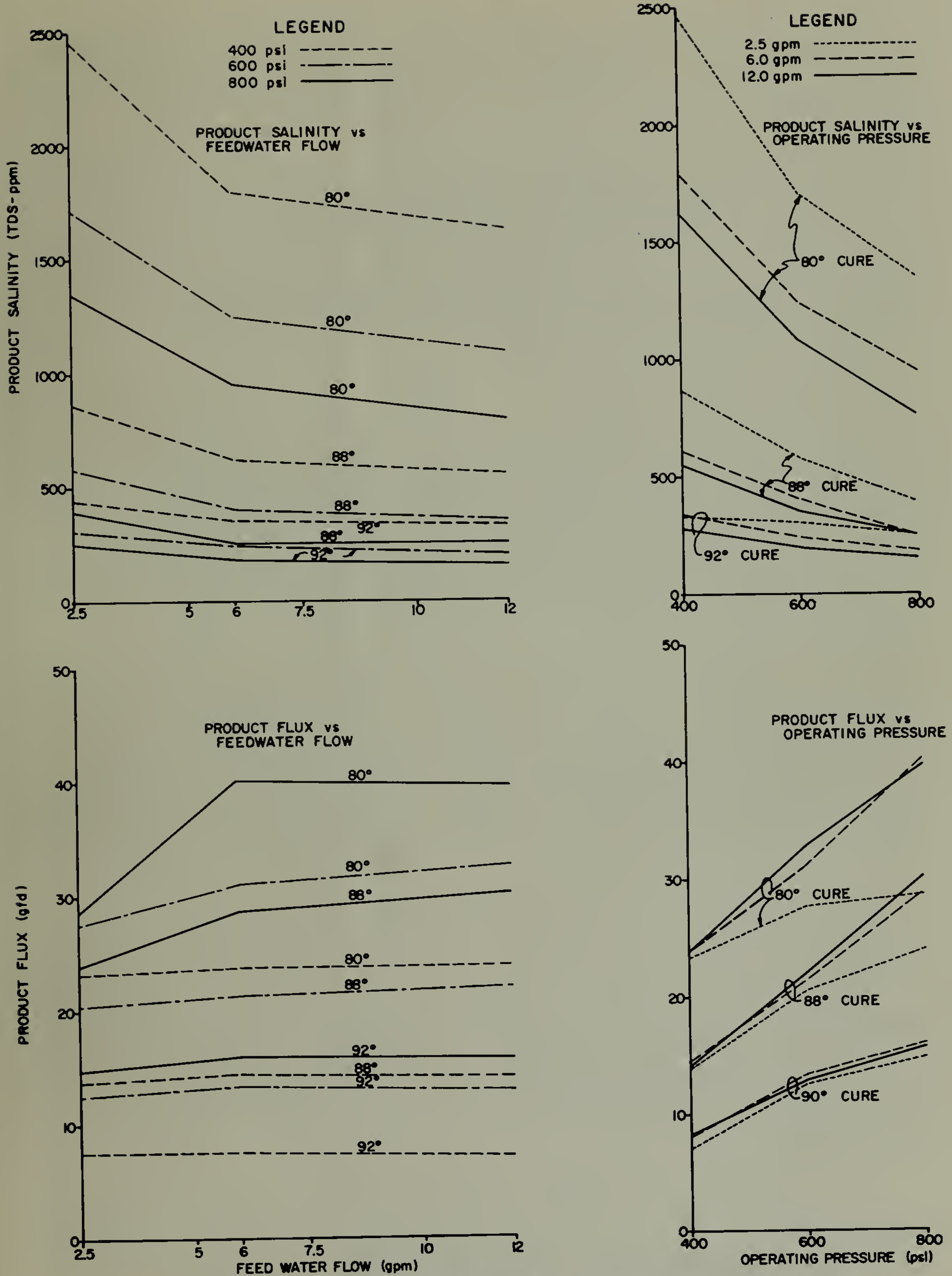

FIGURE 5 - 72 HOUR PRESSURE-FLOW VARIATION TESTS

Evaluation of test results showed that membrane performance was in general agreement with findings of other studies of pressure-flow effects on membrane permeability and is summarized in the following observations: (a) with increased pressure, product flow increased and product salinity decreased; (b) increasing pressure had a greater effect on product flow than increasing the feedwater flow rate; (c) for low-temperature-cured membranes, significant increases in product flow were observed with increases in feed flow, which was attributed to the effect of velocity upon concentration polarization (the boundary-layer effect); and (d) for low-temperature-cured membranes, significant reductions in product water salinity were observed whenever the feed flow was increased.

180-tube RO Unit Operation

For the next part of the study, the basic equipment was expanded to accommodate 180 tubes and operated to evaluate the technical capability of the RO concept to desalt agricultural waste water. Experience acquired in the operation of the 24-tube RO unit was used to make a number of improvements in the design and operation of the 180-tube RO unit. This production unit began operating on November 6, 1971, on a 12-month test schedule.

To obtain optimum product yield, the tube membranes were arranged throughout the unit according to cure temperatures. Membranes cured at 176° F (80° C) to 182° F (83° C) (and having high permeability) were placed along the first sections of the unit, while those cured at 200° F (93° C) (and having low permeability and high salt-rejecting property) were placed in the last sections. Membranes with an immediate temperature cure generally were located along the middle.

An operating pressure of 600 psi (4,140 kPa) was estimated to be the optimum for brackish water desalting. Since no previous studies had been made at 200 psi (1,380 kPa), however, it was decided to begin at this pressure and then increase it to 400 psi (2,760 kPa), then 600 psi (4,140 kPa), and possibly 800 psi (5,520 kPa). The unit began operating at 45-psi (310-kPa) pressure for an overnight break-in period. On the following day, the pressure was raised to 200 psi (1,380 kPa) and feedwater flow set at 7.5 gpm (0.47 l/s). These settings were maintained until November 22, 1971 (17 days).

Feedwater treatment consisted of chlorination at 1.0 ppm (mg/l) and the addition of H_2SO_4 to reduce the pH from about 7.4 to 5.8. Composite samples of product flow and quality were taken daily, and individual samples from each tube on a weekly basis. Samples of feed, brine, and product water were collected for mineral analyses during the study. A typical mineral analysis for water samples taken on January 18, 1972, is shown in Table 2.

TABLE 2

MINERAL ANALYSIS OF WATER SAMPLE
FOR 180-TUBE REVERSE OSMOSIS UNIT
January 18, 1972

Constituent	Concentration (ppm or mg/l)		
	Feed	Product	Brine
Calcium	154	8.3	495
Magnesium	314	3.5	380
Sodium	1,270	145	2,420
Potassium	5.7	0.4	8.0
Sulfate	3,670	83	6,470
Bicarbonate	0	4	0
Chloride	424	155	678
Nitrate	79	64	617
Boron	15	12	18
TH as $CaCO_3$	1,680	35	2,800
TDS	6,250	520	11,300
pH	4.5	5.5	4.1

The membranes were cleaned once a week by passing the spongeball through the 1,800-foot-long (550-metre-long) system under the unit pressure of 45 psi (310 kPa). The time required for passing the spongeball through the system varied from 12 to 14 minutes. The last portion of the effluent was caught and inspected for color and colloidal matter.

The following observations were made from the data collected during this period. The feedwater averaged about 4,780 ppm (mg/l) over the 17-day period. As expected, product flow rate and product salinity varied widely among the membranes having different cure temperatures. Product flow varied from 2.3 gfd (9.4 ml/cm^2, day) for membranes cured at 200° F (93° C) to 23.4 gfd (93.7 ml/cm^2, day) for membranes cured at 176° F (80° C), and product salinity varied from 200 ppm (mg/l) to 1,825 ppm (mg/l) for the same membranes. For membranes of the same cure temperature, product flow generally declined as the feedwater salinity increased. This was due to the higher salt concentration along the membrane wall (concentration polarization) which caused a reduction in permeability and an increase in product salinity. The overall production and corresponding water quality of the feed, brine, and product water are given in Table 3.

TABLE 3

OVERALL PRODUCTION AND WATER QUALITY
180-TUBE REVERSE OSMOSIS UNIT

Constituent	Production (gpm) (l/s)			Water Quality TDS (ppm or mg/l)		
	Min.	Max.	Avg.	Min.	Max.	Avg.
Product water	1.6 (0.10)	2.3 (0.15)	1.9 (0.12)	720	1,025	843
Brine water	5.0 (0.32)	6.0 (0.38)	5.5 (0.35)	6,200	6,780	6,375
Feedwater	6.6 (0.42)	8.3 (0.52)	7.4 (0.47)	4,675	4,900	4,780

On November 22, 1971, unit operations were adjusted to provide a feedwater flow of 7.0 gpm (0.44 l/s) and pressure of 400 psi (2,760 kPa). At this new pressure, the product flow increased from about 3,200 to 7,200 gpd (12.11 to 27.25 m^3/day) and product salinity decreased from 775 to 675 ppm (mg/l). Several days later, however, product flow declined to 5,040 gpd (19.08 m^3/day) as a result of $CaSO_4$ precipitation on the membranes -- a problem that persisted for the remainder of the operation.

The deposits of $CaSO_4$ on the tube walls combined with severe membrane deterioration eventually caused membrane performance to become erratic and production data unreliable. Further operation of the RO unit would have been of no value, and operations were terminated on March 28, 1972. Figure 6 provides a summary of the performance data and important occurrences during the operation of this unit.

60-tube RO Unit Operation

The next unit installed by UCLA was a 60-tube configuration designed specifically to investigate the scaling and membrane deterioration problems that developed during operation of the 180-tube RO unit. The multiple-chemical treatment and precipitation studies were two special investigations made into the use of various treatment chemicals for preventing deterioration of the CA membrane or inhibiting scale formation within the RO tubes. Also, a modified procedure for low-level chlorine pretreatment of the feedwater was set up for evaluation of three types of synthetic membrane backing materials tested for their resistance to chemical deterioration.

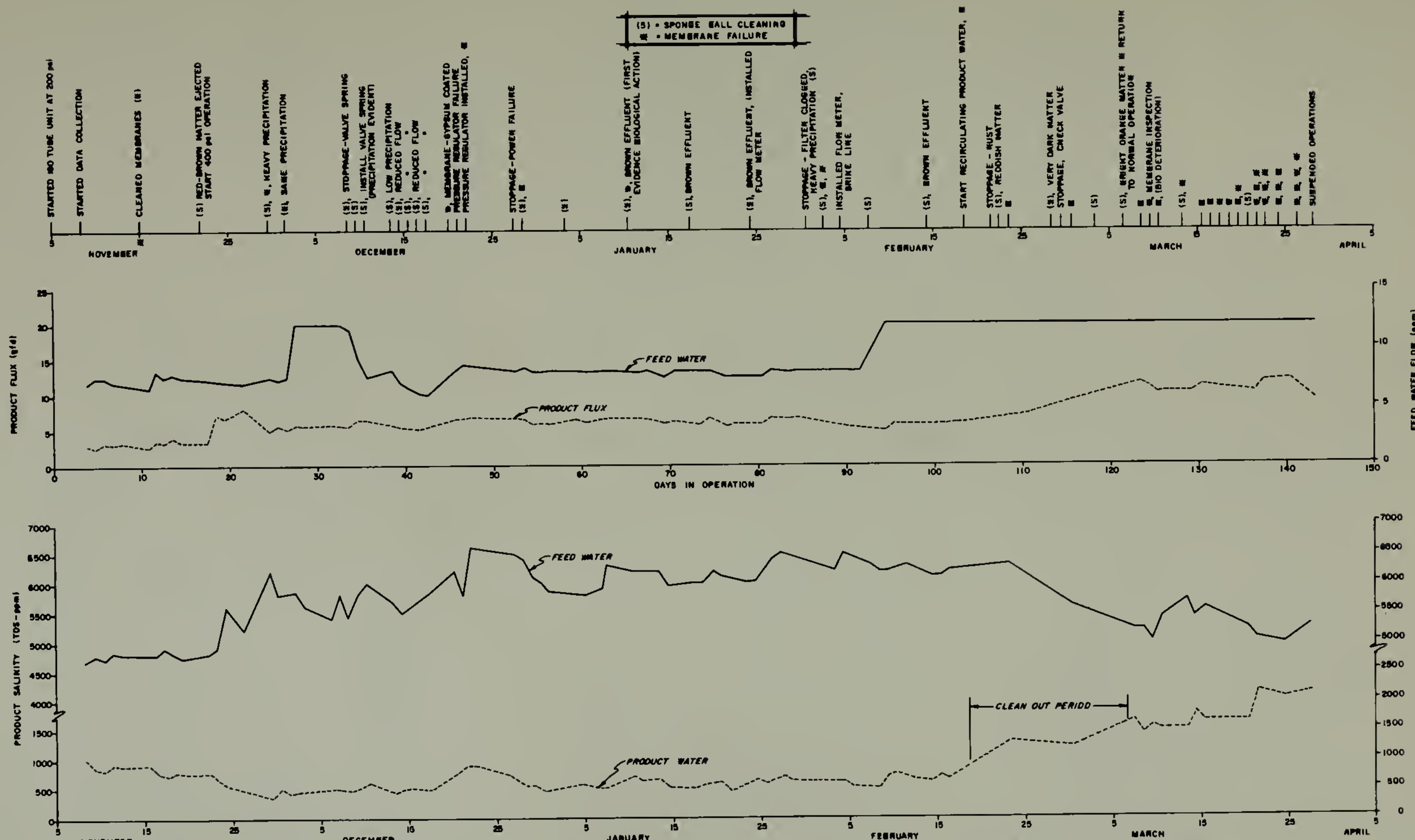

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FIGURE 6 - PERFORMANCE OF 180 - TUBULAR REVERSE OSMOSIS UNIT UTILIZING AGRICULTURAL WASTE WATER

The 60-tube RO unit was divided into five subunits operating in parallel and at equal pressures and flow rates. Each subunit was made up of an assembly of 12 tubes (schematically shown on Figure 7). The 12-tube assembly contained a selection of CA membranes of various cure temperatures and three types of membrane backing materials (nylon, dacron, and polypropylene). The subunits were designed to receive injections of chemical additives from high-pressure dosing pumps. The chemicals were investigated for their effectiveness as a bactericide or antiprecipitant.

The first step in this unit operation was the low-level chlorine treatment given to the feedwater. The raw feedwater was pretreated with 0.2 ppm (mg/l) of chlorine, then detained in a holding tank (at least 40 minutes) to insure complete disinfection. This was followed by dechlorination through an activated carbon filter to supply chlorine-free feedwater for the treatment tests to follow.

At the RO unit, the dechlorinated feedwater was delivered to the five subunits for use in the multiple-chemical treatment and precipitation studies according to the following arrangement. The feedwater entered the first unit (A) without any treatment since it served to evaluate the 0.2-ppm (mg/l) chlorine pretreatment procedure as a bacterial control. One ppm (mg/l) of chlorine was injected into the feedwater of the second unit (B) to assess the effects of this treatment level on the CA membrane and its backing material. Two different chemicals were injected into each of the other three units (C, D, and E), one for evaluation as a bactericide and the other as an antiprecipitant. The treatment chemicals and their applications are listed in Table 4.

TABLE 4

TREATMENT CHEMICALS

Unit	Chemical	Purpose
A	None	Control
B	Chlorine	Effect on cellulose acetate membrane and nylon
C	Sodium hydrosulfite Cyanamer P35	Bactericide (oxygen scavenging) Antiprecipitant
D	Catalyzed sodium sulfite Sodium hexametaphosphate	Bactericide (oxygen scavenging) Antiprecipitant
E	Zephiran Magnesium chloride	Bactericide (disinfectant) Inhibit precipitation

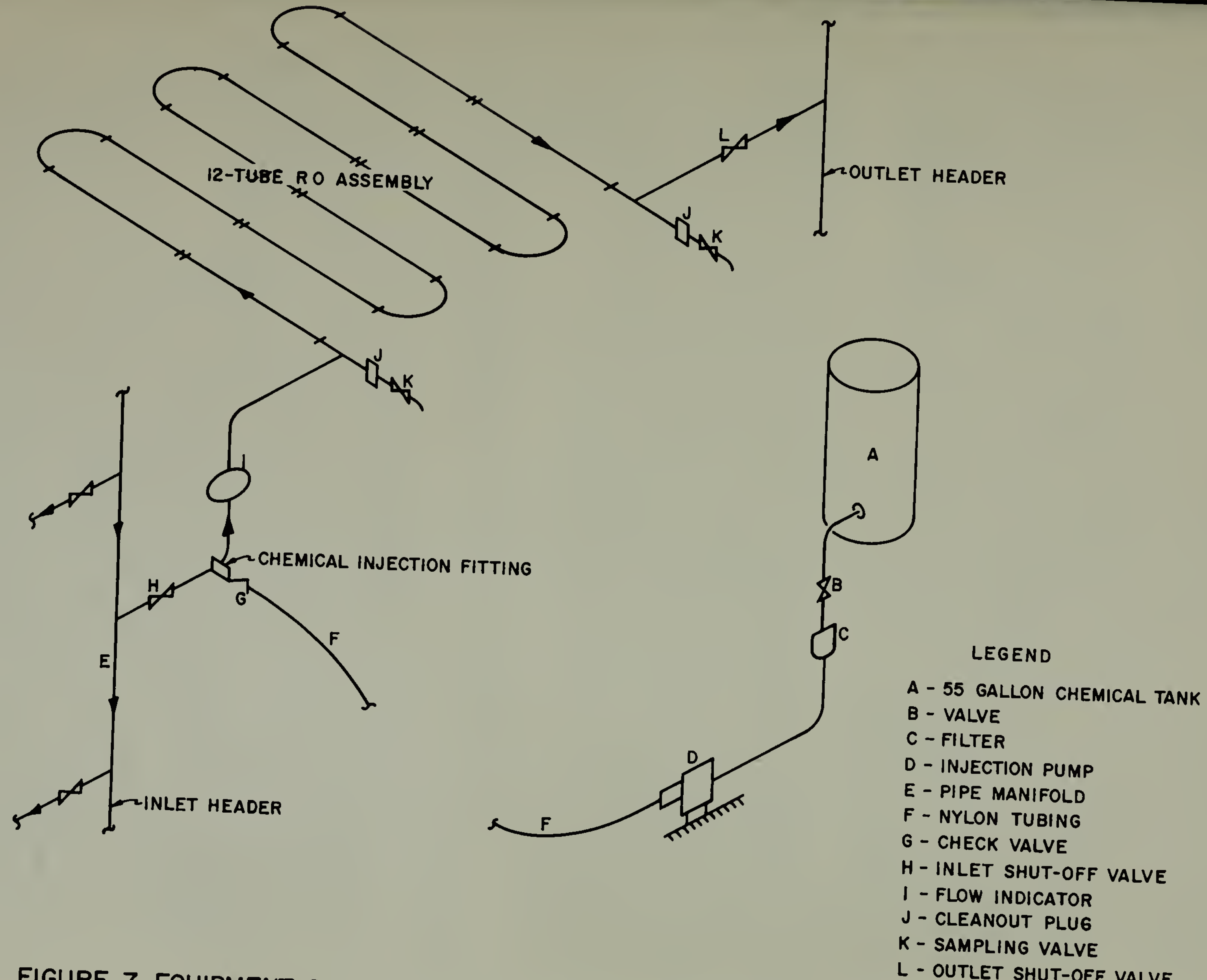


FIGURE 7-EQUIPMENT SCHEMATIC FOR TYPICAL 12-TUBE RO ASSEMBLY

Test operation of the 60-tube RO unit began on June 2, 1972, and was used for the multiple-chemical treatment study for four months. In October 1972, the precipitation study was included in the operation, and both studies were conducted concurrently until they were concluded in December.

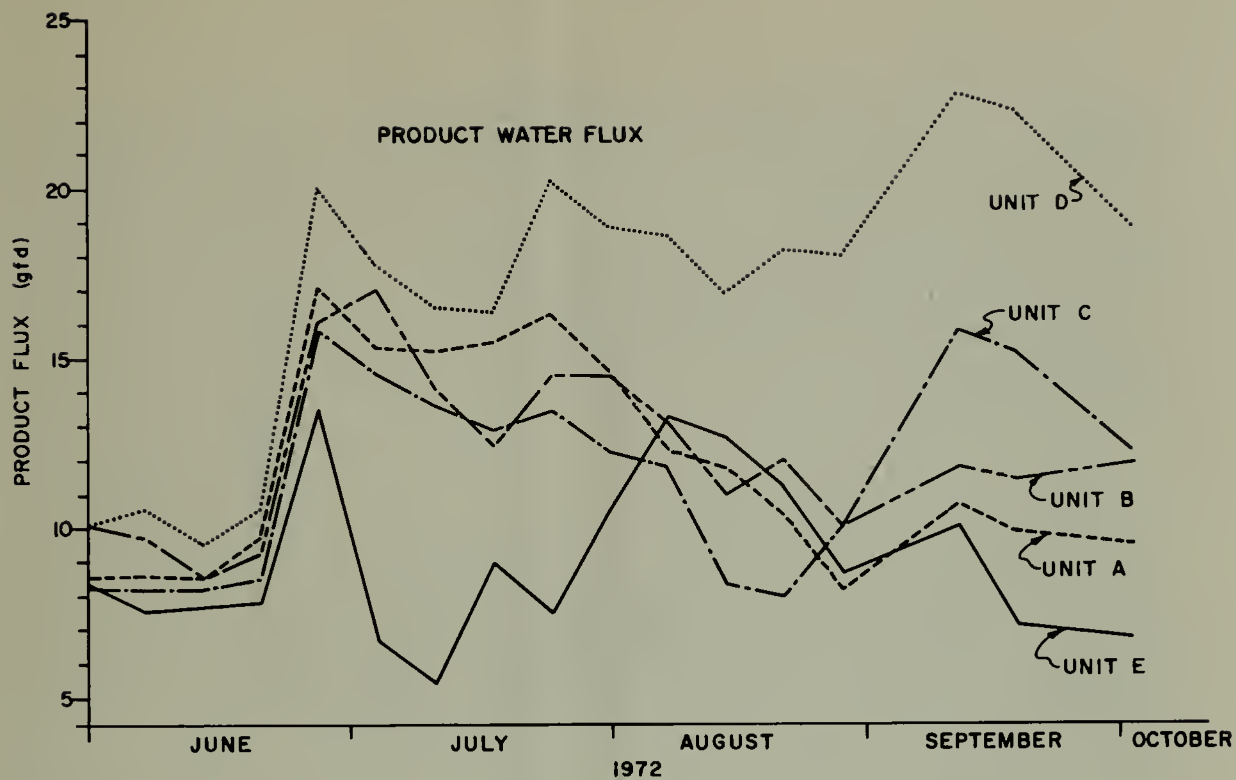
Evaluation of the five 12-tube units undergoing chemical treatment tests was based on factors such as membrane performance, tube failures, and visual inspection of the membrane and backing material. Membrane performance was reflected in the data on product flux and quality collected from the five units throughout the test period. Curves derived from these data are plotted on Figure 8. After the test operation was completed, the unit was dismantled and its tubes examined to establish the condition of the membrane and backing material. Some of the more important findings of the multiple-chemical treatment study are summarized in the following paragraphs.

The feedwater pretreatment procedure consisting of 0.2-ppm (mg/l) chlorination followed by a detention period to insure disinfection appears to be effective in controlling bacterial growth. The removal of residual chlorine by the carbon filter eliminates possible damage from this source. This conclusion is based upon the test results of Unit A. The performance of this unit, as shown by the curves of its product flux and quality on Figure 8, compares favorably with the other units. No tube failures were recorded, nor did inspection of the tubes reveal deterioration of the membrane or backing material for this unit.

A continuous dosage of 1.0 ppm (mg/l) of chlorine to Unit B was detrimental to the CA membrane and nylon backing material but not to the dacron or polypropylene material.

Tube failures resulting from deteriorated membrane or backing material occurred only with this unit. The dacron and polypropylene materials were found to be in excellent condition, while the nylon material was completely deteriorated and possessed an unpleasant odor and a yellow color probably caused by reacting with chlorine. It was concluded that chlorination at this level was unacceptable as a bactericidal treatment, and while dacron and polypropylene were acceptable, dacron was the preferred backing material because of its better handling qualities.

Evaluation of the effect of the treatment chemicals injected as bactericides in Units C, D, and E was precluded by the success of the low-level chlorine treatment given to the feedwater. Although these chemicals would be desirable because they lack the corrosiveness associated with chlorine, the low-level chlorination approach was adopted because it was found to be safe, effective, and relatively economical.



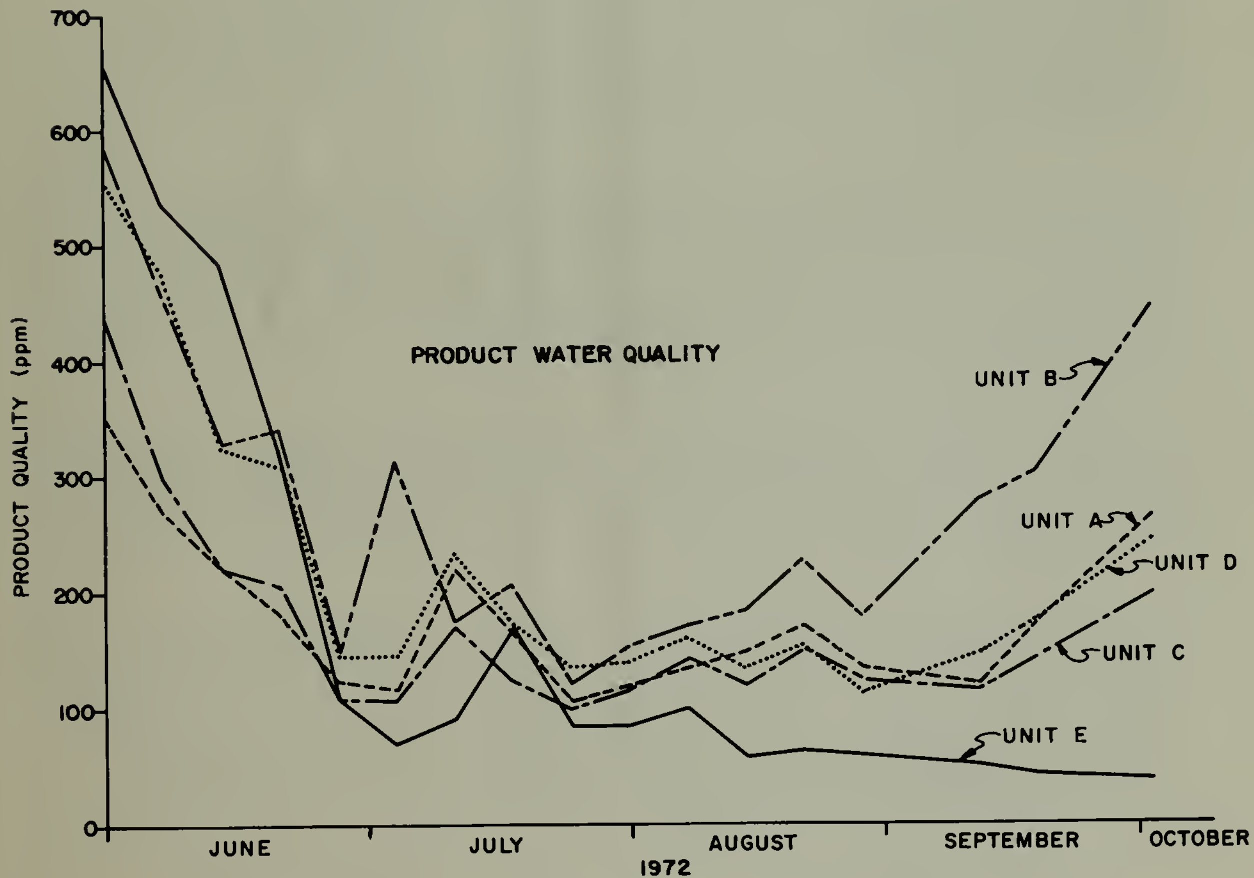


FIGURE 8 - MULTIPLE CHEMICAL TREATMENT TEST

Since there was no visual evidence of scale formation on the membrane surface of the tubes during the four-month test period, the effectiveness of the injected chemicals as antiprecipitants could not be determined by this means. However, the above-average performance of the product flux curve of Unit D (see Figure 8) suggests the influence of SHMP in inhibiting scale formation. Also, the results from the precipitation studies that were available later showed that these chemicals did inhibit scaling to a limited degree.

The precipitation studies were set up to further evaluate the antiprecipitant chemicals and to develop data for predicting the occurrence of precipitation. To perform these studies, the salinity of the brine within the RO tubes was purposely increased to a level exceeding the solubility limit of $CaSO_4$, thereby causing the salt to precipitate. This was done by throttling the flow through the RO tubes to very low rates while maintaining a high unit operating pressure.

The tests were performed on a trial-and-error basis since there was no previous experience upon which to set up a procedure. For these tests a pressure of 600 psi (4,140 kPa) was maintained while the brine flow through the tubes was gradually reduced by throttling the outlet valve. The flow rate was decreased over a period of time until the brine salinity reached a predetermined level where it was then held until precipitation became evident.

$CaSO_4$ was successfully precipitated during several test runs. On the first successful run, with a brine salinity target of 10,000 ppm (mg/l), precipitation was so great that the tubes became clogged and it was necessary to shut the unit down to flush out the precipitates. On subsequent runs, the target salinity was lowered and, as a result, moderate to incipient precipitation was achieved.

In the initial test run that resulted in excessive precipitation of $CaSO_4$ in all the units, it was noted that Unit A, which had received no treatment chemical, experienced the largest decrease in its product flux, thus indicating that precipitation was greatest in its tubes.

In a later test run, during which incipient precipitation occurred, the precipitates were removed from the tubes with a spongeball. Substantial amounts were recovered from Unit A, while only small amounts were recovered from Unit D and trace amounts from Units C and E. This measure of relative quantities recovered showed that the chemicals did inhibit precipitation.

After the precipitation studies were completed, the unit was operated for a period of time without treatment chemicals. Data collected during this period showed a gradual decline of product flux in Units C, D, and E, a condition attributable to the buildup of scale on the membrane wall. This was confirmed by the samples of scale deposit taken when the tubes were dismantled and inspected following termination of the test operation. The amounts of deposit varied from 0.0173 to 0.0552 pound per square foot (0.00084 to 0.00269 gram per square centimetre) of membrane surface. A similar examination of membrane samples taken during the period when chemical treatment was applied showed no such scale formation, thus demonstrating that the antiprecipitant chemicals were effective.

After the first precipitation test, during which excessive amounts of $CaSO_4$ were deposited within the RO tubes, the deposits were flushed out by passing feedwater through the tubes at high flow rates (approximately 10 gpm [0.6 l/s] and 35 psi [240 kPa]). In subsequent operations, the tubes returned to their normal production levels, thus demonstrating that the flush cleaning procedure was not harmful and thus is an acceptable method for removing precipitates from the RO tubes.

The multiple-chemical treatment and precipitation studies were completed in November 1972, and the 60-tube unit continued to operate without treatment chemicals until February 1973. This operating period thus provided data on membrane performance using feedwater without chemical treatment.

Test operations were concluded on February 9, 1973, when the 60-tube unit was dismantled and its tubes examined to establish the condition of the membrane and backing material. Twenty-eight tubes that were found satisfactory for further use were retained for inclusion in the next operating unit to provide more extensive data on the service life of the CA membrane. The next operation utilized a 140-tube RO unit made up of the 28 salvaged tubes and an additional 112 titanium tubes containing membranes cured at temperatures from 190° F (88° C) to 200° F (93° C). All 140 tubes were lined with dacron backing material.

CHAPTER V. REVERSE OSMOSIS EVALUATION STUDY -- TEST INSTALLATION AND PROCEDURES

The operations of three RO desalting plants described in this evaluation study were carried out as a cooperative test program with OWRT. The RO plants selected for testing were of different designs; the hollow-fine-fiber and spiral-wound designs were supplied by OWRT, and the tube-type design was supplied by DWR. The study was made at the WWTEF during an 18-month period in 1973 and 1974.

The purpose of the test program was to evaluate the RO plants under similar operating conditions and to develop preliminary information for the selection and operation of a larger-sized prototype RO plant. Specifically, the plants were operated to determine (a) the life and performance of the semipermeable membrane, (b) the effect of agricultural waste water on the RO process, (c) feedwater pretreatment procedures, and (d) the product recovery obtainable under various conditions of feedwater salinity and treatment with chemicals including softening (ion exchange).

Feedwater Pretreatment

Figure 9 is a flow diagram of the feedwater supply and treatment arrangement used at the WWTEF during the RO test program. The water is supplied from the Alamitos tile drainage system, which was previously described in Chapter IV. The feedwater drawn from the storage pond is treated with three chemicals before the desalination process: concentrated H_2SO_4 to maintain a feedwater pH of between 5.5 and 6.5; lithium hypochlorite to provide a 0.2-ppm (mg/l) concentration of chlorine; and a scale inhibitor (SHMP) at a 5.0-ppm (mg/l) concentration. The feedwater is detained in a holding tank for about 40 minutes to provide for chlorine disinfection, dechlorinated by the activated carbon filter, and then softened with the ion-exchange unit. The feedwater booster pump provides the necessary pressure and flow through the system, supplying water to the RO units at a pressure of about 40 psi (280 kPa).

Chemical feed pumps are used to meter the three treatment chemicals into the feedwater. The H_2SO_4 is taken directly from a supply carboy at a 95-percent concentration and fed into the mixing tank. A dry crystal form of lithium hypochlorite containing 35 percent available chlorine is prepared in a concentrated water solution and fed at the mixing tank. Dry crystalline SHMP containing 67 percent phosphorous pentoxide (P_2O_5) is prepared as a water solution at the appropriate concentration and metered into the feedwater stream after the softening step.

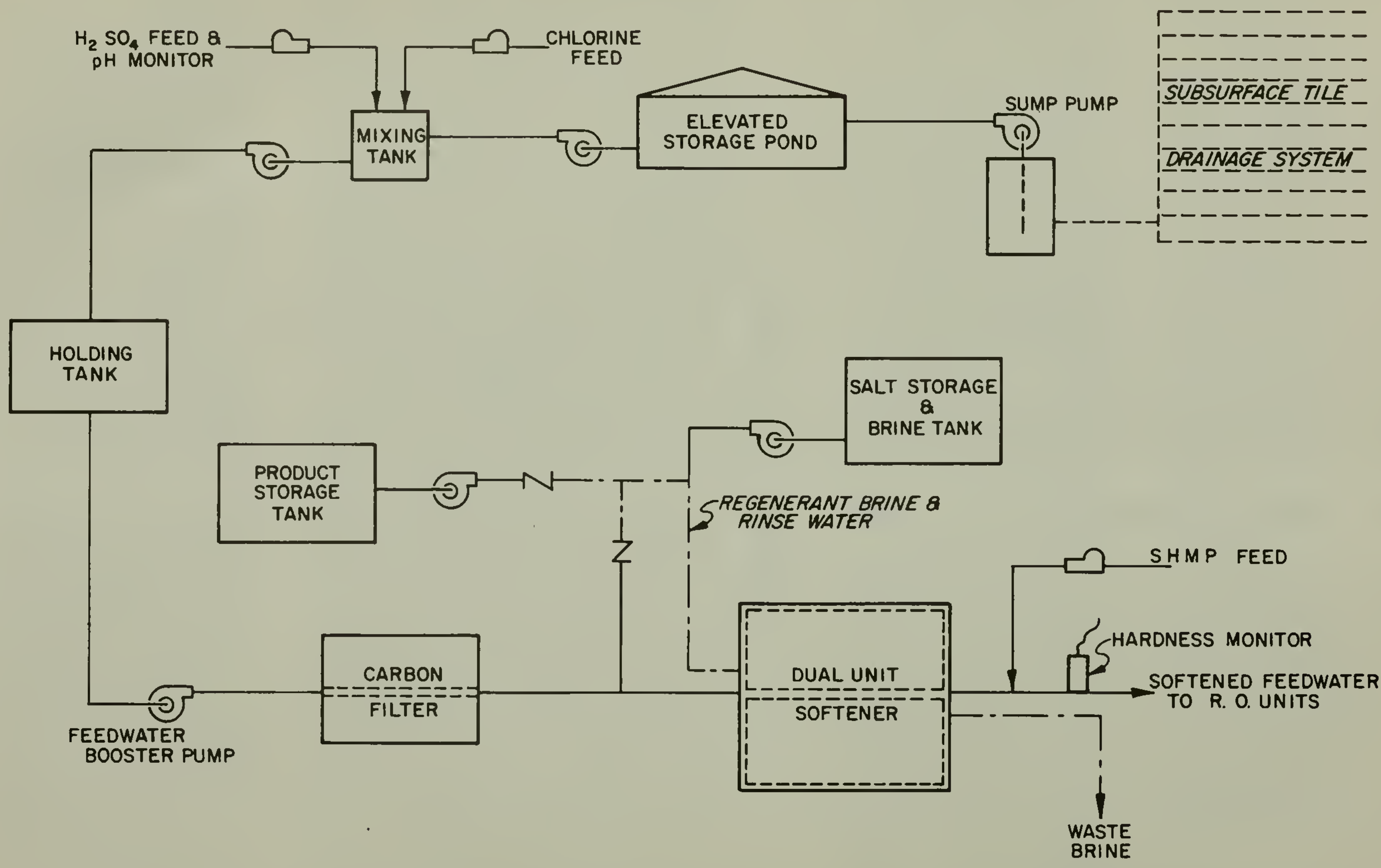


FIGURE 9- FLOW DIAGRAM - FEEDWATER SUPPLY AND TREATMENT ARRANGEMENT

The activated carbon filter is a dual unit (Bruener Model AC-24) with a capacity of 28 gpm (1.8 l/s) when both columns are operating simultaneously in parallel. Each column contains 7 cubic feet (ft^3) (0.2 m^3) of reconstituted activated carbon of 10 x 40 mesh size.

The water softener is a Wynhausen Model 12C1-½X duplex unit of 30-gpm (1.9-l/s) processing capacity, instrumented to provide continuous feedwater deionization. Each column contains 30 ft^3 (0.85 m^3) of the synthetic zeolite resin polystyrene-DVB sulfonate (Rohm and Haas Amberlite IR-120S) that removes the hardness constituents (Mg^{++} and Ca^{++} ions) from the feedwater. Saturated sodium chloride brine is used for resin regeneration.

Professor Theodore Vermeulen and Mr. Gerhard Klein with the University of California, Berkeley, assisted in the design specifications for the water softening unit and reviewed the bid proposal for DWR. Their assistance and expertise in selecting this component is appreciated.

The ion-exchange unit was installed and made operational in December 1973, and softened feedwater was then available for the RO operation. Figure 10 illustrates the ion-exchange unit and an 8,000-gallon (30-m^3) salt storage and brine supply tank.

A Hach hardness monitor was used to monitor the feedwater stream leaving the softener. This device was designed to shut down RO operations when it detected hardness levels exceeding 100 ppm (mg/l) as $CaCO_3$ to prevent $CaSO_4$ scaling in the RO units and possible damage in the event of a softener malfunction. This monitor was installed in May 1974 as a replacement for the Honeywell hardness sensor supplied with the ion-exchange unit which could not be made to operate properly on the Alamitos tile drainage water.

The chlorine content of the feedwater was monitored by the orthotolidine sampling method using a visual comparison of colors. Feedwater pH level was controlled by a Foxboro Model 699 pH reader and a Mec-O-Matic Model H60JI acid feed pump. The Foxboro reader was replaced in May 1974 by a Beckman Model 940 pH analyzer. A Hach chemical analysis kit was used to measure water hardness of the two softener columns.

Tubular Reverse Osmosis Unit

The tubular (UCLA) RO unit supplied by DWR for the test evaluation program was the fourth of this type of design obtained from UCLA. Chapter IV of this bulletin summarizes the test operation of the first three units at the WWTEF (5). Improvements in equipment design and feedwater pretreatment methods developed during prior RO operations were incorporated in the fourth unit.

30-gpm-capacity
Dual Unit Ion Exchanger

8,000-gallon-capacity
Combination Salt Storage
and Brine Supply Tank

FIGURE 10. ION-EXCHANGE SYSTEM

The fourth unit was installed and made operational at the WWTEF in early March 1973, before the two RO units contributed by OWRT for the test program. The UCLA unit was initially installed as a 140-tube unit but was subsequently enlarged to 180 tubes. When this unit was assembled in the 140-tube configuration, 28 tubes were carried over from the previous RO unit (60-tube) operation. These transferred tubes were found acceptable for further use, and their inclusion provided extended data on the service life of the CA membrane.

Unit Description

The simplified schematic arrangement of Figure 11 shows the various elements that make up this unit, and Figure 12 illustrates the unit's pump control section and the desalting section. The main element of the pump control section is the Worthington KFB triplex pump driven by a 15-horsepower (hp) (11-kilowatt [kW]) US motor through a varidrive. The varidrive provides a range of pump operation with feedwater flow rate and system pressure as high as 15 gpm (0.95 l/s) and 1,000 psi (6,900 kPa), respectively. System pressure is maintained at preselected levels by a gas-operated back-pressure regulator.

The treated feedwater is passed through a 10-µm particulate filter and delivered to the triplex pump at about 40-psi (280-kPa) inlet pressure. The pump delivers the feedwater to the desalting section at a pressure of 600 psi (4,140 kPa) and a 10-gpm (0.63-l/s) flow rate. The desalination process takes place as the feedwater flows through the series of tubular RO assemblies in a single pass. The desalted water exits from perforations along the tubes, drains onto corrugated sheets, and is collected by end troughs.

Figure 13 shows the design of a typical tubular assembly in the desalting section. The assembly consists of a tube-shaped CA semipermeable membrane wrapped in three layers of porous dacron cloth and enclosed in a perforated titanium tube. Each tubular assembly is 10 feet long (3.1 metres), has a 1-inch (2.5-centimetre [cm]) outside diameter, and has 2.24 square feet (ft^2) (0.208 square metre [m^2]) of effective membrane surface area. The CA membranes used in these assemblies were prepared from cellulose acetate material using Eastman Chemical Company formulations E-398-10 and E-400-25 and were cured at temperatures ranging from 190° F (88° C) to 200° F (93° C). Methods for casting the membrane and fabricating the tubular assembly were developed by the engineering staff at UCLA (5, 8).

The unit had pressure-activated controls that automatically shut down operations in case of abnormally high or low pressure or the loss of water supply. The unit was

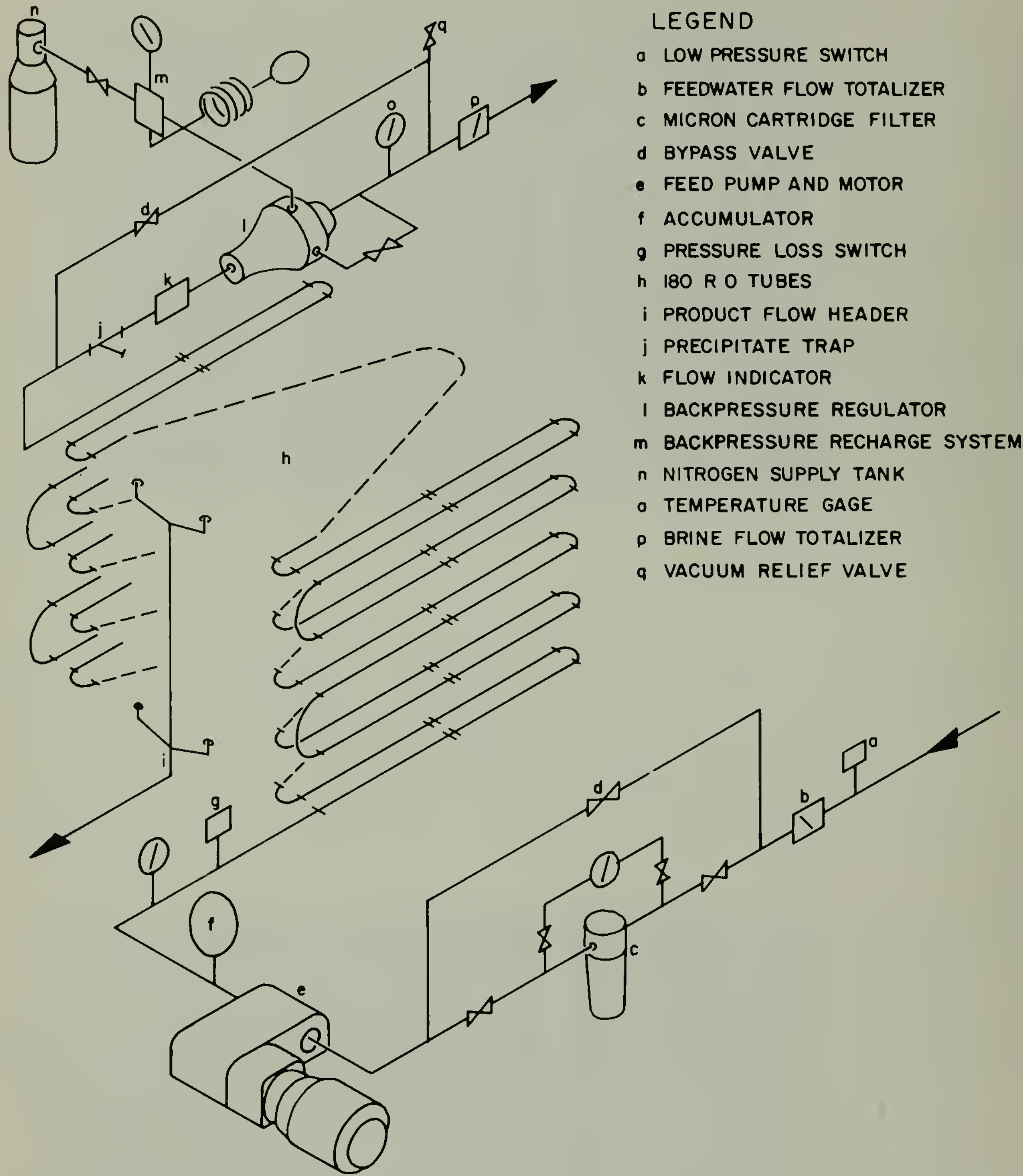
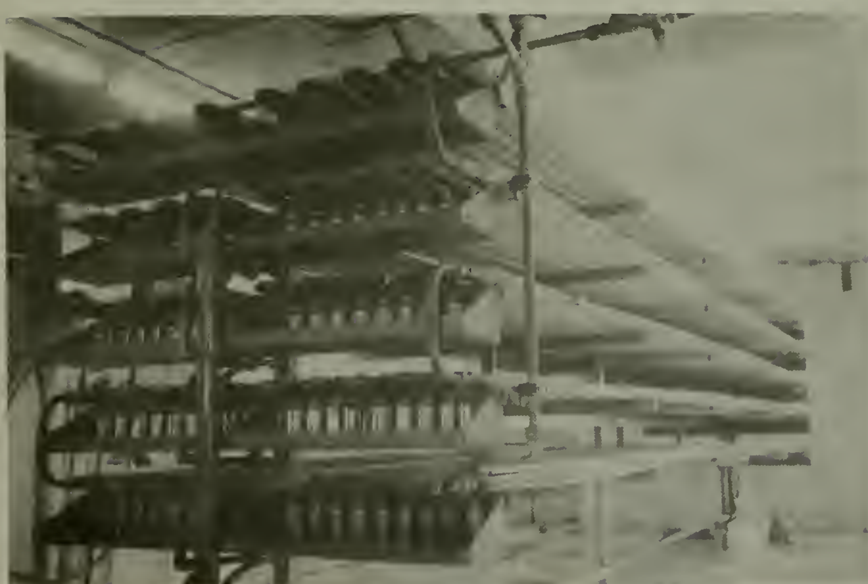


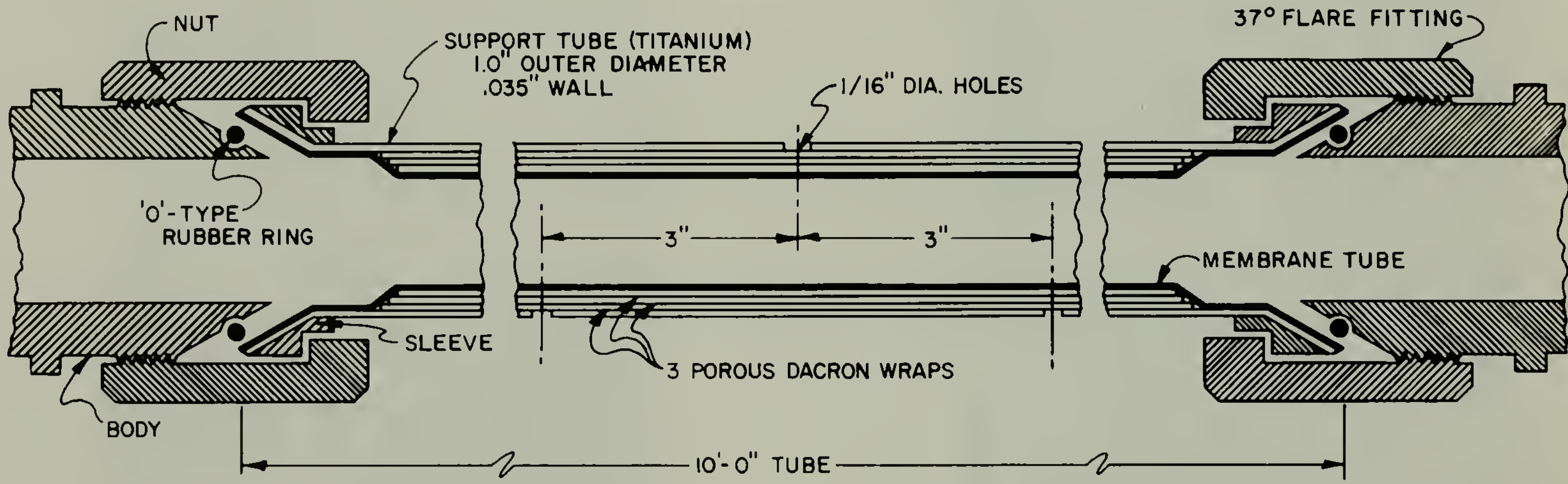
FIGURE 11- SCHEMATIC ARRANGEMENT 180-TUBE (UCLA) R O UNIT

Pump/Control Section



Desalting Section

FIGURE 12. THE 180-TUBE (UCLA) RO UNIT



NO SCALE

FIGURE 13 - TYPICAL TUBULAR ASSEMBLY - 180-TUBE (UCLA) R O UNIT

restarted manually whenever it was shut down for emergency reasons or because of an external power outage. This unit was designed primarily for experimental use and consequently had a somewhat complicated and sophisticated arrangement of equipment and controls. The variables in pressure and flow rate were necessary to provide test capability over a wide range of operating conditions. The desalting section was designed for convenient installation and removal of individual tubes as well as the capability to vary the total number of tubes. A collection trough with separate collection containers was provided so that the performance of each tube could be monitored individually.

Data Collection

Data were collected on a daily basis and served to monitor equipment operation and to obtain a measure of RO performance. Data taken to assure proper operation of equipment included system pressure, temperature, pH and chlorine content of the feedwater, total operating time, and power consumption of the unit. Appropriate gages and meters located on the operating unit provided these data. Sampling tests were used to determine the chlorine content of the feedwater, and pH measurements were made with a Corning Model 17 pH meter.

RO performance was monitored with data on flow rates and salinities of RO feed, product, and waste brine. Feedwater and waste brine data could be taken only on the basis of total unit production. Since this unit was designed for experimental applications, product water data could be taken for the individual tubes, as a composite value for each rack, and for total unit production. The schematic sketch of Figure 14 shows the arrangement of the 180 tubes on the five racks.

Feedwater and brine flow measurements were read from in-line totalizing flowmeters, while product flows were measured with graduated containers and stopwatch. All water salinities were determined with a battery-operated Myron L dissolved solids (DS) meter. This meter had self-compensating features for temperature changes and a triple-scale range of TDS measurements up to 5,000 ppm (mg/l). TDS measurements beyond the 5,000-ppm (mg/l) reading required dilution of the sample with distilled water. Calibration of WWTEF instrumentation for reading water salinity values in ppm was based on methods prepared by the engineering staff at UCLA (5).

Plant Maintenance

Routine plant maintenance was concerned primarily with measures to control membrane surface fouling, such as

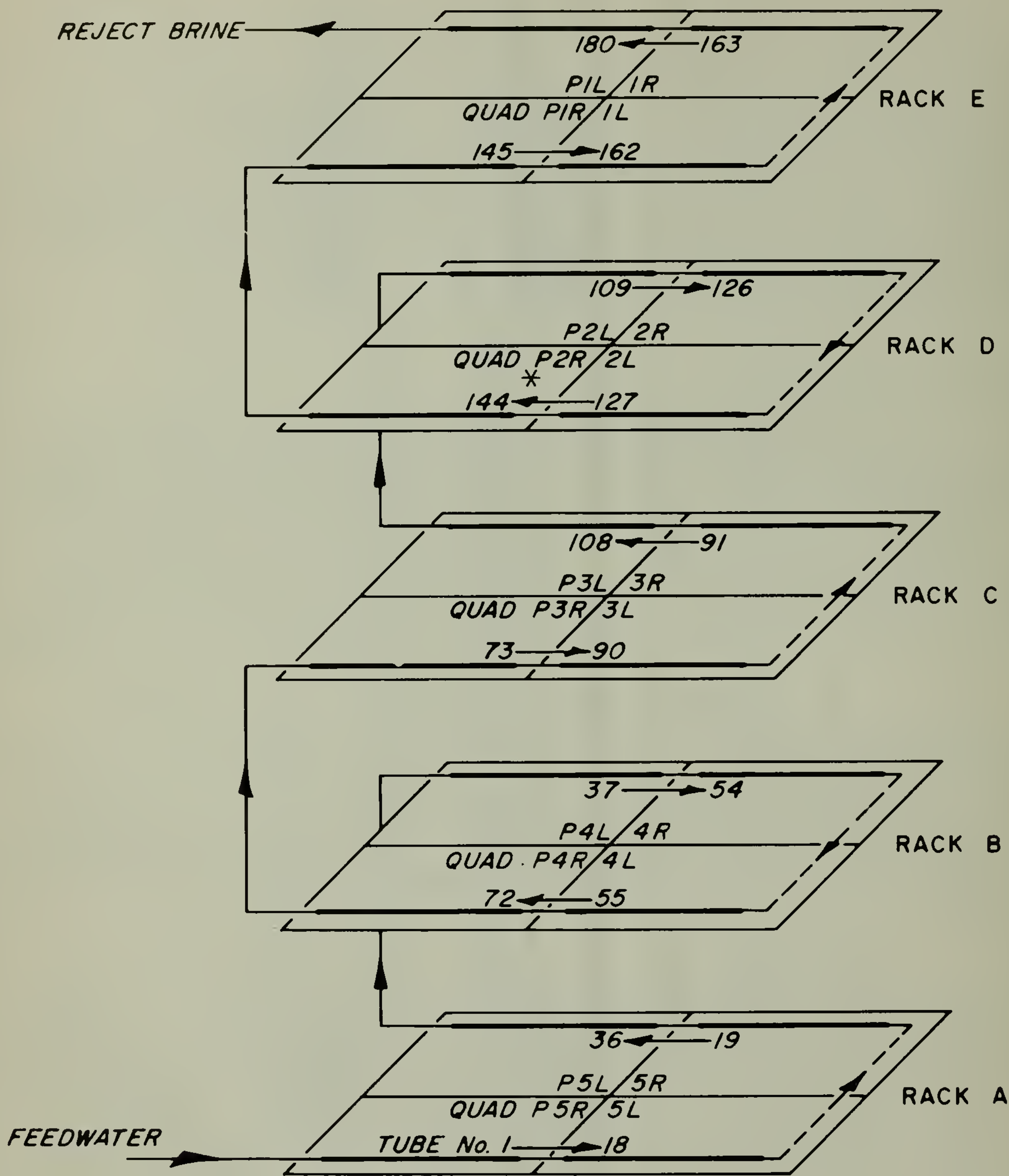


FIGURE 14- TUBE ARRANGEMENT OF DESALTING SECTION
180-TUBE (UCLA) R. O. UNIT

*QUAD P2R IS ONE QUADRANT OF RACK D CONTAINING 9 TUBULAR MEMBRANES periodic changes of the particulate filter cartridge, scrubbing the tube membranes with a spongeball, and flushing the tubes with a citric acid solution. The tube assemblies were also replaced when needed.

The in-line filter assembly located ahead of the triplex pump contained a filter cartridge of 10-μm pore size to remove particulate matter. The cartridge was replaced whenever excessive pressure drops across the filter caused the inlet pressure to the triplex pump to fall below the allowable minimum of 30 psi (207 kPa).

Spongeball cleaning was performed weekly and consisted of passing an oversized polyurethane foam ball through the tubular array under 40-psi (280-kPa) pressure supplied by the feedwater booster pump. In passing through the tubes, the spongeball scrubbed the walls, removing deposited material from the membrane surface.

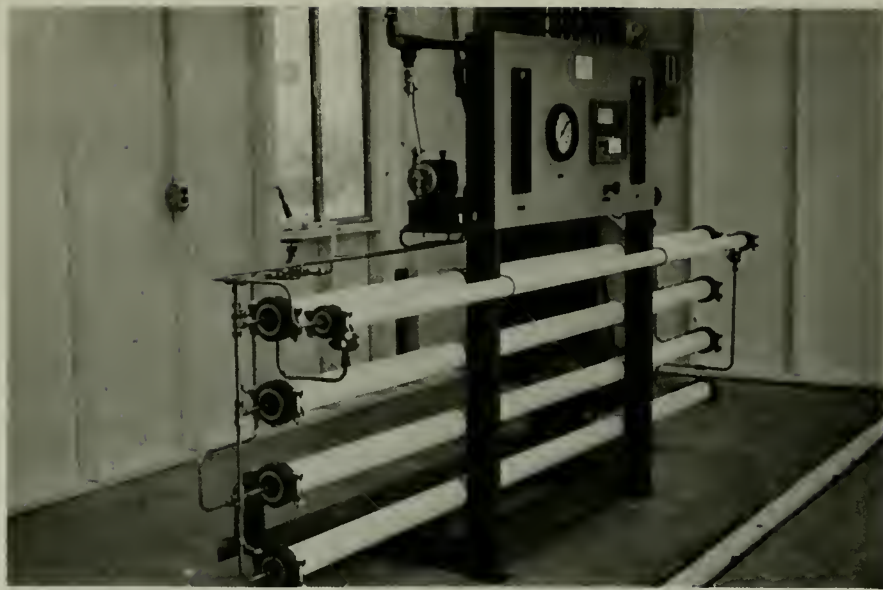
The RO tubes were treated with a citric acid solution that removed certain fouling materials deposited on the membrane surface. This cleaning method was used several times to remove mineral deposits such as aluminum and iron oxide compounds and $CaCO_3$ which are soluble at acid pH (13, 18).

The cleaning solution included 2 percent by weight of citric acid with sufficient ammonium hydroxide added to raise the solution pH to 4.0. The prepared solution was held in a 500-gallon (1.9-m^3) tank from which it was drawn and circulated through the tubular array under a pump pressure of 60 psi (414 kPa). The tubes were flushed with the acid solution for two hours, then rinsed with feedwater for one and one-half hours at 60 psi (414 kPa) and for another half hour at 800-psi (5,520-kPa) pressure.

Tube replacements were routinely made for various reasons, but most commonly because of damaged membrane or deterioration of the membrane's desalting capacity. Some membranes had fabrication defects, and others were damaged during installation or by passage of the spongeball during cleaning operations.

Spiral-wound Reverse Osmosis Unit

The spiral-wound (GESCO) RO unit, which uses the spiral wrap design of semipermeable membrane, was one of two units contributed by OWRT. This unit (Figure 15) was built by the ROGA Division of Universal Oil Products Company (formerly the Gulf Environmental Systems) and rated as a 5,400-gpd (20.4-m^3/day) high-recovery system (10).



Assembled RO Unit

Installation of Desalting Cartridge

FIGURE 15. THE SPIRAL-WOUND (GESCO) RO UNIT

Unit Description

The schematic arrangement of Figure 16 shows the unit made up of five desalting modules, four of 3-inch (7.6-cm) diameter and one of 2-inch (5.1-cm) diameter size. Each module contains three spirally wrapped, removable desalting cartridges as shown on Figure 15. The semipermeable membranes for these cartridges are made of cellulose acetate which is similar in composition to the CA membrane of the UCLA unit. The spiral wrap configuration of the membrane and supporting elements that make up the cartridge result in a compactly designed desalting module. Each 3-inch (7.6-cm) cartridge contains 38 ft^2 (3.5 m^2), and the 2-inch (5.1-cm) cartridge contains 20 ft^2 (1.9 m^2) of effective membrane surface area (19).

The unit operates as a four-stage system. The brine flows through the two modules in parallel (first stage) and then through three modules in series (second, third, and fourth stages). The 2-inch (5.1-cm) module is positioned last (fourth) in the series because of the reduced brine flow at this stage. In each module the feedwater enters at one end, passes through the three desalting cartridges in succession, and leaves at the other end as waste brine. Passing through each cartridge, the feedwater enters at the end face and flows axially along the passageways between the spiral layers of semipermeable membrane where the desalting process takes place.

The feedwater provided to the GESCO unit is rechlorinated at a 0.3-ppm (mg/l) level and passed through a 10-μm particulate filter. A minimum suction pressure of 10 psi (69 kPa) must be maintained for the high-pressure feed pump. Normal operating pressure is 600 psi (4,140 kPa) with pressure and flow regulation maintained by adjusting the needle valves located on the feedwater supply and reject brine lines. Pressure-activated controls provide emergency shutdown of the unit in case of system overpressure or loss of pressure or water supply.

Equipment and Operating Data

Unit: GESCO 5,400-gpd (20.4-m^3/day) high-recovery unit.

Supplier: ROGA Division, Universal Oil Products Company, San Diego, California.

Permeator: Four GESCO Type 4050 modules of 3-inch (7.6-cm) diameter; three cartridges per module; 38 ft^2 (3.5 m^2) of effective membrane area per cartridge.

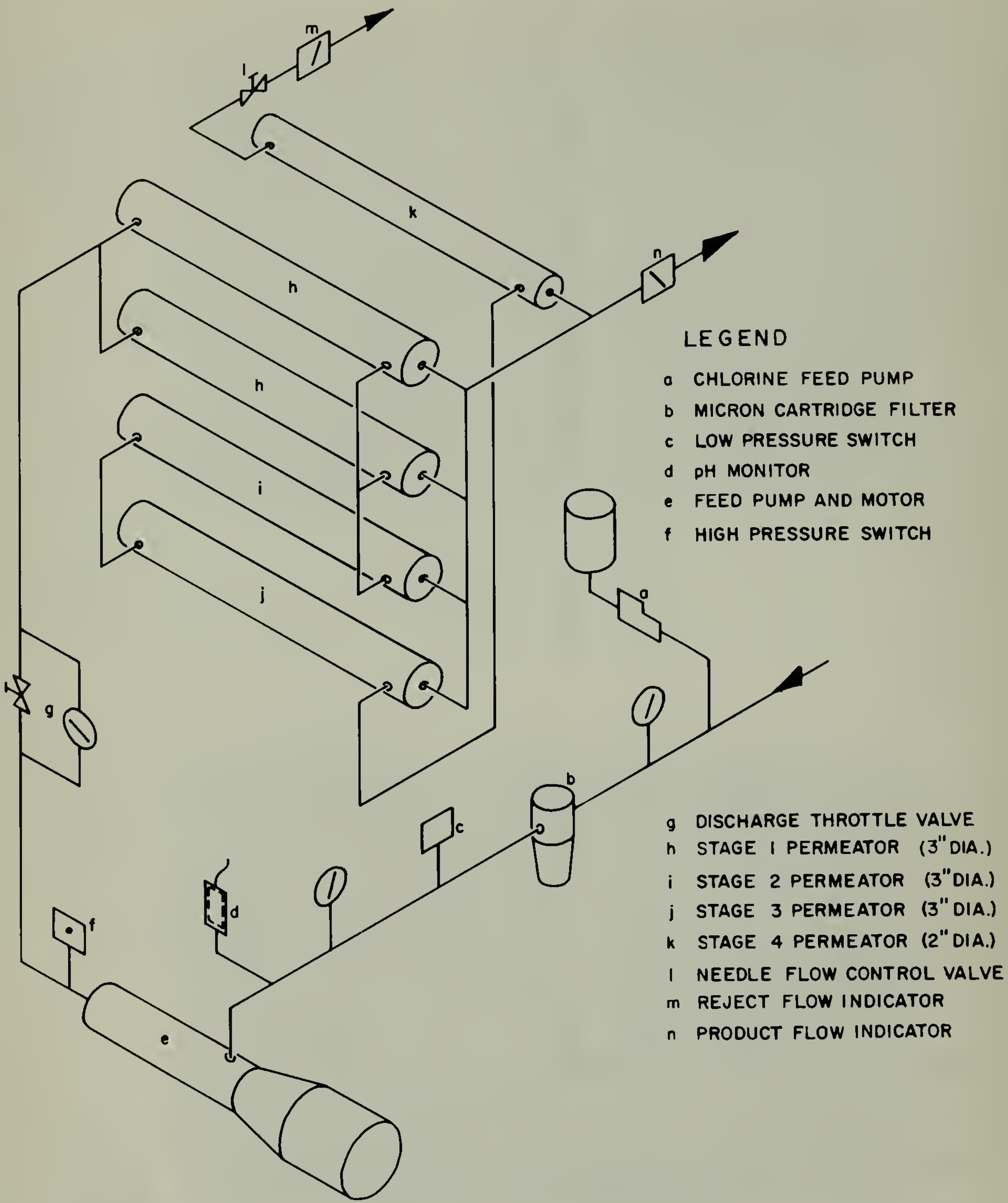


FIGURE 16 - SCHEMATIC ARRANGEMENT - SPIRAL-WOUND (GESCO) R O UNIT

One Type 8019 module of 2-inch (5.1-cm) diameter; three cartridges per module; 20 ft^2 (1.9 m^2) of effective membrane area per cartridge. (Both cartridge sizes use spirally wrapped cellulose acetate membrane of one chemical formulation and cure temperature.)

Operating control: Needle valve throttling on the feedwater or brine line for pressure and flow regulation.

Operating pressure limits: 10-psi (69-kPa) minimum, 600-psi (4,140-kPa) maximum.

Pump and motor: Gould Model 13500 centrifugal pump, 10-hp (7.5-kw) Reliance motor.

Particulate filter: Cartridge type of 10-μm pore size.

Installation and Startup

The RO equipment was delivered to the WWTEF on October 2, 1972, as a skid-mounted, completely assembled unit. Preparatory work was minimal, involving only electrical and piping connections and placement of the cartridges in the desalting module. Preparations for operation were made by DWR personnel with the assistance of a GESCO field representative.

The unit was started up on April 4, 1973, at which time the motor for the high-pressure feed pump was found to be defective. The defective part, cracked bell housing, is shown on Figure 17. Following repair of the motor, the unit was restarted and made operational on May 24, 1973. At this time, a defective pH meter was repaired and one module was dismantled for repair of a brine-side seal.

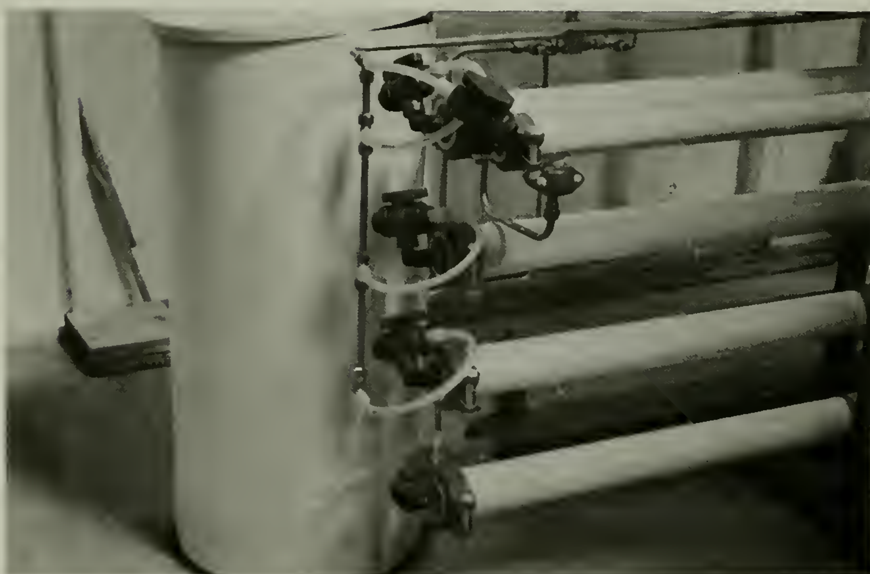
Equipment Modification

Several equipment modifications were made on the unit during the period of test operation. A high-pressure shutoff switch was added as a protective device, and a totalizing clock was installed to record unit operating time. In early August 1973, the product water manifold was modified to include the three-way ball valves shown on Figure 17. This arrangement allowed individual sampling of the five modules for product water flow and quality.

Data Collection

Data were collected on this unit to monitor equipment operation and obtain a measure of RO permeator performance.

Cracks in Pump Motor Bell Housing



Three-way Sampling Valves
Added to Product Manifold

FIGURE 17. GESCO RO UNIT

Appropriate gages and meters located on the RO unit and portable measuring instruments provided data on pressure, temperature, flow rates, water salinities (in electrical conductivity and TDS readings), pH, and total operating time. Since the feedwater for this unit was rechlorinated, it was necessary to monitor the chlorine content to maintain it at a level below 0.5 ppm (mg/l).

Fischer and Porter flowmeters located on the unit measured total composite flow for the product water and reject brine. Three-way valves on the product water manifold allowed product water sampling for flow and salinity data on each of the five desalting modules. Product flow for each module was measured using a graduated flask and stopwatch.

All water salinity data were taken with a Myron L DS meter using the procedure given for the UCLA unit. Electrical conductivity (EC) measurements were taken with a YS Model 33 EC meter.

Plant Maintenance

Routine maintenance was primarily directed toward control of membrane surface fouling. Maintenance included periodic change of the particulate cartridge filter, citric acid treatment of the desalting module, and replacement of brine-side seals.

The in-line filter assembly in the feedwater supply line to the high-pressure feed pump contained filter cartridges of 10-µm pore size for removal of suspended solids. Replacement of this cartridge was necessary whenever an excessive pressure drop across the filter caused the inlet pressure to the feed pump to drop below the allowable minimum of 10 psi (69 kPa).

The RO membrane was cleaned with a citric acid solution to remove deposits on its surface and thereby maintain permeability. The cleaning operation was performed monthly on the GESCO unit and served primarily to remove ferric hydroxide ($Fe(OH)_3$) or $CaSO_4$ deposits.

The cleaning solution was 2 percent by weight of citric acid with sufficient ammonium hydroxide added to raise the solution pH to 4.0 (for $Fe(OH)_3$ cleanout) or to 8.0 (for $CaSO_4$ cleanout) (16). The prepared solution was held in an 80-gallon (0.30-m^3) storage tank from which it was drawn and circulated through the RO module under low pump pressure. The five modules of the unit were simultaneously flushed with the acid solution for one hour, then rinsed with product water for one-half hour.

After several months of operation, the brine-side seals of this unit gradually deteriorated and required periodic replacement. Seal failure causes a stagnant flow condition in the permeator passageway and subsequent fouling with precipitated $CaSO_4$. Therefore, a routine schedule for inspection and replacement of the brine-side seals was instituted.

Hollow-fine-fiber Reverse Osmosis Unit

The hollow-fine-fiber (PermuRo) RO unit was one of two contributed by OWRT and used the polyamide base material in the form of hollow fibers as the semipermeable membrane. It was fabricated by the Permutit Company and designated the PermuRo Model S43-67 Micro Pak Assembly (16). The desalting module for this unit was the Permasep Model 044 containing the "B-9" hollow-fine fiber, manufactured by the Du Pont Company.

Unit Description

Figure 18 illustrates the unit, and Figure 19 is a schematic arrangement of the assembly as installed at the WWTEF. The unit uses a two-stage arrangement in its desalination operation. The feedwater flows first through the two first-stage modules in parallel, and the first-stage reject brine then becomes the feedwater for the single second-stage module.

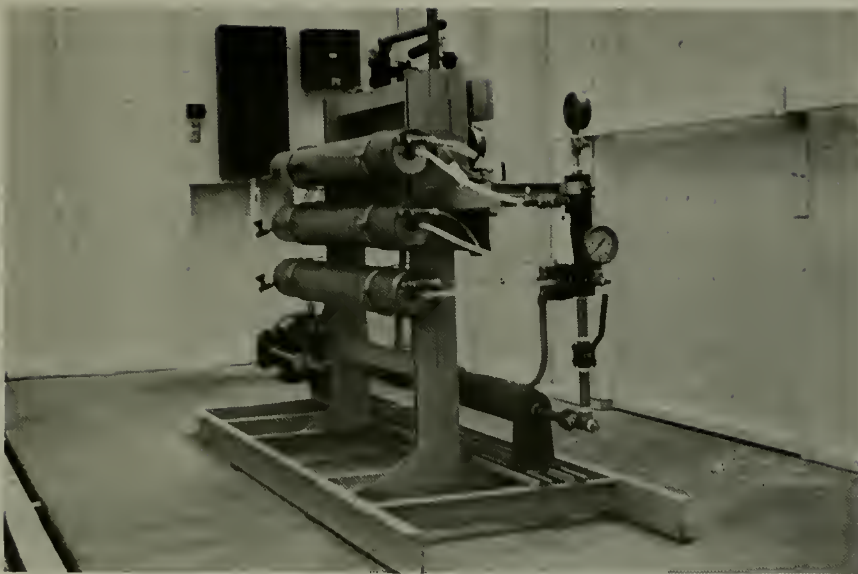
The feedwater delivered to the RO unit is first passed through a 10-μm filter to remove particulate matter. A minimum inlet pressure of 10 psi (69 kPa) must be maintained for the high-pressure feed pump. Normal operating pressure is 400 psi (2,760 kPa) with pressure and flow rate regulated by the throttling valves located on the feedwater and reject brine lines. Pressure-activated switches provide emergency shutdown in case of excessively low or high pressure or loss of water supply.

The distinguishing feature of the PermuRo unit is its hollow-fine-fiber semipermeable membrane. The fibers are made from an aromatic polyamide material (nylon) and fabricated into thin, hollow tubes about the dimensions of a human hair. A bundle of these fibers is fitted into a desalting module and, in the Permasep Model 044, provides about 1,800 ft^2 (167 m^2) of effective membrane surface area (9).

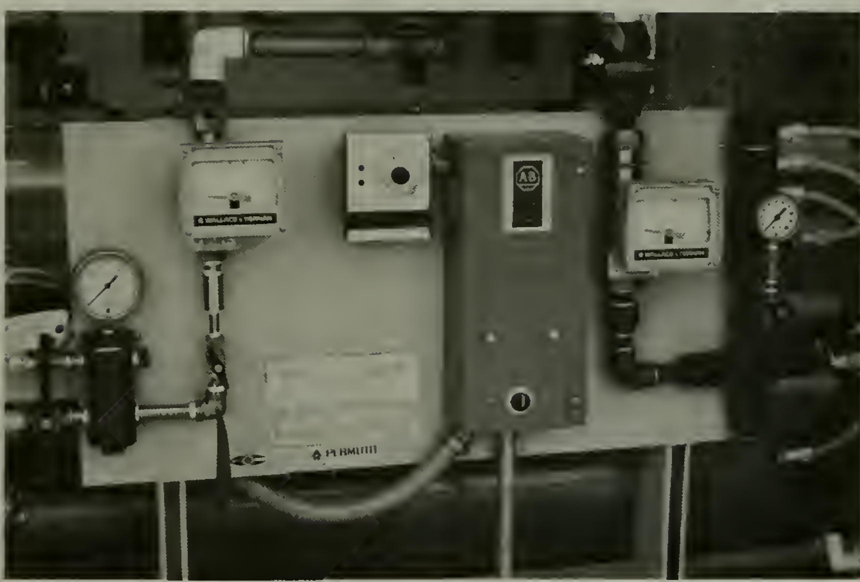
Equipment and Operating Data

Unit: PermuRo Model S43-67 Micro Pak Assembly.

Supplier: Permutit Company, Paramus, New Jersey.

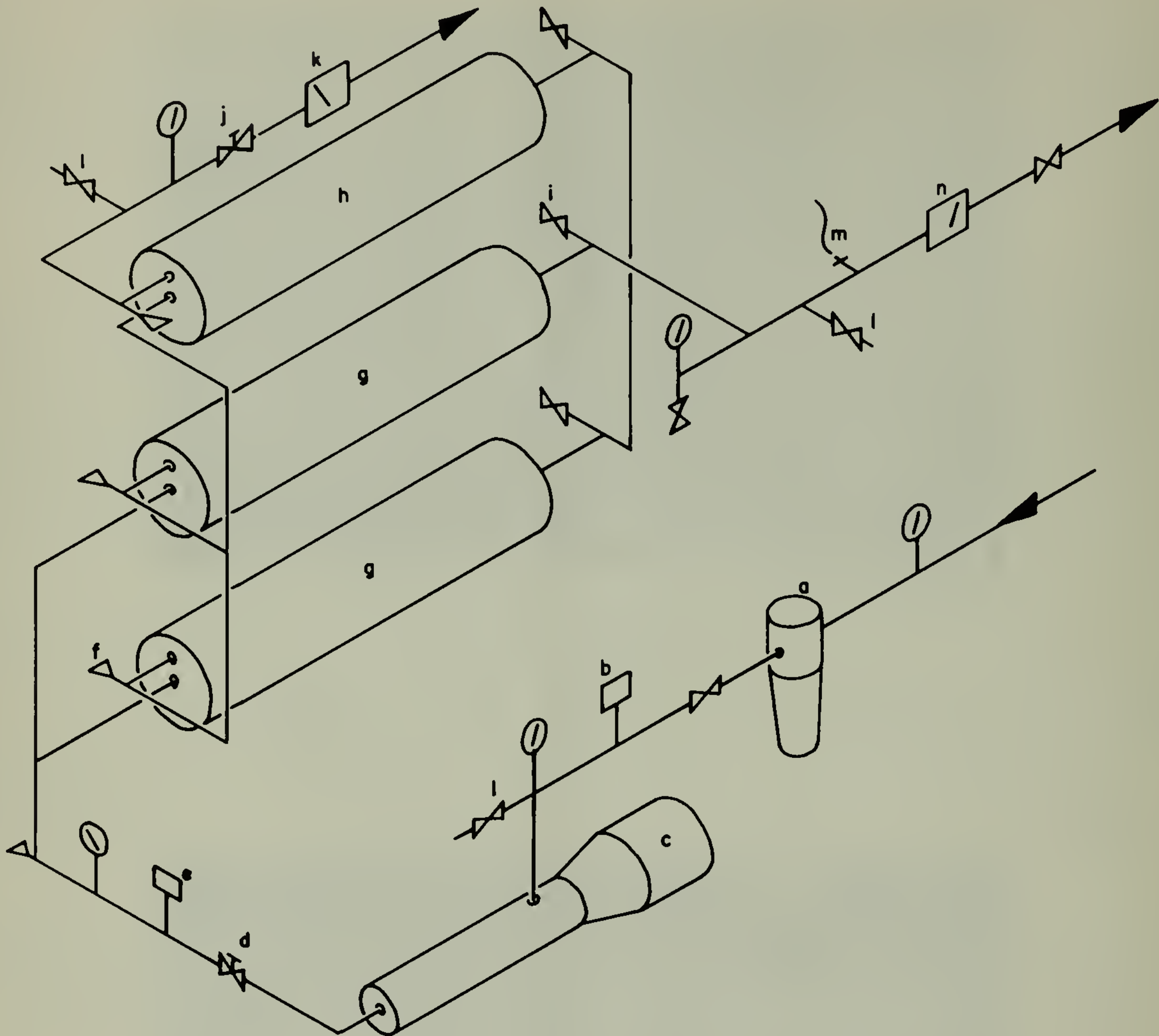


Assembled RO Unit



Instrument Panel

FIGURE 18. THE HOLLOW-FINE-FIBER (PERMURO) RO UNIT



LEGEND

a	MICRON CARTRIDGE FILTER	h	STAGE 2 PERMEATOR
b	LOW PRESSURE SWITCH	i	PRODUCT SAMPLING VALVE
c	FEED PUMP AND MOTOR	j	NEEDLE FLOW CONTROL VALVE
d	DISCHARGE THROTTLE VALVE	k	REJECT FLOW INDICATOR
e	HIGH PRESSURE SWITCH	l	FLUSHING VALVE
f	REJECT SAMPLING PROBE	m	CONDUCTIVITY CELL
g	STAGE I PERMEATOR	n	PRODUCT FLOW INDICATOR

FIGURE 19 - SCHEMATIC ARRANGEMENT - HOLLOW-FINE-FIBER (PERMURO) R O UNIT

Permeator: Du Pont Permasep Model 044 of 4-inch (10-cm) diameter containing the "B-9" hollow-fine-fiber membrane with 1,800 ft^2 (167 m^2) of effective surface area.

Operating control: Ball valve throttling on the feedwater or brine line.

Operating pressure limits: 10-psi (69-kPa) minimum, 450-psi (3,100-kPa) maximum.

Pump and motor: Gould Model 13400 centrifugal pump, 7½-hp (5.6-kw) Reliance motor.

Particulate filter: Cartridge type of 10-µm pore size.

Installation and Startup

The main component of this unit was a skid-mounted assembly that was delivered to the WWTEF on December 5, 1972. Several accessory items were shipped separately and installed by site personnel while preparing the unit for operation. A Permutit Company field representative was present to check out the installation and assist in starting up the unit.

When the unit was started up on May 16, 1973, the high-pressure shutoff switch and one desalting module were found to be defective. The defective module was replaced by a spare shipped with the unit. The high-pressure shutoff switch was disconnected to allow the RO unit to operate without the switch while it was being replaced.

Equipment Modification

Several modifications were made to the equipment during the test period to facilitate the evaluation procedure. A Millipore test rig, which was not provided with the RO unit but considered essential to unit evaluation, was purchased separately. The unit was not originally provided with the interstage flushing connection required for the citric acid cleaning operation, and necessary valves and fittings were purchased locally to make up this connection. The electrical control circuitry was changed from automatic to manual restart to provide a uniform restart procedure for the three RO units. A totalizing clock was installed in late November 1973 to record total operating time.

Data Collection

Data were collected daily on this unit to monitor equipment operation and obtain a measure of RO permeator performance. Data were also collected weekly from several auxiliary tests performed on the permeators of the unit, primarily as a check on membrane fouling.

Appropriate gages and meters located on the RO unit and portable measuring instruments provided data on pressure, temperature, flow rates, salinity (in TDS and EC readings), and total operating time. The unit was equipped with Wallace and Tiernan flowmeters that measured the total composite flows of the product water and reject brine for the three permeators.

All water salinity data were taken with a Myron L DS meter according to the methods described under "Data Collection" of the UCLA unit. EC measurements of water quality were also taken using a YS Model 33 EC meter.

<u>Auxiliary Tests</u>

Several weekly tests were performed on the PermuRo unit, primarily to indicate membrane fouling and thereby prevent damage to a permeator. These were the Langelier Saturation Index, Millipore filter, and differential pressure tests (16). As a part of the tests, chemical analysis was also made of water alkalinity, total hardness, and calcium hardness using the appropriate Hach chemical analysis kit.

<u>The Langelier Saturation Index (I)</u> was used to predict the tendency for the RO brine to precipitate $CaCO_3$. The value of the Index, I, is determined from the actual measured feedwater pH and the calculated saturation pHs, the value at which $CaCO_3$ precipitation is expected to occur. The saturation pHs must be derived from the calcium (Ca), alkalinity (HCO_3), and TDS content of the water and its temperature.

The relationship between pHs and these constituents of the water is set up in nomograph (20) and slide rule form (Langelier Saturation Index calculator) with which the value of I can be readily calculated. The calcium and alkalinity levels are found as P (Ca) and M (alk), respectively, in ppm (mg/l) as $CaCO_3$. Hach chemical analysis tests are used for the following test procedures:

1. Alkalinity, Phenolphthalein and Total
Titration Method for Water and Wastewater
APHA Standard Methods, 13th ed., 52 (1971)

2. Hardness, Calcium
Titration Method - CalVer II for Water and Wastewater
APHA Standard Methods, 13th ed., 84 (1971)

3. Hardness, Magnesium and Total
Titration Method - ManVer II for Water and Wastewater
APHA Standard Methods, 13th ed., 179 (1971)

Saturation Index tests were made weekly of the feedwater and first-stage and second-stage reject brines of the PermuRo unit.

The Millipore filter test indicates the amount of suspended solids entering the RO system with the feedwater and leaving the system with the reject brine. It is a measure of the rate of fouling within the permeator and determines the required citric acid cleaning cycles.

The test apparatus requires the use of a Millipore filter holder containing a 0.45-μm filter. The water sample being tested is passed through the filter under 30-psi (207-kPa) pressure, and the time required to pass a given sample provides a measure of the fouling properties of the water defined in terms of a plugging factor.

Millipore filter tests were performed weekly on the three permeators of the unit to determine the value of the plugging factor.

The differential pressure test measures the pressure drop across the permeator between the feed inlet and reject outlet of the permeator. The normal pressure drop is expected to be 8 psi (55 kPa) to 12 psi (83 kPa) and is an indication of the proper functioning of the permeator. An excessive pressure drop may be an indication of fouling, while mechanical failure of the permeator may be detected by an unusually high or low pressure differential.

Differential pressure tests were performed weekly on the PermuRo unit. Pressure drops across the three permeators and EC readings of the product and reject brines of each permeator were recorded.

Plant Maintenance

Routine plant maintenance was performed primarily to control membrane surface fouling. These procedures involved periodic changes of the particulate filter cartridge and citric acid treatment of the permeator and are essentially the same as those described under "Plant Maintenance" for the GESCO unit.

CHAPTER VI. REVERSE OSMOSIS EVALUATION STUDY -- TEST OPERATIONS

Feedwater Supply and Treatment

Feedwater Supply

Following the pattern of previous years, the flow of tile drainage water from the Alamitos sump varied considerably throughout the 1973-74 test period. Table 5 provides a comparison of ionic constituents of the tile drainage water during periods of extreme high and low salinity, and Figure 20 illustrates the annual variation of several constituents and other drainage water characteristics.

TABLE 5

ALAMITOS TILE DRAINAGE WATER
CHEMICAL ANALYSIS OF LOW AND HIGH TDS FLOWS
AND SOFTENED FEEDWATER

Constituent	Drainage Water Concentration (ppm or mg/l)		Softener Water Concentration (ppm or mg/l)	
	Sample Date		Sample Date	
	9-14-73	12-31-73	4-5-74	
	Low TDS	High TDS	Raw	Softened
Calcium	149.0	365.0	392.0	11.0
Magnesium	57.0	255.0	199.0	10.0
Sodium	406.0	1,340.0	1,320.0	2,130.0
Potassium	3.3	5.7	5.7	1.7
Carbonate	--	--	--	--
Bicarbonate	334.0	234.0	309.0	20.0
Sulfate	849.0	3,780.0	3,620.0	3,850.0
Chloride	197.0	522.0	455.0	403.0
Nitrate	96.0	48.0	82.0	79.0
Boron	3.9	15.0	13.0	14.0
pH	7.8	8.2	7.7	6.0
TH as $CaCO_3$	606.0	1,960.0	1,800.0	69.0
TDS	2,010.0	6,990.8	6,510.8	6,780.8

In 1974 the farmland serviced by the tile drainage system was planted to cotton, and since the irrigation of this crop was completed by summer, the drainage flows into the Alamitos sump became insufficient to supply test operations in the late months of the year. Consequently, it was necessary to supplement test requirements with water from the Delta-Mendota Canal interceptor drain after September 1974.

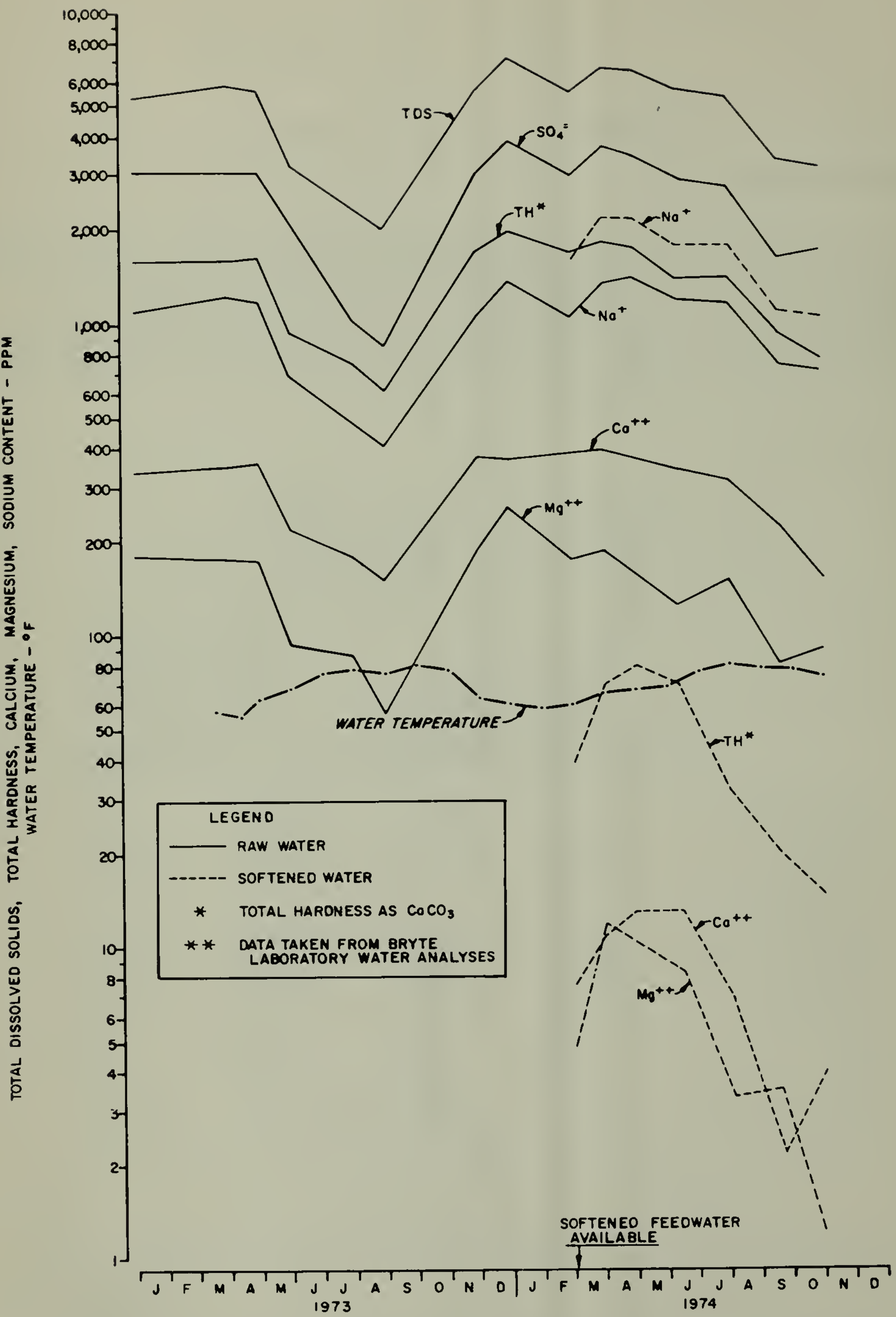


FIGURE 20-ALAMITOS TILE DRAINAGE WATER - SEASONAL VARIATIONS IN TOTAL DISSOLVED SOLIDS, TOTAL HARDNESS, TEMPERATURE AND SEVERAL IONIC CONTITUENTS - RAW AND SOFTENED FEEDWATER **

Feedwater Pretreatment

The feedwater pretreatment system was operated essentially as previously described under the procedure for feedwater pretreatment. A significant change in feedwater quality resulted with the inclusion of the softening process. The changes in the calcium, magnesium, and sodium content as a result of softening are indicated in Table 5 and on Figure 20. Prior to the use of softened feed, the RO units generally were operated below the 70-percent recovery level to avoid $CaSO_4$ concentrations beyond the saturation limit and possible precipitation of the salt. The removal of substantial amounts of Ca^{++} ions by the softening process allowed the RO units to operate at recovery levels as high as 90 percent.

Temporary adjustments in the feedwater pretreatment procedure were required while special investigations were carried out on the UCLA unit. These adjustments were made during the maximum recovery study, the 95-percent recovery study, and the SHMP additive study.

Equipment Modification

A number of equipment modifications were made to the feedwater treatment system during the test operation. The feedwater booster pump was replaced twice to meet the increased feedwater supply requirements. The Foxboro pH reader was replaced with a Beckman pH controller in May 1974, and the original feedwater holding tank was replaced in August 1974. No addition to the softener resin was required during the test period. The carbon filter was not backflushed on a scheduled basis, nor was there a need to replace the activated carbon.

The softener unit was delivered in September 1973 and made operational in December 1973. Some delay in startup was experienced because of improperly installed components that took considerable time to identify and correct.

Because the softening of feedwater of the quality found at the WWTEF had no precedent, there was little experience available from manufacturers and water conditioning operators to guide in selecting the equipment and operating criteria. Consequently, the selected equipment and mode of operation for the softening process were not fully proven, and a number of deficiencies developed that required correction.

One of the first problems was with the Honeywell hardness sensor used to detect feedwater hardness at the completion of the exchange cycle. This sensor and its replacement could not be made to operate properly, most likely because they were not designed for use on water of the quality available at the WWTEF. The sensor served as a safety device to prevent hard water from entering the feedwater stream and was replaced with a Hach hardness monitor. This hardness monitor continuously sampled the feedwater hardness and was designed to shut down RO operations in case the monitor detected feedwater hardness levels greater than 100 ppm (mg/l) (as $CaCO_3$).

The original four-hour timing device installed to control the operating cycle of the softener was replaced by a 30-hour infinitely variable timer on June 27, 1974. This change extended the service time between regenerations, which considerably reduced salt consumption and provided a more flexible operation to meet the changes in feedwater TDS.

An original implementation of the softening process was the use of product water for the regenerant brine and rinse water. This improved the efficiency of resin regeneration when compared to using feedwater with its high TDS and calcium content. However, it was later found that the supply of product water was limited because of periodic outages of the RO units and the use of this water for citric acid cleaning of the modules.

On December 18, 1973, a shortage of product water resulted in an incomplete regeneration of one softener column and subsequent discharge of regenerant brine into the feedwater stream and RO units. The influx of brine caused the desalting modules to become heavily fouled and forced the RO units to shut down.

This problem was corrected by supplementing the regeneration water supply with treated feedwater. To provide this backup supply, the capacity of the feedwater booster pump was increased and sections of the feedwater piping were enlarged. These modifications accommodated the increased feedwater needs for RO operation at higher recovery levels. Site operations were shut down for seven days in early March 1974 for this modification work.

Operational Downtime

Generally, equipment failures or problems with the feedwater treatment system resulted in shutdowns of the test operation and thus contributed to the downtime experienced by the RO units. Problems associated with the softener startup and operation caused most of the feedwater system downtime. The Hach hardness monitor required considerable adjustment and attention for proper operation. The device tended to shut down the RO operations from false signals, and this contributed to the operating downtime, especially when shutdown occurred over the weekend when site personnel were not in attendance. Other factors contributing to the downtime were feedwater pump replacement and repair needs and a seven-day period when operations were down for plant modification.

Downtime caused by support equipment outages amounted to approximately 33 days for the UCLA unit, 46 days for the GESCO unit, and 30 days for the PermuRo unit. This downtime is different for each RO unit because it did not necessarily affect them concurrently.

UCLA Reverse Osmosis Unit Operations

Summary

This unit was operated on a continuous basis from March 1973 through December 1974 and did not experience any significant problems that adversely affected its desalted water production. The unit did incur routine downtime as a result of those equipment repair and maintenance needs associated with continuous operation.

For most of the test period, the unit was operated to provide optimum desalted water production under the prevailing conditions of feedwater TDS. In addition, the unit was periodically taken from its normal mode of operation and used to perform special studies on various aspects of desalination of interest to DWR and UCLA investigators.

A series of investigations was conducted to establish the maximum recovery levels attainable as limited by the scaling tendency of the feedwater. These tests were conducted on both the 140-tube and 180-tube RO configurations utilizing feedwater at extreme levels of TDS, with and without SHMP treatment.

When softened feedwater became available, the 180-tube unit was operated at the 90-percent recovery level using feedwater at a TDS of more than 6,000 ppm (mg/l) and at 95-percent recovery with feedwater supplied at 3,000 ppm (mg/l). A final study was conducted with the unit using unsoftened feedwater treated with a high concentration of SHMP.

Unit Performance

Overall performance of the UCLA unit is shown by the operating data given on Figures 21A, 21B, and 21C. Figure 21A shows plant performance under various conditions of feedwater TDS, operating pressure, and flow rate. Desalting performance is reflected in product flow, recovery, and

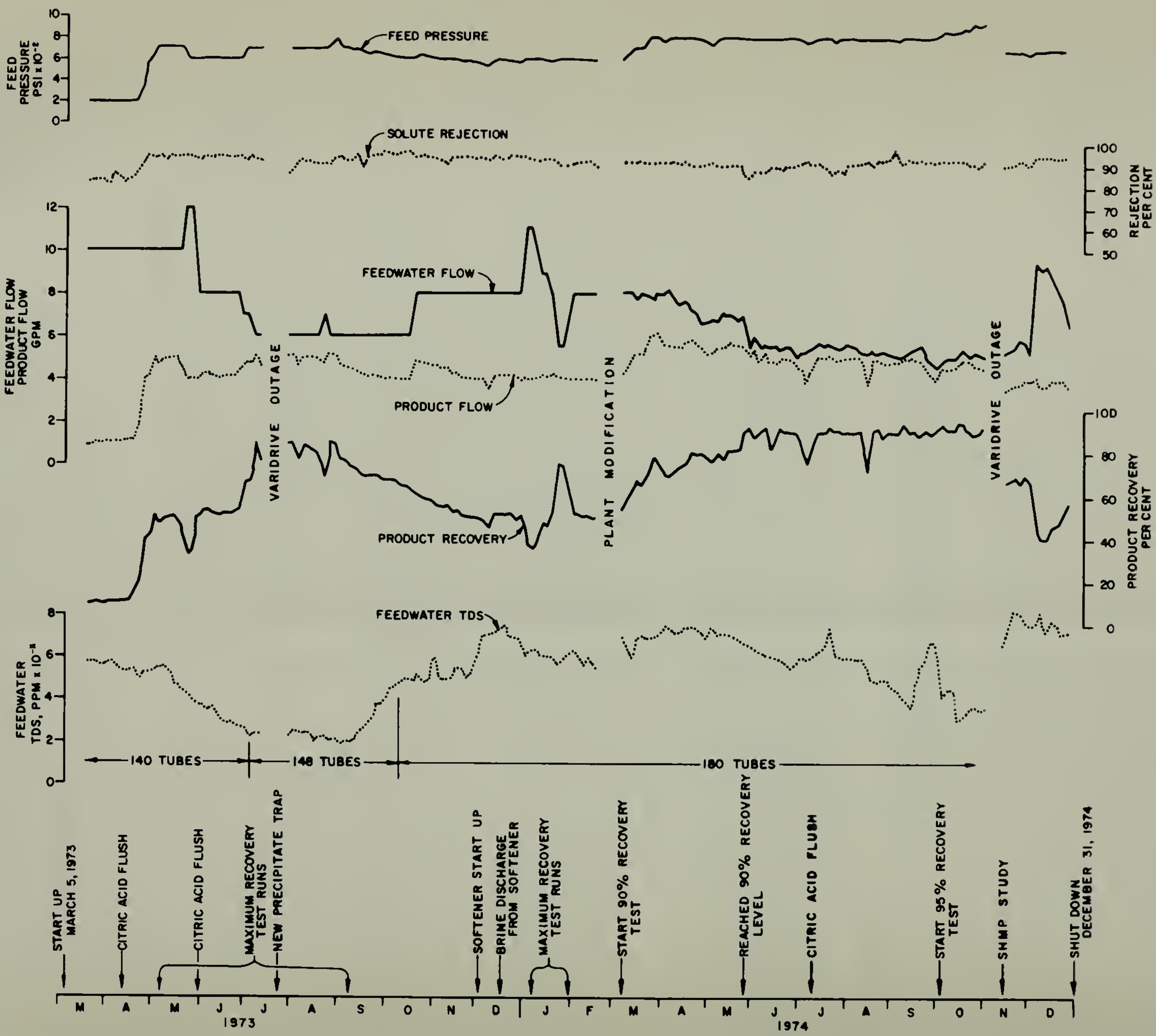


FIGURE 21A- 180-TUBE (U C L A) R O UNIT PERFORMANCE

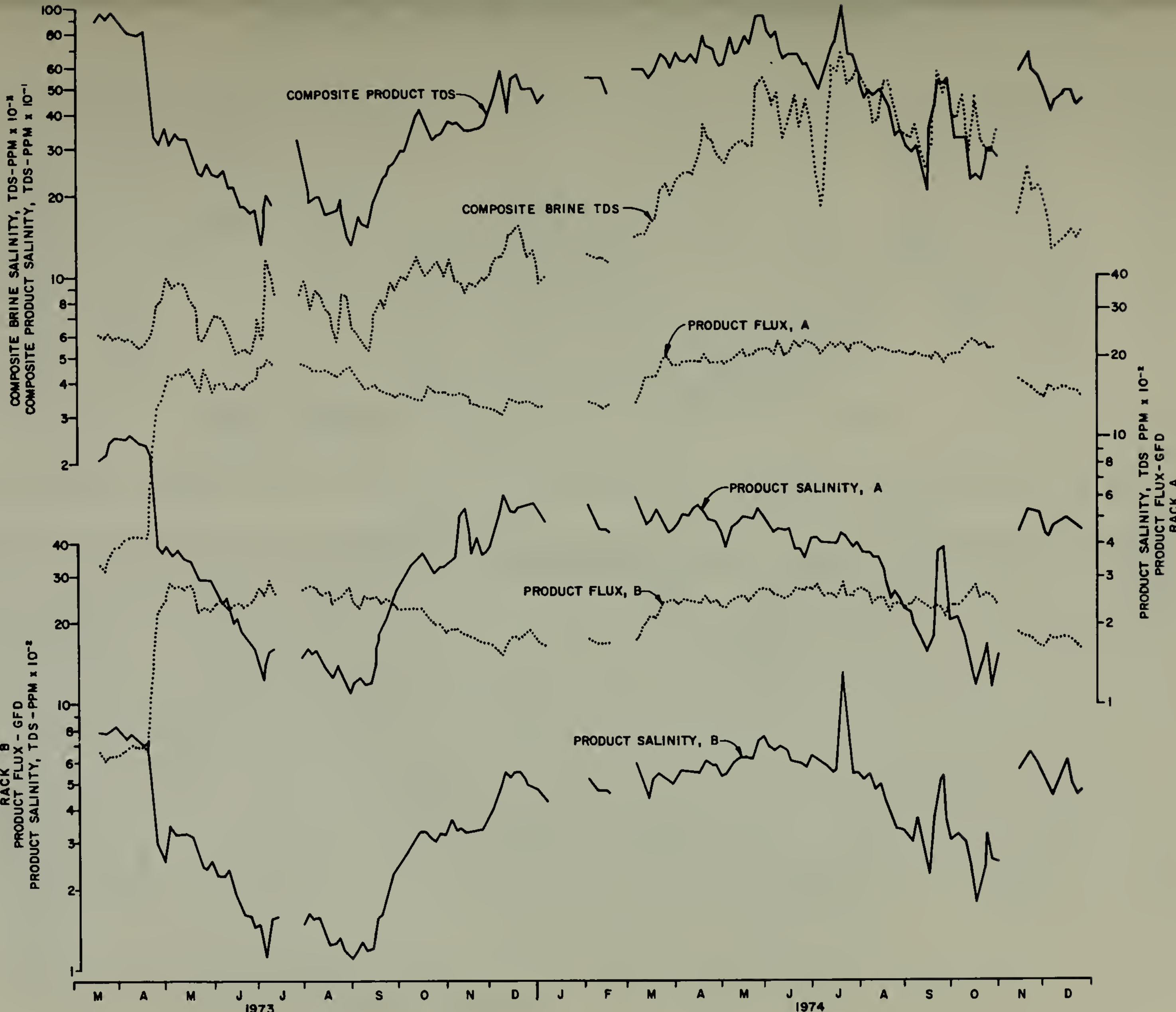


FIGURE 21B- 180-TUBE (UCLA) R O UNIT PERFORMANCE

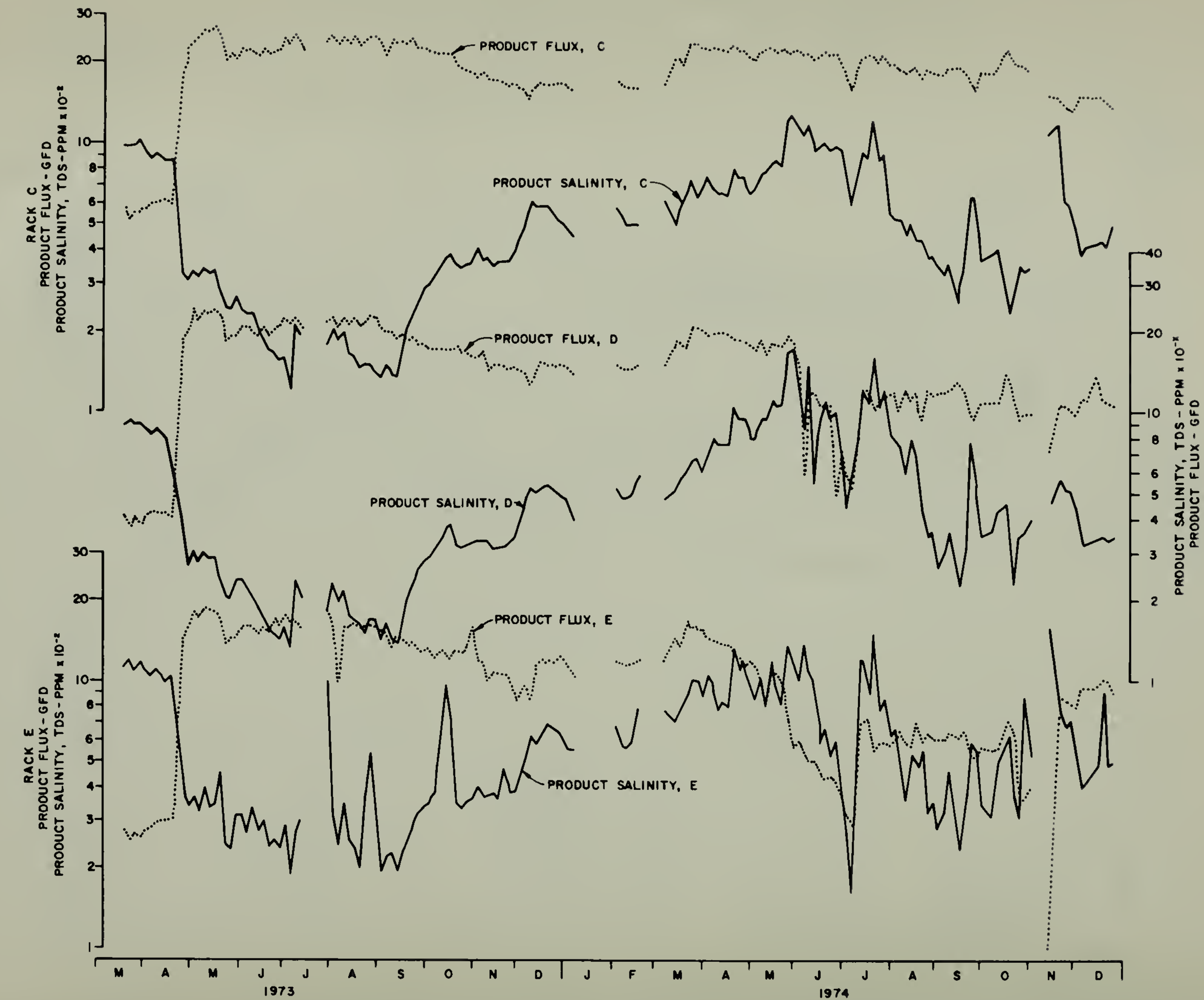


FIGURE 21C- 180-TUBE (UCLA) R O UNIT PERFORMANCE solute rejection. Figures 21B and 21C provide summaries of composite project and waste brine salinity as well as the product flux and salinities of the five individual racks. The plots of the five racks clearly show the change in desalting performance along progressive sections of the RO unit.

Percent recovery was determined by the ratio: product flow rate/feed flow rate x 100. Salt rejection efficiency, which was consistently above the 90-percent level for this unit, was calculated as follows:

$$\text{Percent rejection efficiency} = \frac{\text{Feedwater TDS} - \text{Product TDS}}{\text{Feedwater TDS}} \times 100$$

Figure 21A lists important occurrences (such as changes in tubular configuration, outages, special investigations, etc.) during the operation of this unit. Following startup, the unit was operated 45 days at 200-psi (1,380-kPa) feed pressure. The purpose of this run was to gather data at low operating pressures because of the special interest held in this aspect of RO desalination. Pressures between 600 psi (4,140 kPa) and 800 psi (5,520 kPa) were maintained for the remainder of the operation except for the period when it was raised to 900 psi (6,205 kPa) for the 95-percent recovery test. The variations in feedwater flow rate were primarily the result of its manipulation during the maximum recovery test. Composite product flux and salinity were maintained at 20 gfd (82 ml/cm^2, day) and 400 ppm (mg/l) respectively when operating at the 90-percent recovery level.

The performance data of this unit show that the tubular membrane maintained satisfactory desalting characteristics throughout the operating period. There were no adverse effects upon membrane performance resulting from compaction, fouling, or other causes of membrane deterioration. This unit maintained a high operating efficiency through timely replacement of tubes that showed unacceptable performance. The ease with which faulty tubes could be identified and replaced and the low replacement costs made this practice feasible. Weekly cleaning with the spongeball kept membranes free of surface fouling.

Operational Downtime

This unit was operated on a continuous basis including weekends and holidays. During the period between May 1, 1973, and November 18, 1974, there were 566 operating days available, of which the unit was in service 487 days or 86 percent of the time. Factors contributing to the 14-percent downtime are shown in Table 6. Most of the RO unit's downtime was caused by problems with the pump varidrive, which resulted in a total of 25 days of outage. The remaining downtime was due to minor mechanical repairs and maintenance, tube replacements, and spongeball cleaning operations. Softener startup and operational problems caused much of the support equipment downtime.

TABLE 6

UCLA RO UNIT OPERATION DOWNTIME

Cause of Downtime	Percent Downtime
RO equipment outage	5.9
Power supply outage	2.3
Support equipment outage	5.8
Total outage	14.0

Equipment Modification

The UCLA unit was initially installed with 140 tubes, a shortened configuration that limited the desalting capacity. This arrangement allowed operation of the unit without the risk of intensive scaling while investigating performance at maximum recovery levels. Eight tubes containing special formulations of the CA membrane were added to the unit for field testing in July 1973, and 32 tubes were added in October 1973 to give it a full complement of 180 tubes.

A new design of precipitate trap shown on Figure 22 was installed in July 1973. The trap performed satisfactorily except for a brief period in July 1974 when it was clogged with algal growth and during the 95-percent recovery test when it became plugged with precipitated salt. The original pump, which had been in service since 1971 and was subjected to high operating loads during the maximum recovery test operations, was replaced in May 1974.

A new design of spongeball was evaluated for use in membrane cleaning during August 1973. Its use, however, resulted in a significant increase in tube failures, especially at the last tube position of the unit. These failures were attributed to the collapse of the membrane caused by negative pressure that developed in the tube during passage of the spongeball. To resolve this problem, the cleaning procedure was modified to prevent this negative pressure from developing, and the size of the spongeball was reduced. The cleaning procedure finally adopted used three 1-inch (2.5-cm) diameter spongeballs inserted in the tubular array at spaced time intervals.

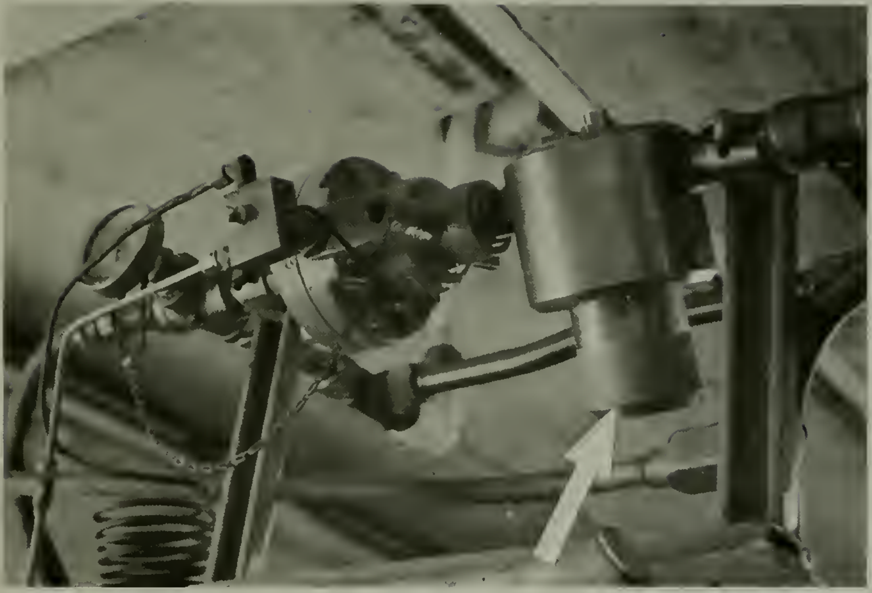


FIGURE 22. UCLA RO UNIT, NEW DESIGN OF PRECIPITATE TRAP

Operating Problems

Tube Failures. Seventy-four tube replacements were made for various reasons during the test operation of the unit. Fifteen tubes were damaged during attempts to improve the performance of the spongeball cleaning procedure. Twelve tubes were replaced as a result of leakage around the O-ring seal of the tubular assembly. The brass fittings joining the assemblies had corroded around the O-ring as a result of electrolytic action, causing water leakage and some membrane damage. Tubes were also replaced because of mechanical failure from spongeball cleaning and fabrication defects.

A number of tubes began to show poor desalting characteristics during the early stages of the 90-percent recovery operation and were replaced by tubes with membranes with better properties for operation at high recovery rates.

Softener Malfunction. The UCLA unit did not develop any problems as a result of the accidental discharge of softener regenerant brine into the feedwater stream. When this accident occurred on December 12, 1973, the unit shut down automatically as a result of high pressure that developed in the tubular system, most likely caused by the accumulation of precipitated brine. The unit was flushed with softened feedwater for an hour and then returned to service. The flushing procedure was apparently effective since there was no subsequent deterioration of RO performance.

Varidrive. The only equipment problem that resulted in significant downtime for the UCLA unit during this test operation was the malfunctioning varidrive component of the triplex pump. The unit was inoperative for 13 days in July 1973 and 12 days in November 1974 because of problems with the varidrive component.

Special Studies

Tube Service Life. When the UCLA unit was assembled for operation, 28 tubes that already had a service life of nine months from the prior unit (60-tube) operation were included in the assembly. These 28 tubes were installed in Rack A (see Figure 8) and, with the exception of four tubes that were replaced, accrued a service life of 30 months during the test period ending December 1974. This compares with 21 months for 53 original tubes that were not replaced in Racks B through E of the 140-tube configuration. Any difference in performance among the five racks should be attributed to the relative position of the racks rather than differences in tube service life.

Maximum Recovery Tests. Two series of tests were carried out by UCLA investigators to establish the maximum product recoveries attainable under different conditions of feedwater TDS and treatment with SHMP additive. The first series of these tests was conducted using the 140-tube unit configuration, and a second series was carried out with the 180-tube unit. The wide range of feedwater TDS available throughout the year was favorable to conducting these tests.

A maximum limit of product recovery was considered attained when $CaSO_4$ precipitated on the membrane surface. Since this precipitation would drastically reduce permeation through the membrane, continued operation would not be advisable without first removing the precipitate. Incipient precipitation on the membrane surface was recognized by a conspicuous drop in product flux which was then confirmed by passing a spongeball through the tubes to remove the precipitate. Operation at the maximum level was for a short period of time and consequently did not reflect a normal operating condition which would necessarily be at a lower recovery level to avoid scaling.

These maximum recovery tests were part of the UCLA study to determine the scaling threshold limits of $CaSO_4$ in agricultural waste water. UCLA has developed a computer program that predicts the concentration factors at which the Alamitos tile drainage water of a given ionic strength will precipitate $CaSO_4 \cdot 2H_2O$ (gypsum) (6). The series of tests with the 140-tube unit was of a preliminary nature, serving to establish the validity of the computer program. The shortened configuration of 140 tubes provided data for the program in predicting scaling conditions while protecting the tubes from damage by gross scaling.

The second series of tests was carried out in September 1973 and January 1974 when the feedwater had a TDS of 2,000 ppm (mg/l) and 6,000 ppm (mg/l) respectively. These tests were conducted on the 180-tube configuration using feedwater treated with SHMP. The results of these tests are summarized in Table 7.

These results indicated that, during periods of high (6,000 ppm [mg/l]) and low (2,000 ppm [mg/l]) feedwater TDS, about 45-percent and 70-percent levels of product recovery, respectively, represent the point of incipient scale formation using untreated feedwater. Using feedwater treated with 5 ppm (mg/l) of SHMP, the product recoveries increased substantially, with levels of 75 percent at high and 87 percent at low feedwater TDS conditions representing the point of incipient scale formation. The effectiveness of SHMP was demonstrated by calculations based on data of these test runs which indicated that the scaling concentrations of water treated with the scale inhibitor increased to two times that of untreated water.

TABLE 7

MAXIMUM RECOVERY TEST RESULTS

Pressure (psi)	Feedwater Flow Rate (gpm) (l/s)	Feedwater TDS (ppm or mg/l)	Product Water Flow Rate (gpm) (l/s)	Product Water TDS (ppm or mg/l)	Recovery (Percent)	SHMP (ppm or mg/l)
700	6.5 (0.41)	2,000	4.6 (0.29)	155	70	none
800	6.0 (0.38)	2,000	5.2 (0.33)	185	87	5.0
595	8.9 (0.57)	6,000	4.0 (0.25)	455	45	none
600	5.5 (0.35)	5,800	4.1 (0.26)	625	75	5.0

<u>90-percent Recovery Operation</u>. The ion-exchange unit was added to the feedwater pretreatment operation in December 1973 to supply softened feedwater to the three RO units. The change was made to evaluate the calcium-removal capability of the ion-exchange step as a means to prevent scaling in the RO desalting modules.

It had been estimated that a 90-percent level of recovery could be attained by the RO unit without incurring $CaSO_4$ scaling during periods of seasonally high TDS when utilizing feedwater with 95 percent of the Ca^{++} ions removed. Figure 23 (5) shows the extent of Ca^{++} removal required to attain 90-percent recovery during an annual period for the Alamitos tile drainage water. The extent of Ca^{++} removed by the ion-exchange process (shown in Table 5) indicated that the 90-percent recovery goal was attainable.

The UCLA unit was then operated at progressively higher rates of recovery to test the limit of its desalting capability using softened feedwater. This procedure would determine if the removal of Ca^{++} ions by the softener had been sufficient to allow the RO operation at the 90-percent recovery level.

Starting at 55-percent recovery in March 1974, the desalted water production of the UCLA unit was steadily increased until a 90-percent level was attained in late May 1974. During this time there were no indications of $CaSO_4$ precipitation even though the feedwater TDS was consistently above 6,000 ppm (mg/l). However, the performance of a number

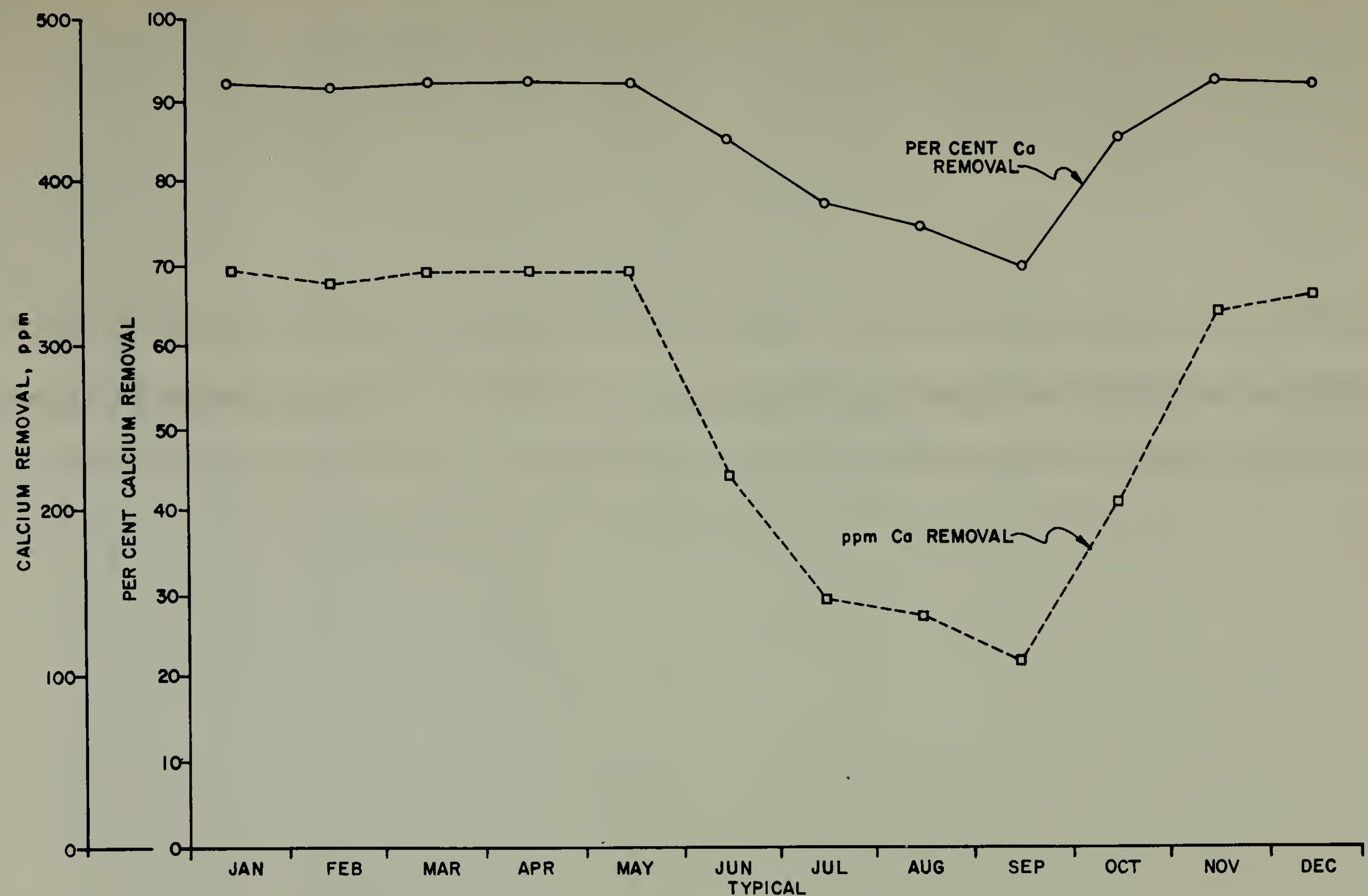


FIGURE 23 - CALCIUM REMOVAL FROM TILE DRAINAGE WASTE WATER TO ATTAIN 90 PER CENT WATER RECOVERY

of tubes deteriorated, and they were replaced by tubes with membranes with improved desalting properties at high recovery levels. The unit was then operated at the 90-percent level from May to October of 1974, during which time the TDS of the feedwater dropped to lower levels. Figures 21B and 21C indicate that composite product flux and salinity averaged 20 gfd (82 ml/cm^2, day) and 400 ppm (mg/l), respectively, during this period.

95-percent Recovery Operation. The purpose of this study was to demonstrate the feasibility of RO desalting above the 90-percent recovery level. A target level of 95-percent recovery was selected, and the operation was supplied with treated and softened feedwater at a TDS of about 3,000 ppm (mg/l). The TDS was maintained at this level by combining the flows from the Alamitos sump, the Delta-Mendota Canal interceptor drain, and RO product water returned to the storage pond. The UCLA unit was selected for use because of its general suitability for experimental applications.

This operational study began on October 1, 1974, and continued with only minor interruptions until October 31, 1974, when it was ended by mechanical failure of a pump component. During the test the unit was operated at ranges of pressure from 800 psi (5,520 kPa) to 950 psi (6,550 kPa) and a feed flow rate of from 4.5 to 5.5 gpm (0.28 to 0.35 l/s), resulting in a brine flow rate of from 0.08 to 0.67 gpm (0.005 to 0.04 l/s).

Unit recovery could be maintained consistently above the 90-percent level, and by taking incremental increases in recovery, the 95-percent level was reached and temporarily exceeded several times. However, the 95-percent level could not be consistently held, largely because of a general instability in the RO operation. The main cause of this unstable condition was believed to be the changing permeability (product flux) of the membrane with time as a result of progressive surface fouling. This was especially evident when the unit was given a spongeball cleaning treatment. Major adjustment to the unit controls was required to accommodate the change in membrane permeability because of cleaning effects. Other contributing factors were the continuing change in feedwater TDS (2,700 to 4,700 ppm [mg/l]) and the poor response of the unit to pressure adjustments, probably because of the compaction effects at high pressure.

Sodium Hexametaphosphate Study. It has been recognized that the injection of appropriate amounts of SHMP additive into the feedwater of an RO system effectively raises the scaling threshold limit of $CaSO_4$. This study was intended to evaluate the effect of SHMP on $CaSO_4$ scaling when using treated but unsoftened feedwater supplied at a TDS above 5,000 ppm (mg/l). Specific objectives were to establish a maximum recovery level and an optimum SHMP injection rate.

The study began on November 14, 1974, when the UCLA unit was placed in operation to provide 70-percent recovery at 700-psi (4,830-kPa) pressure. Unsoftened feedwater was supplied at 6,000 ppm (mg/l) and contained 50 ppm (mg/l) of SHMP. This test run was maintained for about 24 hours, during which time the unit experienced a gradual loss of production. At the end of the 24-hour period, recovery was about 66 percent and several end tubes of the unit showed considerable loss of product flux. The RO unit was shut down, and examination of the tubes showed them to be heavily precipitated. In addition, the precipitate had carried over into the brine strainer, causing it to clog and become inoperative. The study was then terminated because of this mechanical problem.

GESCO Reverse Osmosis Unit Operations

Summary

This unit was operated on a continuous basis from May 24, 1973, to November 12, 1974. After startup problems were resolved, the unit performed satisfactorily, maintaining an efficient level of desalted water production throughout its operating period. Settings of feedwater flow rate and pressure were adjusted to maximize product water recovery within the limits specified for this unit.

The unit incurred a nominal amount of downtime related to equipment maintenance and repair and from outages due to external causes. A short outage period was experienced as a result of a delay in replacing a damaged desalting cartridge.

For the first three months of operation, unit recovery was maintained at the 55-percent level with feedwater pressure at 250 psi (1,720 kPa) and flow rate at 2.5 gpm (0.16 l/s). During September 1973, unit recovery was progressively increased from 55 percent to a 70-percent level. At this level there were indications of reduced production because of membrane surface fouling; thus the operating recovery rate was returned to lower levels. Feedwater at a TDS of 2,000 ppm (mg/l) and treated with 5 ppm (mg/l) of SHMP was used during this test run. Recovery was then maintained at the 50-percent level as the feedwater salinity increased on a seasonal basis.

With softened feedwater available, the unit began operating in late March 1974 from 50 percent to progressively higher recovery levels until 90 percent was reached in mid-June. Unit recovery was then held at the 90-percent level until the test operation was completed in November 1974. The feedwater TDS was consistently above 6,000 ppm (mg/l) during the early phase of this high-recovery operation but later receded.

Unit Performance

Performance of this unit is summarized by the operational data presented on Figures 24A, 24B, and 24C. Figure 24A shows the relationship between feedwater TDS, the operating parameters of pressure and flow rate, and those that characterize the desalting performance of the unit. Figures 24B and 24C summarize the data on composite product and brine salinity as well as product flux and salinities of the five desalting modules. Sampling data for the five modules became available in August 1973 when three-way sampling valves were installed on the product manifold of the unit.

Figure 24A shows that an operating pressure of 300 psi (2,070 kPa) was required to maintain recovery at 60 percent, while 600 psi (4,140 kPa) was required for 90-percent recovery. Normal operating pressure for this unit is 600 psi (4,140 kPa), but generally, during the first year of production, a lower operating pressure is preferred for efficient desalted water production. A higher pressure is required after one year of operation when membrane compaction has taken effect.

When operating at 90-percent recovery, product flux was maintained above 10 gfd (41 ml/cm^2, day) for the first three stages of the unit. Production was lower for the fourth stage because of the reduced flow and high TDS of the feed brine for this stage. Product flux was based upon 114 ft^2 (10.6 m^2) of membrane surface area available for the 3-inch (7.6-cm) module and 60 ft^2 (5.6 m^2) for the 2-inch (5.1-cm) module. Rejection efficiency was 90 percent at lower operating pressures (300 psi [2,070 kPa]) and was 85 percent at higher pressures (600 psi [4,140 kPa]) when production was at 90-percent recovery.

Performance data of Figures 24B and 24C indicate that satisfactory desalting characteristics were maintained by the five modules throughout the operating period. There were no signs of progressive membrane deterioration from the effects of compaction or bacterial or chemical attack. Monthly treatment with citric acid kept the unit free of membrane surface fouling. Only one desalting cartridge was replaced in the unit during its period of operation. The cartridge was damaged from $CaSO_4$ scaling caused by a brine-side seal failure.

Operational Downtime

This unit was started up on May 24, 1973, and operated on a continuous basis until shutdown on November 12, 1974. During this period, there were 536 operating days

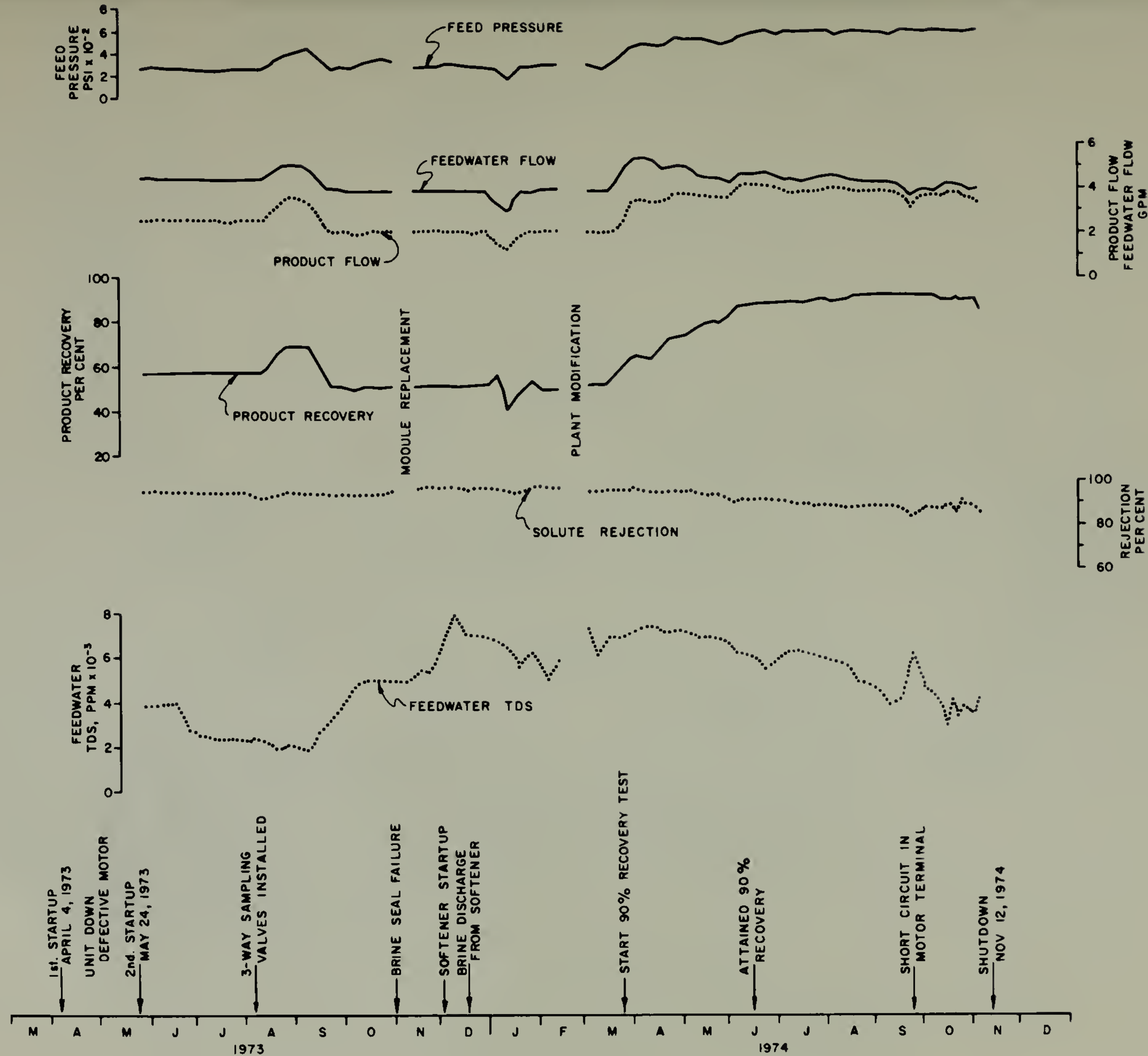


FIGURE 24A- SPIRAL-WOUND (GESCO) R O UNIT PERFORMANCE

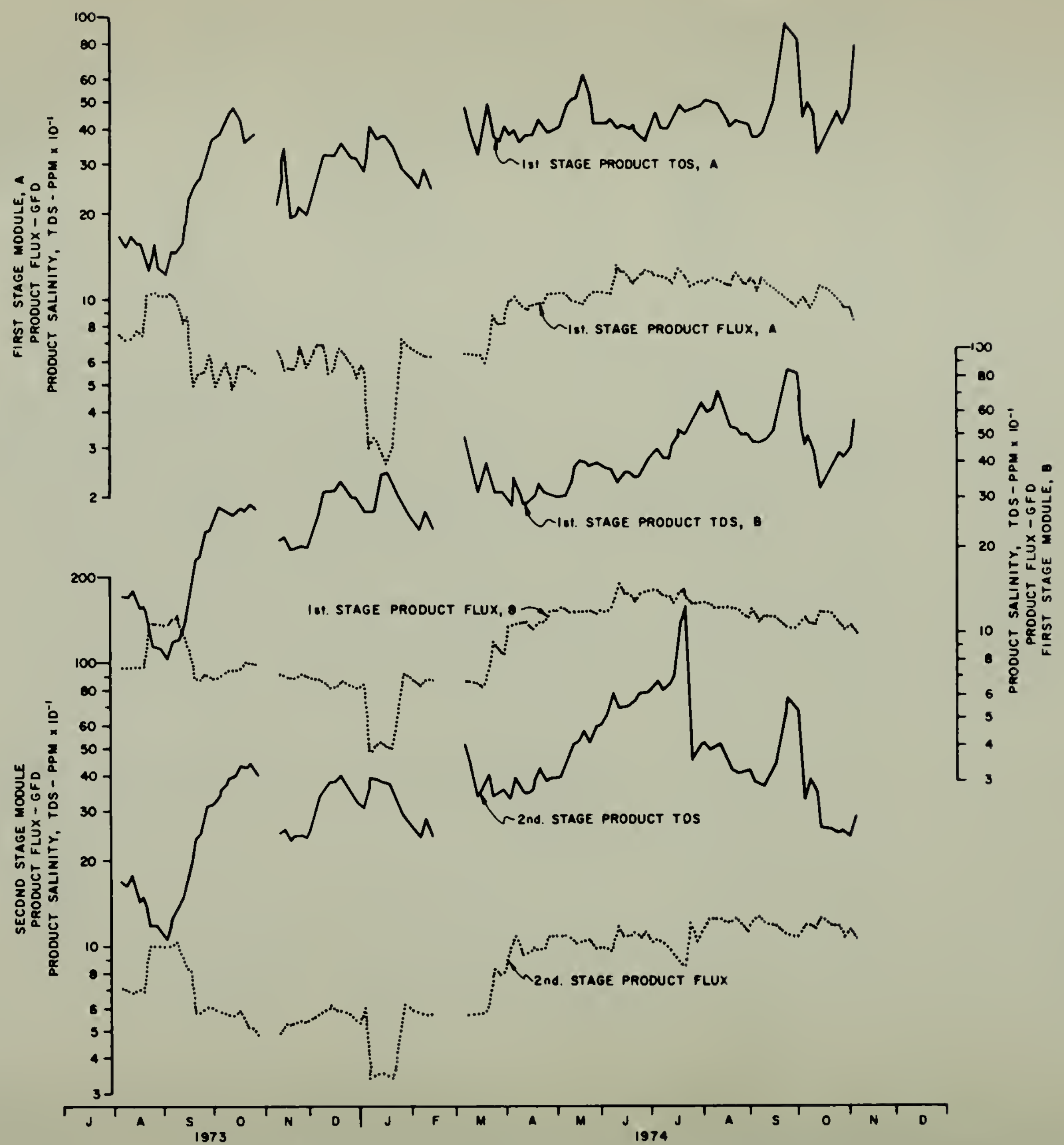


FIGURE 24B- SPIRAL-WOUND (GESCO) R O UNIT PERFORMANCE

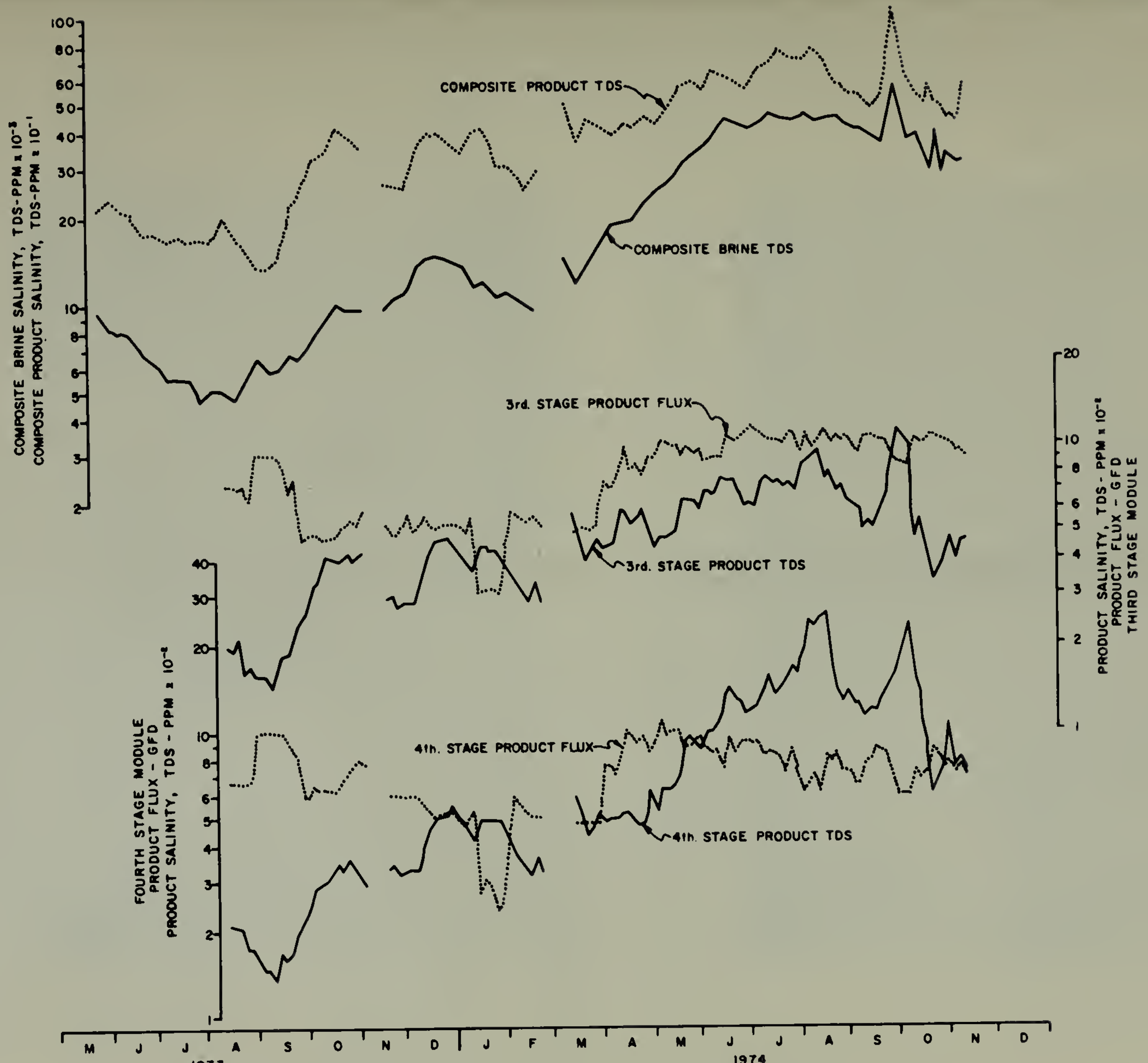


FIGURE 24C- SPIRAL-WOUND (GESCO) R O UNIT PERFORMANCE available, of which the unit was in service 465 days or 86.5 percent of the time. Factors contributing to the 13.5-percent downtime are shown in Table 8. Eleven days were lost in November 1973 from module fouling caused by failure of the brine-side seals. This outage accounted for a large share of the RO unit downtime. Maintenance requirements for seal repair, leakage of product sampling valves, activation of the high-pressure shutoff switch during weekends, and a short circuit in the motor terminal box also contributed to this RO unit downtime. Softener operating problems caused most of the support equipment downtime.

TABLE 8

GESCO RO UNIT OPERATION DOWNTIME

Cause of Downtime	Percent Downtime
RO equipment outage	3.2
Power supply outage	1.8
Support equipment outage	8.5
Total outage	13.5

Operating Problems

The only major shutdown for this unit occurred in November 1973 when leakage through the brine-side seals resulted in fouled modules. After sampling data collected during the month of October indicated a malfunction of the No. 1 module, it was dismantled and inspected on November 1, 1973. The middle cartridge was found to be heavily fouled with $CaSO_4$, and the brine-side seal was badly depressed. This condition is illustrated by Figures 25 and 26.

The unit was shut down until November 12, when a replacement for the fouled cartridge was available for installation. At this time the remaining modules were dismantled for seal repair, and one cartridge of the No. 3 module was found to be partially fouled. This cartridge was not replaced, however, because it was expected that, with the seals repaired, the renewed flow would dissolve the precipitate and the cartridge would regain its desalting capability.

Fouling occurs when the brine flow bypasses the desalting cartridge due to seal leakage and causes the water within the cartridge's brine channel space to become stagnant. Some permeation takes place, however, because the module is under high pressure. This causes a buildup of brine salinity within the channel space to a concentration that results in precipitation.

Unrolled Brine Flow Screen Showing
Accumulation of Precipitated Calcium Sulfate

End View Showing Fouled Passageways

FIGURE 25. GESCO RO UNIT, FOULED PERMEATOR

Typical Condition of Brine-side Seals
After Five Months

Seal Badly Depressed

FIGURE 26. GESCO RO UNIT, DETERIORATED BRINE-SIDE SEALS

Seal repair consisted of placing several wraps of lightweight foam tape around the cartridge as illustrated on Figure 27. Foam tape was used as a temporary measure because the 2-inch (5.1-cm) and 3-inch (7.6-cm) diameter modules used with this unit were not standard production sizes and therefore had no seal of permanent design for their use. Periodic inspection and replacement of the brine-side seals minimized the leakage problem.

Softener Malfunction

This unit was shut down when its modules became fouled from regenerant brine discharged into the feedwater stream by the malfunctioning softener. Following the outage the modules were flushed with product water to restore them to service, but it was necessary to repeat the procedure several times before performance was considered acceptable. After the outage the unit performed satisfactorily; therefore, it was concluded that no permanent damage to the desalting module resulted and that the restoration procedure was a success.

90-percent Recovery

With the availability of softened feedwater, it was possible to operate the RO unit at higher levels of recovery without incurring $CaSO_4$ scaling. Starting in late March 1974 at the 50-percent level, the unit was operated at progressively higher rates of recovery until the 88-percent level was reached in mid-June. Design limitations governing flow rates through the desalting modules made operation beyond the 88-percent level inadvisable. At this recovery level, the product flux and salinity were about 11 gfd (45 ml/cm^2, day) and 600 ppm (mg/l) respectively, and the TDS concentration of the feedwater was consistently above 6,000 ppm (mg/l). In the following months, the feedwater TDS concentration receded, and thus the unit operation was maintained at the 90-percent level for the remainder of the test period.

PermuRo Unit Operations

Summary

Operation of this unit began on May 15, 1973, and was concluded for the purposes of this test program on November 12, 1974. No problems delayed startup of this unit, although several defective components required replacement. The unit operated on a continuous basis, performed satisfactorily, and maintained an efficient level of desalted water production throughout the test period. Operating pressure and feedwater flow rate were adjusted to provide optimum production for the unit.

Installing a Brine-side Seal

Completed Seal Assenbly

FIGURE 27. GESCO RO UNIT, REPAIR
OF BRINE-SIDE SEAL

This RO unit incurred only a nominal amount of downtime as a result of operational maintenance and repair needs and external causes. However, a prolonged downtime developed from a delay in obtaining replacements for damaged permeators.

Initial operation was set at 75-percent recovery, the procedure recommended by the manufacturer for proper break-in of the RO unit. However, DWR personnel subsequently lowered the recovery to the 50-percent level to avoid the risk of $CaSO_4$ scaling.

For the first four months, unit operation was maintained at the 50-percent recovery rate with feedwater pressure between 250 psi (1,720 kPa) and 300 psi (2,070 kPa) and flow rate at 10 gpm (0.63 l/s). During September 1973, the recovery level was raised to 70 percent in a test of the production capability of the unit using feedwater at a TDS of 2,000 ppm (mg/l) and treated with 5 ppm (mg/l) of SHMP. Unit recovery was then returned to the 50-percent level, during which time the feedwater became increasingly saline due to seasonal conditions.

In late December 1973, the unit became inoperative because of fouled permeators and remained so until May 15, 1974, when replacement permeators were delivered and installed. Since softened feedwater was then available, the unit was placed in operation to attain 90-percent product recovery. This was reached in mid-June, and unit operation was held at the 90-percent level for the remainder of the test period.

Unit Performance

Performance of this unit is summarized by the operational data presented in Figures 28A and 28B. Figure 28A describes the feedwater flow rate, pressure, TDS, and those parameters that characterize the desalting performance of the unit. Figure 28B summarizes the data on composite and waste brine salinities as well as the product flux and salinity of each permeator.

As the performance data indicate, product flux was maintained at 1.5 gfd (6.1 ml/cm^2, day) when operating at 50-percent recovery with pressure in the 250-to-300-psi (1,720-to-2,070-kPa) range. Product flux of 2.0 gpd (8.2 ml/cm^2, day) was attainable at 90-percent recovery and 400-psi (2,760-kPa) pressure. Product flux was based on 1,800 ft^2 (167 m^2) of membrane surface available for each permeator. Rejection efficiency was held at 90 percent throughout the entire operating period for this unit.

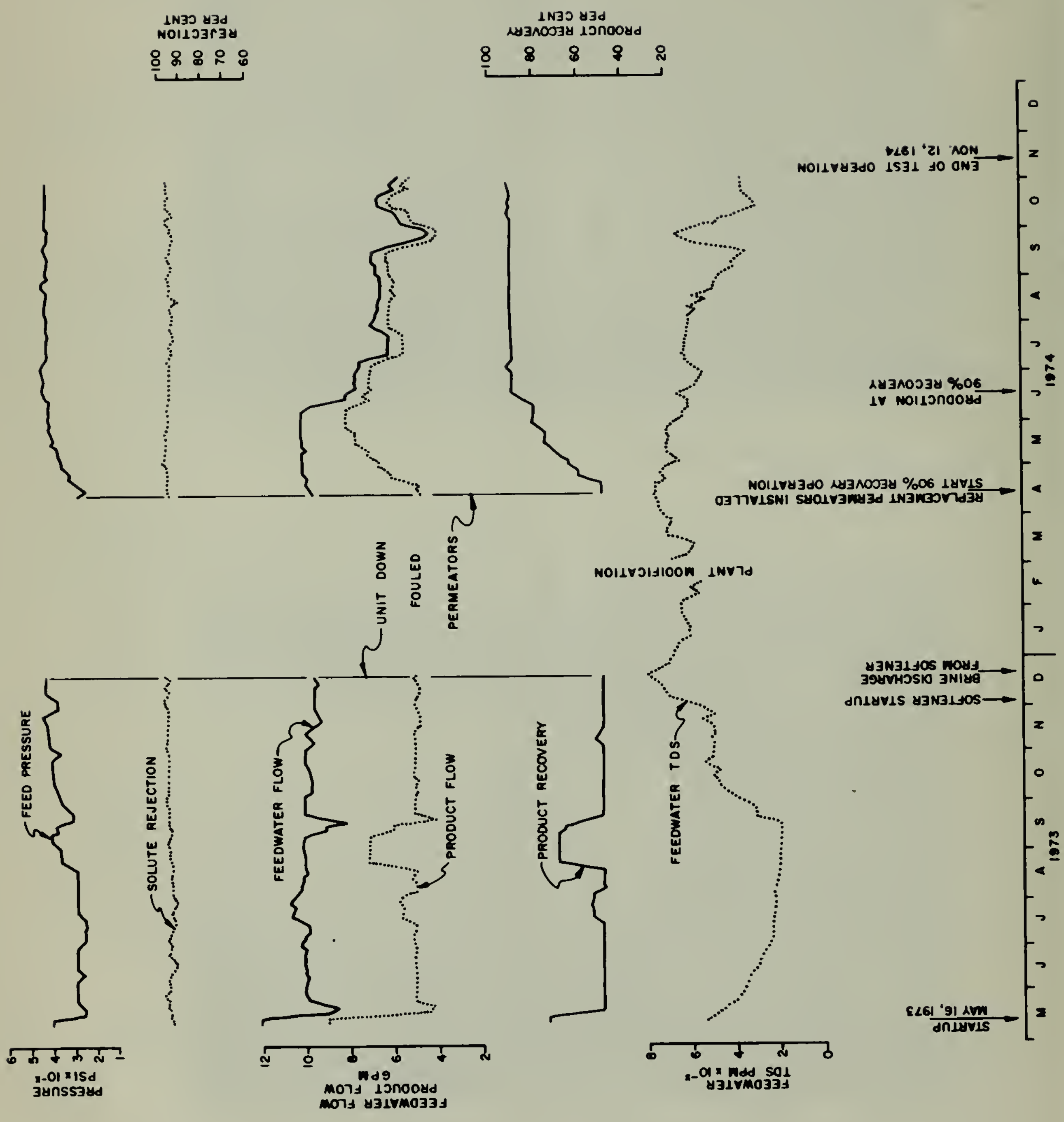


FIGURE 28A- HOLLOW-FINE-FIBER (PERMURO) R. O. UNIT PERFORMANCE

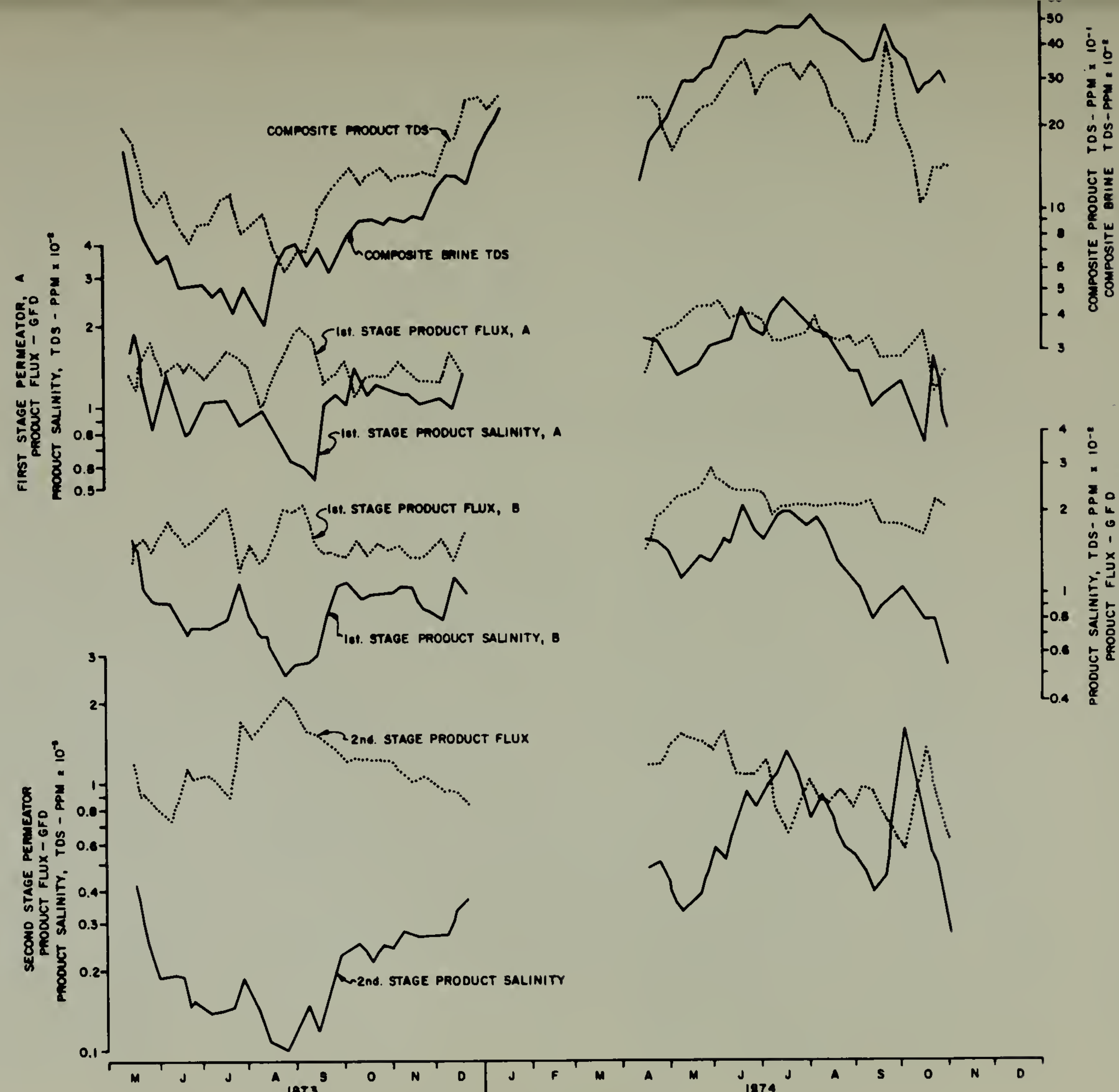


FIGURE 28B- HOLLOW-FINE-FIBER (PERMURO) R. O. UNIT PERFORMANCE

Two sets of permeators were used with this unit, and the data on Figure 28A show that both sets provided satisfactory service during the test period. There were no indications of any decline in desalting performance from fouling, compaction, or membrane deterioration. Monthly cleaning with a citric acid solution minimized loss of production from membrane surface fouling.

Operational Downtime

Operation of this unit began on May 16, 1973, and was completed for test purposes on November 12, 1974. During this period there were 543 operating days available, of which the unit was in service 395 days or 72.5 percent of the time. Factors contributing to the 27.5-percent downtime are shown in Table 9. Most of this downtime was the result of 111 days lost while waiting for delivery of two replacement permeators. The original permeators were permanently damaged when regenerant brine from the softener was inadvertently discharged into the feedwater stream causing the permeators to become fouled beyond recovery. Softener startup problems caused most of the support equipment downtime.

TABLE 9

PERMURO RO UNIT OPERATION DOWNTIME

Cause of Downtime	Percent Downtime
RO equipment outage	20.5
Power supply outage	1.4
Support equipment outage	5.6
Total outage	27.5

Equipment Modification

In July 1973, a hairline crack and subsequent leakage developed in the interstage manifold (made of PVC plastic) which required obtaining a replacement from the RO equipment manufacturer. A totalizing time clock was added to the unit in November and the low-pressure shutoff switch was replaced in December 1973.

Softener Malfunction

On December 18, 1973, a softener malfunction resulted in an incomplete regeneration of one softener column and subsequent discharge of regenerant brine into the feedwater stream. The influx of brine into the permeators of the PermuRo unit caused them to become heavily fouled and the RO unit to shut down.

Several efforts were made to restore the permeators to normal operating condition, but none proved successful. The permeators were first flushed with product water. After this procedure failed, the unit operated at a reduced pressure of 175 psi (1,210 kPa) using product water as feed. The permeators were also given a citric acid cleaning treatment to clear out any $CaSO_4$ precipitate.

No further work was done on the unit until January 30, 1974, when a Permutit Company representative dismantled and inspected the permeators. The cause of the permeator failure was not fully determined, although it could have resulted from contact with chlorine, which is known to be harmful to the polyamide membrane. It was detected in the porous backup disk of the permeator at the time of inspection and was believed to have been brought in with the product water supplied by the other RO units for the flushing operation. Figure 29 shows deposits of $CaSO_4$ on the endplates of the damaged permeators. Two replacement permeators were delivered to the WWTEF on May 15, 1974. DWR personnel installed the two replacements and a spare permeator on the following day and placed the unit in operation.

90-percent Recovery

With the use of softened feedwater, operation of the RO unit was possible at higher levels of recovery without incurring $CaSO_4$ scaling. Starting on May 15, 1974, at the 50-percent level, the recovery rate of this unit was progressively increased, and by mid-June a 90-percent recovery rate was reached. At this level the product flux and TDS were about 2.0 gfd (8.2 ml/cm^2, day) and 300 ppm (mg/l) respectively. The feedwater TDS was consistently above 6,000 ppm (mg/l) during this high-recovery operation. Operation was maintained at the 90-percent recovery level from June to the end of the test period, during which time the feedwater TDS receded to lower levels.

Boron Removal Study

Following completion of the RO evaluation study, a special study on the removal of boron from subsurface tile

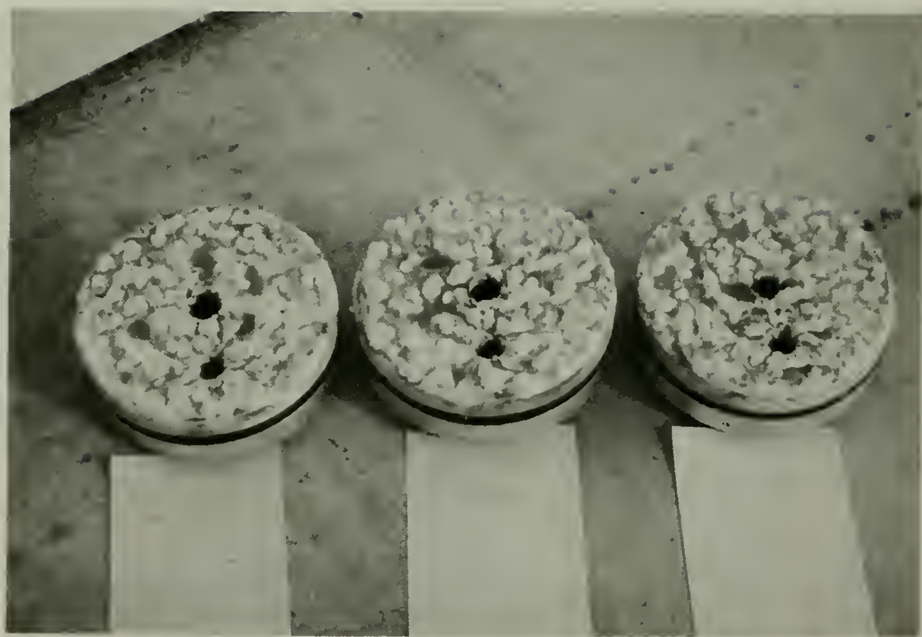


FIGURE 29. PERMURO RO UNIT, $CaSO_4$ DEPOSITS ON ENDPLATES OF DAMAGED PERMEATORS

drainage water was carried out with the PermuRo RO unit during December 1974 and January 1975. This study investigated the effect of several feedwater pH levels upon the ability of aromatic polyamide membrane to reject boron and a blending step to reduce the boron content of the product water. Its purpose was to evaluate these methods as a means to improve the boron-rejecting efficiency of the RO process.

Agricultural waste water of the quality found in some areas of the San Joaquin Valley is considered to be unsuitable for reuse in farm irrigation because of its high TDS content and the presence of mineral constituents that are considered toxic to plants. In particular, the tile drainage water supplied to the WWTEF has an especially high boron content, at times greatly exceeding safe tolerance levels. While traces of boron are essential to normal plant growth, its presence in applied irrigation water can be tolerated at concentrations of only up to 1 or 2 ppm (mg/l) by most agriculturally important crops.

While the test operation of the three RO units carried out under the RO evaluation study had demonstrated excellent capacity to desalt agricultural waste water, the semipermeable membrane itself did not maintain a uniform capability to reject various ion constituents. In this respect, the rejection of boron was relatively low, with the polyamide membrane showing better rejecting performance than the CA membrane.

The feedwater supply and treatment arrangement used for this study is shown on Figure 9. However, because of insufficient flow from the Alamitos sump during the December-January period, the water supply for the study was augmented with water from the Delta-Mendota Canal interceptor drain. During this period the Delta-Mendota Canal was dewatered for repair, and therefore its interceptor drain supplied water essentially of the same quality as the Alamitos sump. For the purpose of this special study, it was necessary to supply feedwater at several values of pH. A water solution of concentrated sodium hydroxide (NaOH) was therefore introduced into the feedwater downstream of the SHMP injection point.

Pretreated feedwater was delivered to the PermuRo RO unit at selected levels of pH which was controlled by the injection of concentrated NaOH. Four test runs were made at different specified feedwater pH levels with the RO unit operating at 50-percent recovery. When stable operation was attained at the selected pH, samples of feed, product, and brine water were taken for analysis at the DWR's Bryte Laboratory.

Three test runs were made on a once-through pass, each with the feedwater at a pH of 7.8, 9.0, and 11.0. A fourth run was made at a pH of 11.0 in which the product water was recycled for a second pass through the RO unit. The product water was returned to the mixing tank and combined with the feedwater in a ratio of 40-percent product water and 60-percent raw water.

Results

The results of the four test runs are shown in Table 10. The data indicate that the effectiveness of boron removal by the RO unit is improved at the more basic feedwater pH levels. It appears, however, that the overall ion-rejection efficiency decreases with higher pH values. The last test run on January 17, 1975, shows that the blending step reduced the boron content to 1.8 ppm (mg/l) in the product water.

TABLE 10

PERMURO REVERSE OSMOSIS UNIT
WATER SAMPLE ANALYSIS FROM TEST RUNS*

Test Date	Sample Source	TDS (ppm or mg/l)	pH	Boron (ppm or mg/l)
12-24-74	Feed	7,540	7.8	18
	Product	273	7.8	11
	Brine	16,200	7.8	27
1- 2 -75	Feed	7,120	9.0	18
	Product	138	9.0	5.0
	Brine	16,300	9.0	33
1-16-75	Feed	7,370	11.0	16
	Product	758	11.0	3.3
	Brine	16,100	11.0	32
1-17-75	Feed**	4,690	11.0	14
	Product	602	11.0	1.8
	Brine	10,400	11.0	29

*Water analysis made at DWR's Bryte Laboratory.

**With recirculation in approximate ratio of 40-percent product to 60-percent raw water.

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APPENDIX

PREVENTION OF BIODETERIORATION AND SLIME FORMATION IN TUBULAR REVERSE OSMOSIS UNITS

by

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July, 1975

PREVENTION OF BIODETERIORATION AND SLIME FORMATION IN TUBULAR REVERSE OSMOSIS UNITS

by

Michael G. Richard and Robert C. Cooper

I. INTRODUCTION

Background

The California Department of Water Resources has been active involved in determining the feasibility of reclaiming agricultural drainage water in the San Joaquin Valley through desalination by the process of reverse osmosis (RO). Such a feasibility study has been in progress since 1971 at the Waste Water Treatment Evaluation Facility (WWTEF) located near Firebaugh, California. In these studies subsurface agricultural drainage water, produced year round, is being desalted by passage under pressure through specially constructed tubular cellulose acetate membranes. This investigation is expected to determine the feasibility of RO as a method for desalting agricultural wastewater and also to provide a basis for comparing desalination with other approaches to wastewater reclamation or disposal. These studies are being conducted under a cooperative test program with the Office of Saline Water and with equipment and technical assistance from the University of California at Los Angeles (UCLA). Details of these investigations have been presented elsewhere (1,4).

Early in these evaluations, it was found that fouling, resulting from the apparent accumulation of bacterial matter and inorganic precipitates along the RO tube wall, significantly reduced the flux rate (product flow). Membrane failure frequently was caused by tube deterioration and was suspected to be due to bacterial activity (1). Membrane fouling has been a significant problem in many applications of reverse osmosis (1-6). Membrane deterioration has been noted previously (1,2,4-8), but the problem certainly is not general; membranes have been exposed to a variety of microorganisms without apparent attack or deterioration in performance (2).

In 1968, Cantor (7) demonstrated that bacteria isolated from biodeteriorated cellulose acetate RO membranes, soil, and lake mud could cause a type of membrane failure in the laboratory similar to that observed in actual RO units which experienced biological degradation in use. The membranes which were biologically degraded in the laboratory study showed considerable loss of acetyl content (acetate groups). The conclusion of Cantor's report was that the biodeterioration of the RO membranes was due to the action of cellulytic microorganisms.

Reese (8) previously had shown that certain species of fungi could attack cellulose acetate resulting in the hydrolysis of this material and that the degree of acetate substitution into the cellulose molecule (important in desalination characteristics) determined the susceptibility of the membranes to biological attack. Reese found that only fully acetylated cellulose (the triacetate) was immune to biodeterioration. This is a higher degree of substitution than previously reported by Siu to be necessary for microbial recalcitrance (9). Reese indicated that the species of fungi involved possessed both esterase activity toward the acetate portion of the cellulose acetate compound and cellulytic activity toward the cellulose portion. Esterase activity toward the cellulose acetate without the cellulytic ability had not been observed.

Results of the Initial Study at Firebaugh, California

In March 1973, the University of California at Berkeley (UCB) in cooperation with the California Department of Water Resources initiated studies on the bacteriological aspects of membrane fouling and membrane failure in tubular reverse osmosis (RO) units operated at the WWTEF located near Firebaugh, California. A monitoring program was conducted in which the types and number of bacteria present in the various steps of the reverse osmosis process were determined and their significance evaluated. These determinations were conducted simultaneously for a reverse osmosis unit in which feedwater pretreatment, including acidification to pH 5.5, chlorination followed by dechlorination by passage through activated carbon, and filtration through a 10μ spun cotton filter were used and one in which no pretreatment of the input water was involved (5).

Bacterial slimes were produced in both units. The membranes in the untreated unit underwent biodegradation while those receiving pretreated water did not. Bacteria similar to those of the genus *Arthrobacter* were shown to predominate in the untreated unit while members of the genus *Bacillus* predominated in the slime produced in the chemically treated unit. Both these groups of bacteria are common inhabitants of many soils.

Membrane biodeterioration was apparent in the untreated RO unit after 79 to 137 days of operation. Upon examination of these failed membranes, it was found that the entire surface of the membrane was covered with a brown slimy material and appeared to be perforated with tiny holes and thin spots. Several sections of the 10-foot tubular membranes were entirely dissolved away. The membranes were difficult to remove and handle as they were extremely brittle and broke easily. An example of a biodegraded membrane is presented in Figure 1 and the sequence of deterioration is shown in Figure 2.

Laboratory studies involving enrichment culture and subsequent isolation and characterization of involved microorganisms indicated that the biodegradation phenomenon was a metabiotic process and would not occur without at least two different groups of microorganisms being present. This process involved several species of the bacterium *Arthrobacter*, a

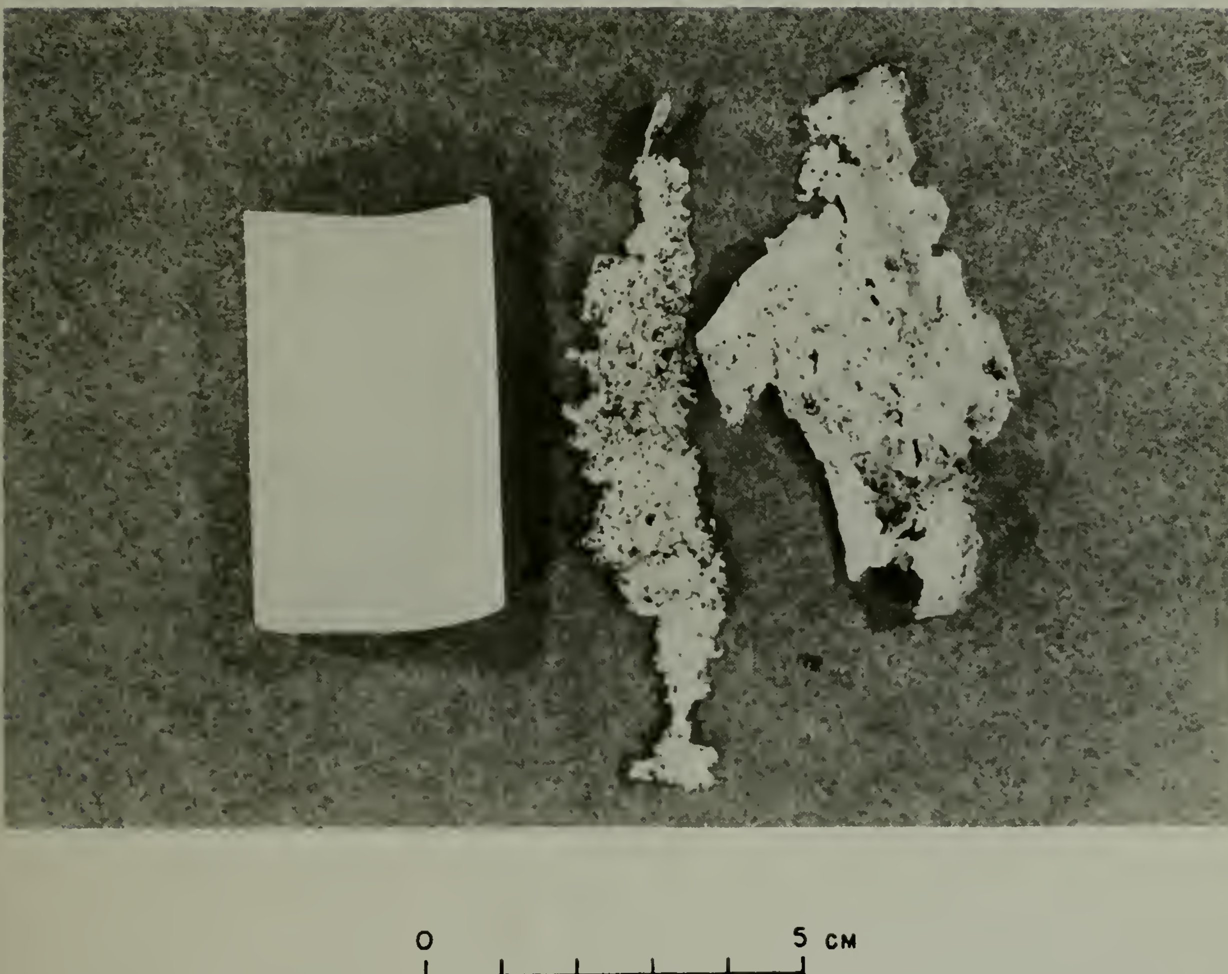


Figure 1. Comparison of Failed and Non-failed Membranes Removed from Service at Firebaugh (approximately 1X magnification). The membrane on the left is a two inch section of a non-attacked membrane while the membrane on the right is a three inch section removed from a failed tube.

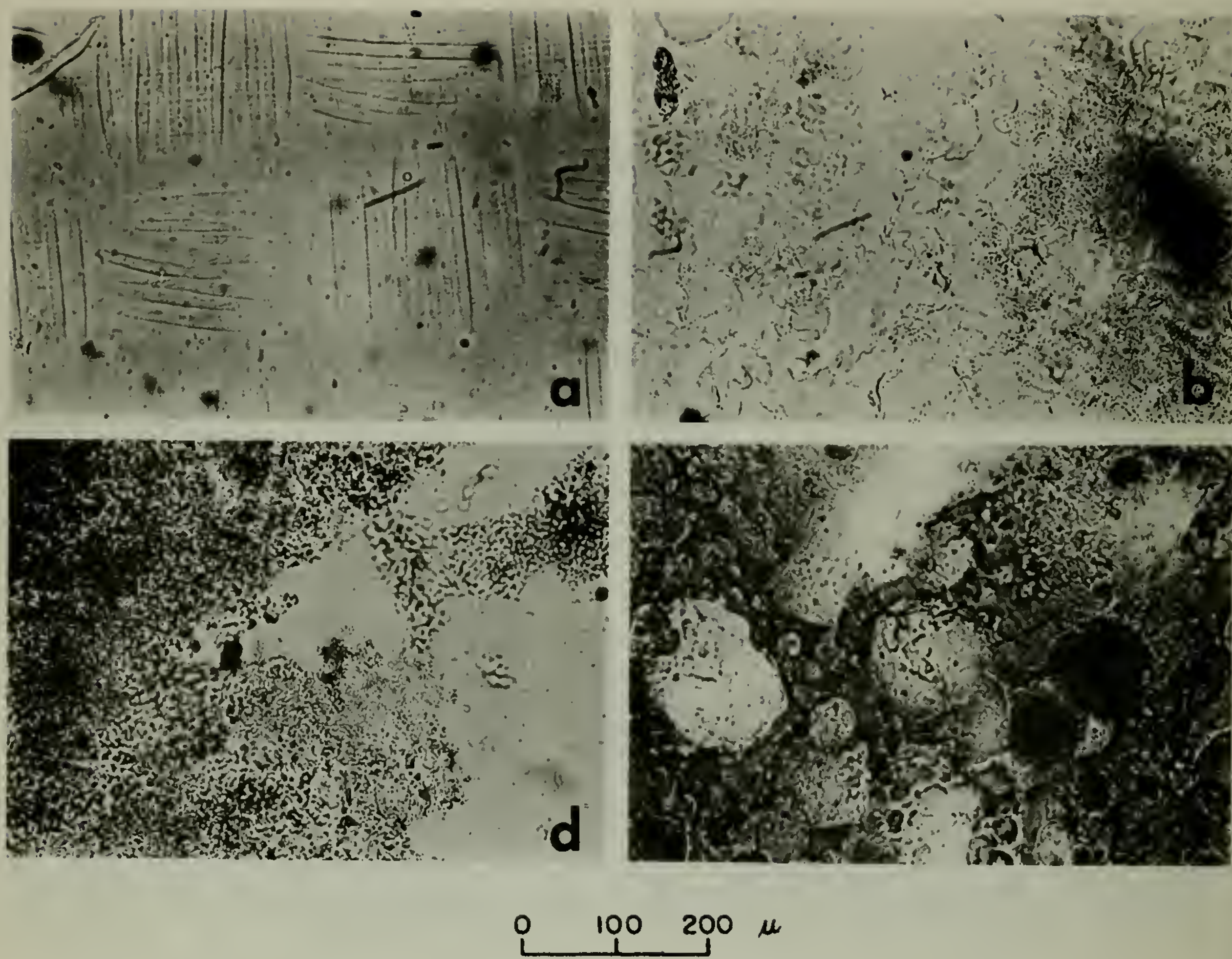


Figure 2. Four-part Sequence Illustrating Membrane Biodegradation (approximately 150X magnification). Picture a shows the surface of an unused cellulose acetate membrane removed from its backing material and metal tube. The peculiar etchings are due to compaction of the membrane against the dacron backing material. Pictures b, c and d are membranes removed from operation at Firebaugh. Picture b shows the surface of a membrane early in biodegradation (note that the grid-like etchings can still be discerned). Picture c shows a later stage in biodegradation (note the characteristic pitting and cratering and especially the darker areas in the right center of the photograph; this membrane has been stained with safranin which stains living cells a deep red). Picture d shows a membrane at the completion of biodegradation.

species of Bacillus, an actinomycete tentatively identified as belonging to the genus Streptomyces, and a fungus resembling Penicillium. Some of these microorganisms are shown in Figure 3.

A possible mechanism for biodegradation of these membranes was presented. It was proposed that a chemical modification of the cellulose acetate membrane is brought about by the metabolism by one group of microorganisms, possibly by metabolizing the acetate groups in the molecule, and that a subsequent group of bacteria, able to hydrolyze cellulose, degrades the remaining modified material. Bacteria of the genus Arthrobacter appeared to initiate the attack while bacteria belonging to the Bacillus, Streptomyces and Penicillium groups appeared to enter the degradation process only after the initial phase. Members of these latter groups could not initiate cellulose acetate membrane biodeterioration.

Cellulose acetate membrane biodegradation was observed to occur only under aerobic conditions, in the presence of nitrate-nitrogen as the sole nitrogen source for microbial growth, and at neutral pH. Methods of control for several important microorganisms in the initial group were evaluated in the laboratory. Of significance was the inability of the tested microorganisms to grow at a pH lower than 5, their inability to grow at salt concentrations greater than three percent (30,000 mg/l salt), and their sensitivity to low dosages of chlorine.

Suggestions for further study included an evaluation of pH control separated from the chlorination procedure as a means of preventing membrane degradation while not increasing slime formation problems and the removal of oxygen from the system for the same reason.

Proposals for the Current Study

The purpose of continuing this study was to further establish the microbial components involved in sliming and biodegradation of RO membranes and to relate the effects of various pretreatment and operational steps upon these microorganisms. The continuation of this study formed the basis of this paper. The study involved two objectives, as follows:

The first objective dealt with monitoring a special 12-tube RO unit, constructed at UCLA and installed at the WWTEF at Firebaugh, California, to determine the effects of various chemical feedwater pretreatments upon slime formation and biodeterioration of the RO membranes. These pretreatment procedures included: (1) continuous chlorination at 0.1-0.2 mg/l (ppm) total chlorine residual; (2) operation with feedwater pH adjusted to pH 4.0-5.0 using concentrated sulfuric acid; (3) oxygen removal from the feedwater using catalyzed sodium sulfite; and (4) no pretreatment (control). In addition, a limited test was to be conducted in the control unit to determine the effects of periodical slime removal by mechanical cleaning versus no periodical cleaning on slime formation and membrane failure.

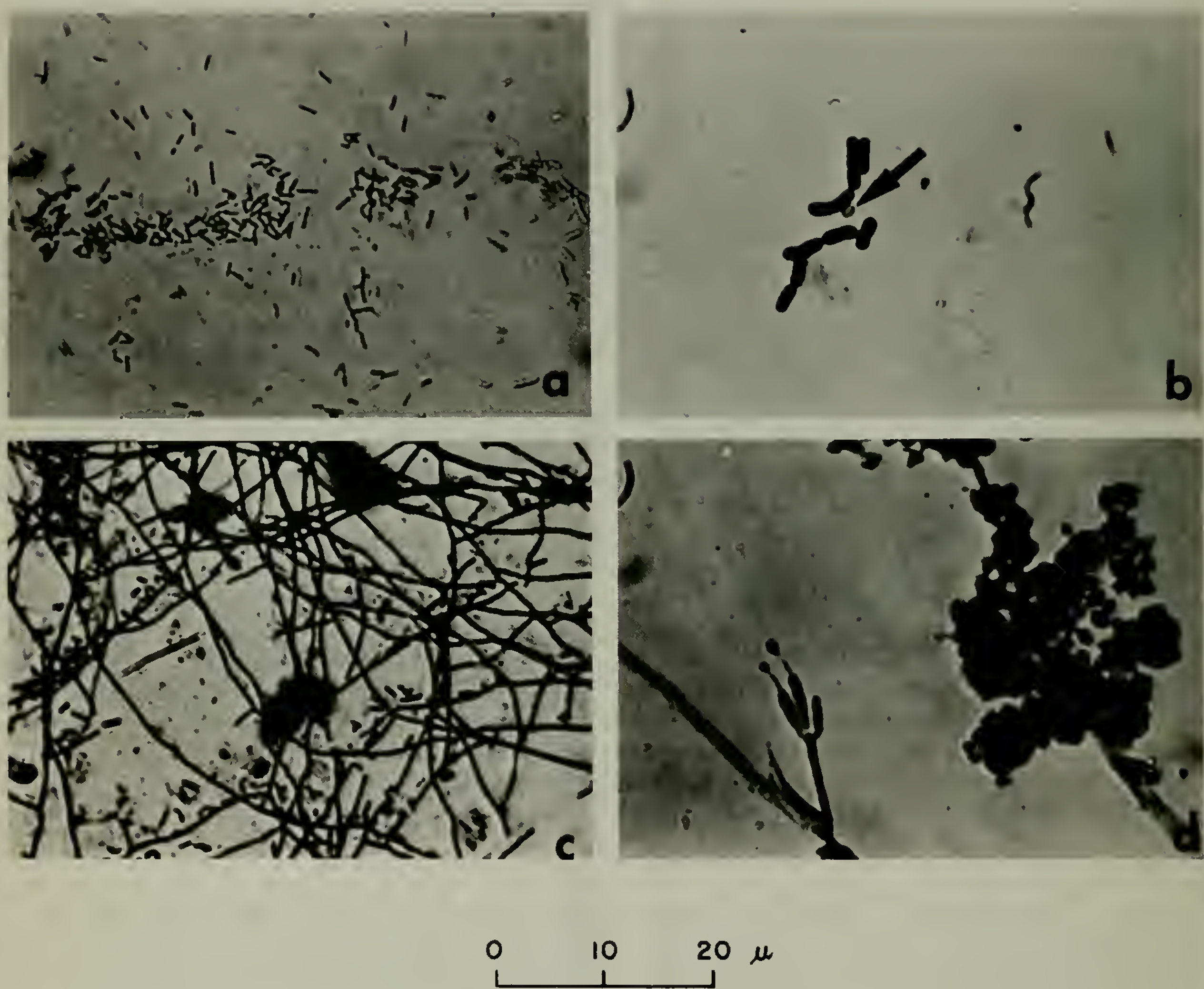


Figure 3. Four Main Morphological Types of Microorganisms Involved in Cellulose Acetate Biodegradation (approximately 1500X magnification; Gram stained). All are pure cultures. *Picture a* shows a species of *Arthrobacter*. *Picture b* shows a species of *Bacillus*. The arrow indicates a released endospore. *Picture c* shows an Actinomycete and *Picture d* shows a fungus .

The second objective dealt with continuation of the attempt to clarify the biological components in membrane operational problems. This included the determination of the effect of various compositions of cellulose acetate RO membranes upon biodegradation. Parameters of interest included the percentage acetate and the viscosity of the parent material and the temperature utilized in the annealing process for the membranes.

II. METHODS AND PROCEDURES

The Bio-Test Unit

The field studies reported herein were conducted at the Waste Water Treatment Evaluation Facility (WWTEF) located near Firebaugh, California. Descriptions of this facility and its source of irrigation return water have been presented elsewhere (1,4). A description of the tile drainage water produced in the Firebaugh area is presented in Table 1. The 12-tube bio-test unit was designed and fabricated at UCLA. This unit was installed at the WWTEF on February 7, 1974, and trial operations began on March 4. Biological studies began on June 17, 1974, and continued until December 1974. Figure 4 illustrates the schematic arrangement of the unit which consisted of a desalting component, duplex reciprocating pump, and treatment chemical supply and injection component.

The desalting component utilized 12 tubes of the standard 1-inch diameter by 10-foot tubular design cellulose acetate membranes fabricated by UCLA. The 12 tubes were arranged in four 3-tube assemblies which operated in parallel at equal pressures and flows. Each of these 3-tube assemblies will be designated as a pretreatment unit.

The first of the four assemblies acted as a control unit, desalting untreated drainage water and was designated the Raw Unit (R). The second assembly received feedwater adjusted to a pH of 4.5 using concentrated sulfuric acid (the untreated feedwater had a pH of 7.2). This unit was designated the Acid Unit (A). The third assembly received feedwater treated with 80 ppm of cobalt chloride catalyzed sodium sulfite as an oxygen scravenger and was designated the Sulfite Unit (SS). The fourth assembly received feedwater treated with chlorine, added as lithium hypochlorite solution to maintain 0.2 ppm chlorine residual in the brine flow from the unit. This was designated the Chlorine Unit (Cl). In the Acid, Sulfite and Chlorine Units, the first tube contained no membrane and functioned as a mixing tube. The second tube in these units contained a membrane of the 383-40-86 C composition (percent acetyl content, viscosity and annealing temperature). The third tube in each unit contained a membrane of the 400-25-88 C composition. The Raw Unit contained no mixing tube and the first and second tubes contained membranes as above. The third tube, designated R_3, contained a membrane of composition similar to the second tube (400-25-88 C); however, this RO tube was not periodically

TABLE 1. CHEMICAL CHARACTERISTICS OF IRRIGATION WATER AND

TILE DRAINAGE WATER IN THE FIREBAUGH AREA

Constituent	Average Concentration[1] in Irrigation Water	Range in Tile[1] Drainage Water
	Mg/1	Mg/1
TDS	300	2500 - 7600
Calcium	20	160 - 390
Magnesium	10	70 - 230
Sodium	50	620 - 2050
Potassium	3	4 - 11
Bicarbonate	90	280 - 330
Nitrate	1	20 - 80
Phosphate	0.5	0.13 - 0.33
Sulfate	65	1500 - 3900
Chloride	60	310 - 640
Iron	0	0.02
Boron	0.3	4 - 15
pH	-[2]	7 - 7.6
DO	-	7 - 9
BOD (5 day)	-	1 - 3
COD	-	10 - 20

[1]California Department of Water Resources, 1971.[1]

[2]No data available.

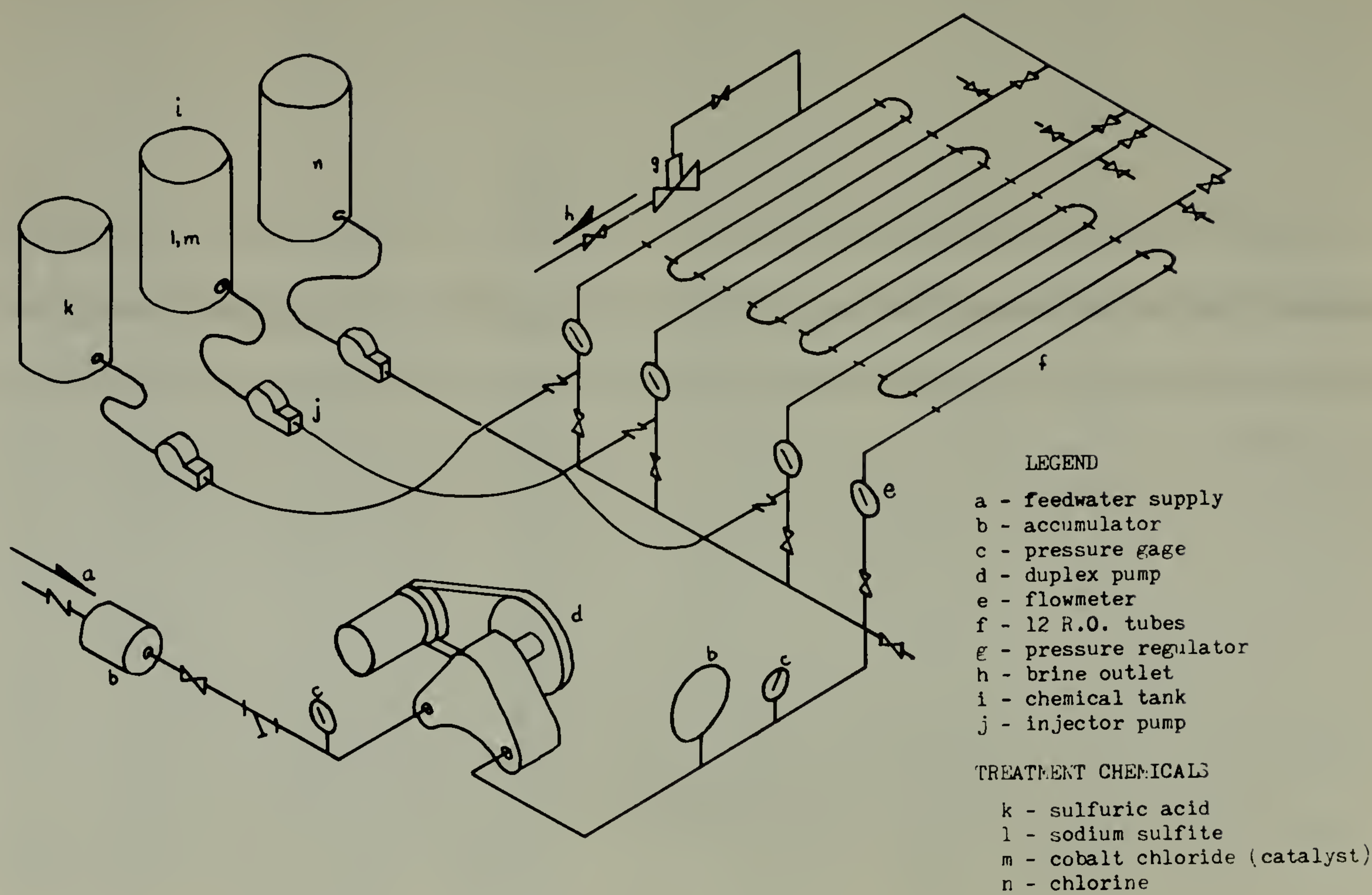


FIGURE 4. 12 TUBE BIO-TEST UNIT

cleaned (the membrane cleaning procedure will be described below).

The pumping unit was a Myers two-cylinder, reciprocating pump that supplied 4 gallons per minute (gpm) flow at 400 pounds per square inch (psi) pressure. It was driven by a 2-horsepower motor through a belt drive that permitted a flexibility in pumping rates. The combination of operating pressure and flow rate utilized in the bio-test unit resulted in approximately a five percent recovery of the feedwater as low TDS product water.

The chemical treatment equipment consisted of 55-gallon-capacity fiberglass tanks and Milton-Roy high-pressure dosing pumps. The treatment chemicals were prepared at the appropriate concentrations in the tanks using untreated drainage water as dilutent from which they were withdrawn and fed into the three-tube assemblies by the dosing pumps through 1/4-inch tubes. Adjustable pressure and injection-rate controls on the pumps provided correct chemical dosages for a wide range of operating conditions.

The membrane-containing tubes in each of the four units were mechanically cleaned at either two-week or three-week intervals. The membrane cleaning technique consisted of passing a two-inch spongeball through the one-inch diameter tubes under applied pressure. The spongeball and the dislodged slime were ejected at the end of the tubular unit. The spongeball cleaning technique has been shown to remove most of the material that accumulates along the RO tube walls during operation (1).

Tube R_3 was used during the first half of this investigation as a test to determine the effect that mechanical removal of accumulated slimes has upon membrane failure and slime formation.

<u>Sampling of the Unit</u>

The 12-tube bio-test unit was operated from March 4, 1974 to January 31, 1975 during which time eleven samples were taken by personnel from our laboratory. From 6/17 through 8/27 samples were taken every two weeks while from 9/17 until 12/17 this period was lengthened to three week intervals. The sampling dates were (1) 6/17, (2) 7/2), (3) 7/16, (4) 7/30, (5) 8/13, (6) 8/27, (7) 9/17, (8) 10/8, (9) 11/7, (10) 12/13 and (11) 12/17.

Sampling consisted of collection of untreated feedwater, composite samples of product water from each unit (a mixture from both RO tubes in each section) and composite samples of slimes ejected during spongeball cleaning. The contents of the RO tubes were replaced with untreated feedwater prior to spongeball cleaning by removing enough water to ensure complete replacement of the partially desalted contents with untreated water. This was done to equalize the feedwater carrier (defined above) in the slime samples so that any increase observed in the weight of the residue removed from the unit could be attributed to increased slime formation and not due to different efficiencies of desalination in the various RO tubes.

Membrane failure was detected by an increase in product water TDS content and flow rate. Upon detection of failure the membrane was removed at the next regular visit by personnel from our laboratory (UCB) and replaced with a new membrane of analogous composition. The failed membranes were taken to UCB for further analysis.

Unit performance was monitored by personnel from the DWR. Daily sampling of RO flow quantities and product water TDS content were performed. In addition, daily measurements were taken of the dissolved oxygen (DO) in the Sulfite unit brine flow, the pH of the Acid unit brine flow, and the residual chlorine concentration in the Chlorine unit brine flow. Daily measurements of the pH, TDS and DO were also performed on the untreated feedwater.

Collected samples were contained in tightly capped bottles and stored upon ice for transportation from Firebaugh to UCB. On arrival the samples were plated in duplicate on plate count agar according to Standard Methods (10), with the sampling-to-plating interval being four to six hours. These plates were incubated at room temperature (20-26 C) for 96 hours.

Two media were chosen for use in plate counting. These included specifically prepared artificial Firebaugh buffer, containing appropriate ion concentrations similar to raw drainage water, plus 0.05% dextrose and 0.05% peptone, and one similar to the above but without the addition of peptone (containing only nitrate-nitrogen as a nitrogen source for microbial growth). These two media were designed to be minimal media with inorganic constituents similar to raw drainage water with high nitrate-nitrogen levels and buffered to pH 7.4. These media have been shown to be quite suitable for the isolation of bacteria from Firebaugh agricultural drainage water. The complete formulation is presented elsewhere (5).

Microorganism isolation and characterization was performed as previously described (5). Essentially, colonies were randomly picked from appropriate agar plates used in routine plate counting and these isolates were Gram stained and described morphologically. All isolates were grouped into one of ten isolate groups on the basis of cellular morphology (to be described later).

Analyses were performed on the collected slimes and raw feedwater for total residue and total volatile solids. These tests were performed by gravimetric analysis according to Standard Methods (10) and Water Chemistry Laboratory Manual (11). Separation of residue into components was necessary in the slime samples as these samples contained the mechanically removed slime accumulations (spongeball removed) resuspended in the feedwater used to push the spongeball through the unit. This volume of feedwater ranged from 3300 to 7600 ml. As care was exercised to replace the contents of the RO tubes with untreated feedwater prior to spongeball cleaning, the feedwater addition of residue to the total residue in the slime-feedwater mix could be determined and subtracted from each slime sample. Thus the residue reported for the slime samples removed from the RO tubes represents the total residue of the slime plus the feedwater carrier minus the equivalent weight of residue for the same volume of untreated feedwater.

Laboratory Studies

Laboratory work was performed essentially as reported previously (5) and will be only briefly mentioned here.

Membranes that failed during operation of the bio-test unit were carefully removed from their holding tube and transported to UCB. These membranes were "dissected" apart and carefully examined to determine the cause of membrane failure. Sections of these membranes were stained and mounted for future reference.

Sections of these membranes were also placed in appropriate cultures containing artificial Firebaugh buffer and sections of new cellulose acetate RO membranes as the sole carbon and energy source for microbial growth. When bioactivity was apparent this process was repeated using the previous culture as an innoculum. In this manner a culture of microorganisms extremely active upon cellulose acetate membrane material was obtained.

In addition, the ability of this laboratory adapted culture to degrade RO membranes of various cellulose acetate compositions was investigated. The test membranes were prepared from cellulose acetate that varied in the percent acetyl substitution and parent material viscosity and in the temperature used to anneal (cure) the membranes prior to use. The membranes were supplied by UCLA. Equal size sections of these membranes were added to separate sterile 250-ml erlenmeyer flasks containing artificial Firebaugh buffer plus 0.1 ml of the cellulose acetate-adapted innoculum and incubated aerobically at 30 C. These tests were performed in triplicate and included appropriate controls. The flasks were allowed to incubate for 60 days and observed daily. Membrane failure was considered positive when membrane deterioration was visually evident.

III. RESULTS AND DISCUSSION

Membrane Failure in the Bio-Test Unit

During the operation of the bio-test unit, three types of membrane failure were observed. These included (1) mechanical failure which resulted from a hole being formed in the membrane due to cleaning (abrasive) operations which may have been potentiated by the chemical pretreatment of the feedwater; (2) extensive biodeterioration in which the membrane was partially dissolved away in an irregular fashion and appeared pitted and covered with a gelatinous light-brown or yellow material; and (3) premature failure due to biological attack along a crease or structural defect in the membrane.

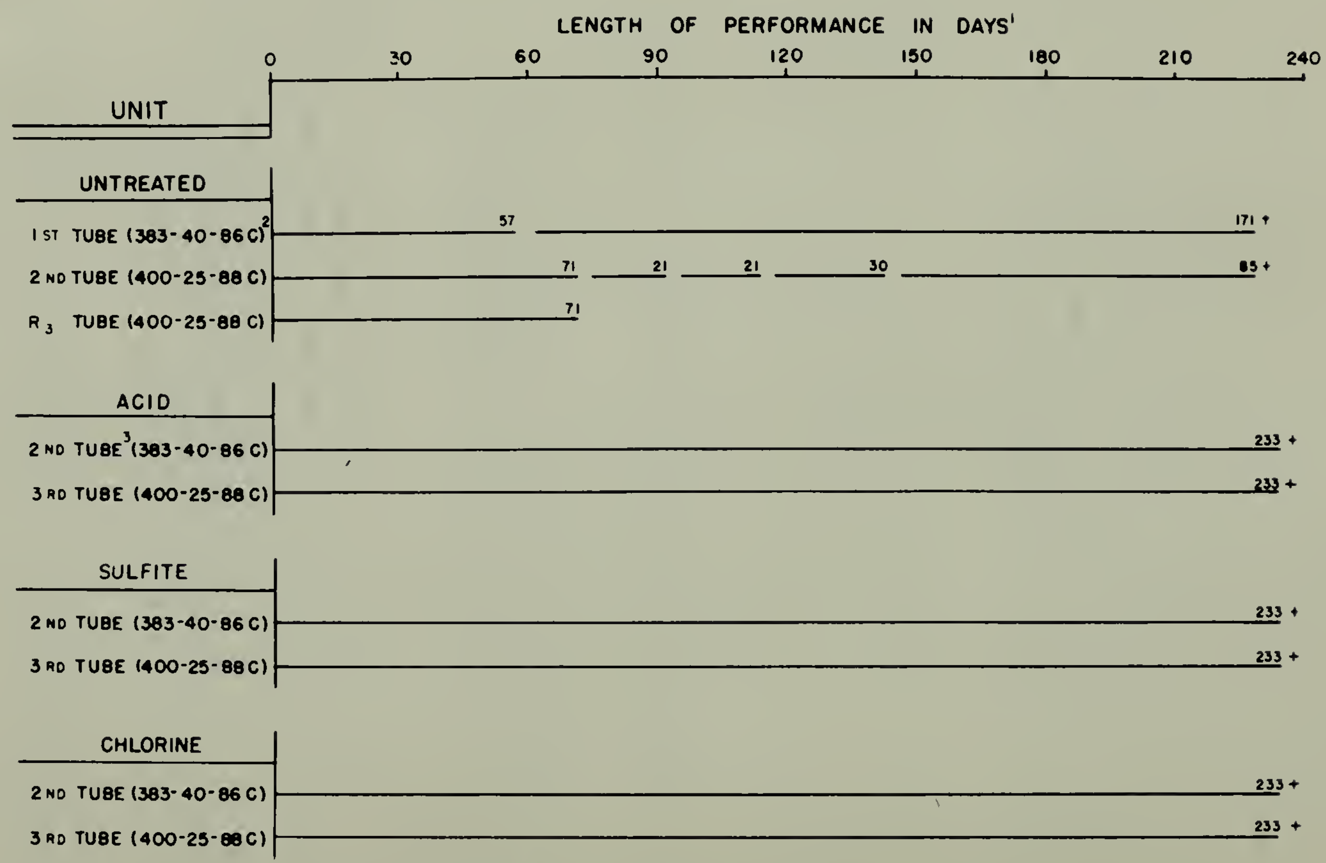
During the eight months of operation of the bio-test unit ten membrane failures were observed. These included six membrane failures in the Raw unit (no pretreatment) attributed to biodeterioration of the membranes and four membrane failures total in the Acid, Sulfite and Chlorine units attributed to membrane-mechanical failure. No biodeterioration was observed in the acid, sulfite or chlorine pretreated units during the study.

Membrane degradation in the untreated unit was dependent upon the cellulose acetate membrane composition utilized. The first tube, of composition 383-40-86C, failed once after 57 days of operation. The second tube, of composition 400-25-88C, failed four times during the same time period after 71, 21, 21 and 30 days of operation. The membrane composition clearly appeared to affect the membrane degradation process in this study. The effect of membrane composition on the biodegradability of the RO membranes was investigated in the laboratory and will be presented later.

The R_3 tube in the Raw unit contained a membrane of composition identical to the second tube in this unit but was not spongeball cleaned. The second tube was cleaned every two weeks. Both these membranes failed after 71 days of operation due to extensive biodeterioration of the membranes. It appears that spongeball cleaning, which is effective in removing slime accumulations from the RO units, does not appreciably delay or affect the biodegradation rate of the RO membranes in operation. The loss of membranes to biodeterioration is illustrated in Figure 5.

Mechanical failure of RO membranes in the bio-test unit occurred four times during the study. One occurred in the Acid unit, while three occurred in the Chlorine unit. The acid treated membrane was in operation for 57 days prior to membrane failure. The chlorine treated membranes were in operation for 57, 71 and 157 days prior to membrane failure. Chlorine has been shown to adversely affect cellulose acetate RO membranes by causing hydrolysis and brittleness in the membranes (1). The acid

FIGURE 5. BIODEGRADATION OF MEMBRANES IN THE BIO-TEST UNIT



[1] INTERUPTION IN LINE INDICATES MEMBRANE BIOFAILURE
[2] MEMBRANE COMPOSITION
[3] IN THE ACID, SULFITE AND CHLORINE UNITS THE FIRST TUBE CONTAINED NO MEMBRANE
"+" INDICATES STILL IN OPERATION AT COMPLETION OF EXPERIMENT

pretreatment resulted in considerable corrosion in the RO system as evidenced by the accumulation of metal corrosion products in the slimes removed from the acid pretreated unit. The adjustment of feedwater pH to values around pH 4-5 has been shown to increase the life of cellulose acetate RO membranes (1, 13). However, occasional pH values of 3-4 were observed in the Acid unit brine samples, and the effect of this lowered pH on the membranes is not known. It may have been that the acid and chlorine solutions in contact with the cellulose acetate RO membranes may have potentiated membrane failure during cleaning operations.

Membrane failure resulted in an increase in the product water flow rate and TDS concentration. The TDS measurement appeared to be the more sensitive indication of membrane deterioration. Membrane failure due to biodeterioration appeared to occur progressively over a period of 7-10 days. Membrane mechanical failure, as opposed to biological failure, manifested itself by a sudden increase in the product water flow rate and TDS content. This observation could be used to diagnose the cause of membrane losses.

Bacteriological Parmeters

The number of microorganisms isolated from the slime samples and product water samples from the four separate pretreatment units was determined at intervals. For the product water samples the data was recorded as the number of bacteria per ml of product water. For the slime samples the total number of bacteria removed from the RO tubes (minus the feedwater contribution to this total) was divided by the surface area of membrane involved so as to arrive at a value independent of the number of RO tubes involved (one RO membrane of the standard one-inch diameter by 10-foot length contains 243,219 square millimeters of membrane surface area exposed to slime). The accumulation of slime and bacteria along the RO tube wall may occur somewhat irregularly, with slime formation and bacterial colonization occurring to a greater extent at one end of the RO tube than the other. However, for these purposes the total number of bacteria isolated from the unit was averaged over the entire length of the RO tube (5). The slime data for the bio-test unit are shown in Figure 6 and the product water counts are shown in Figure 7.

Referring to Figure 6, it can be seen that the number of bacteria capable of colonizing the membrane surfaces varied somewhat within each unit over time. This is understandable as the feedwater characteristics and pretreatment chemical dosages changed considerably during the study, and the membranes themselves aged and may have presented varying surfaces to the colonizing bacteria. Examination of this figure clearly demonstrates the effects of the various pretreatment chemicals upon bacterial colonization. The average value for the number of bacteria per square millimeter of surface for the Raw unit, Acid unit, Sulfite unit, and Chlorine unit was 2200, 259,

FIGURE 6. REDUCTION OF BACTERIA BY THE PRETREATMENTS

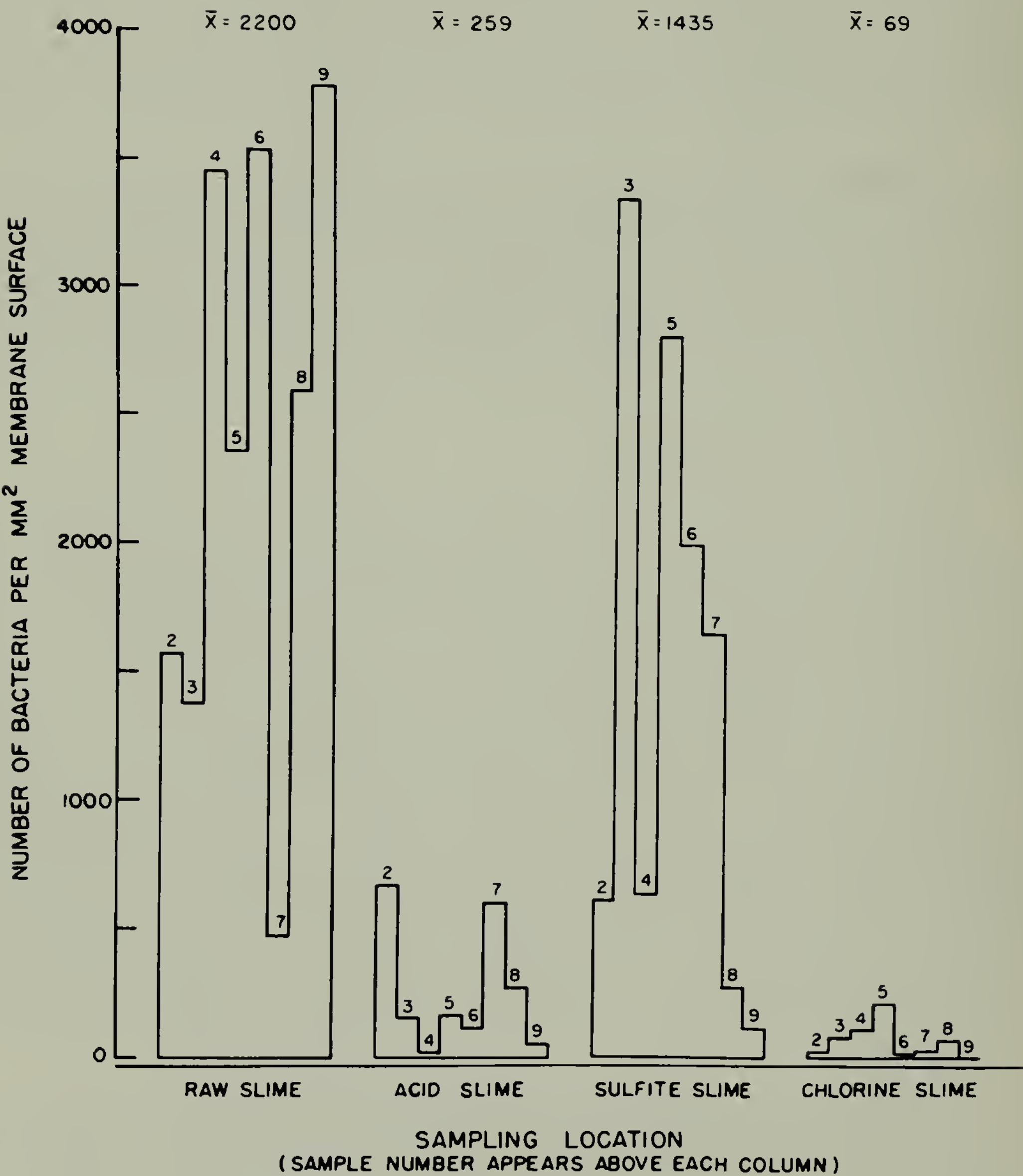
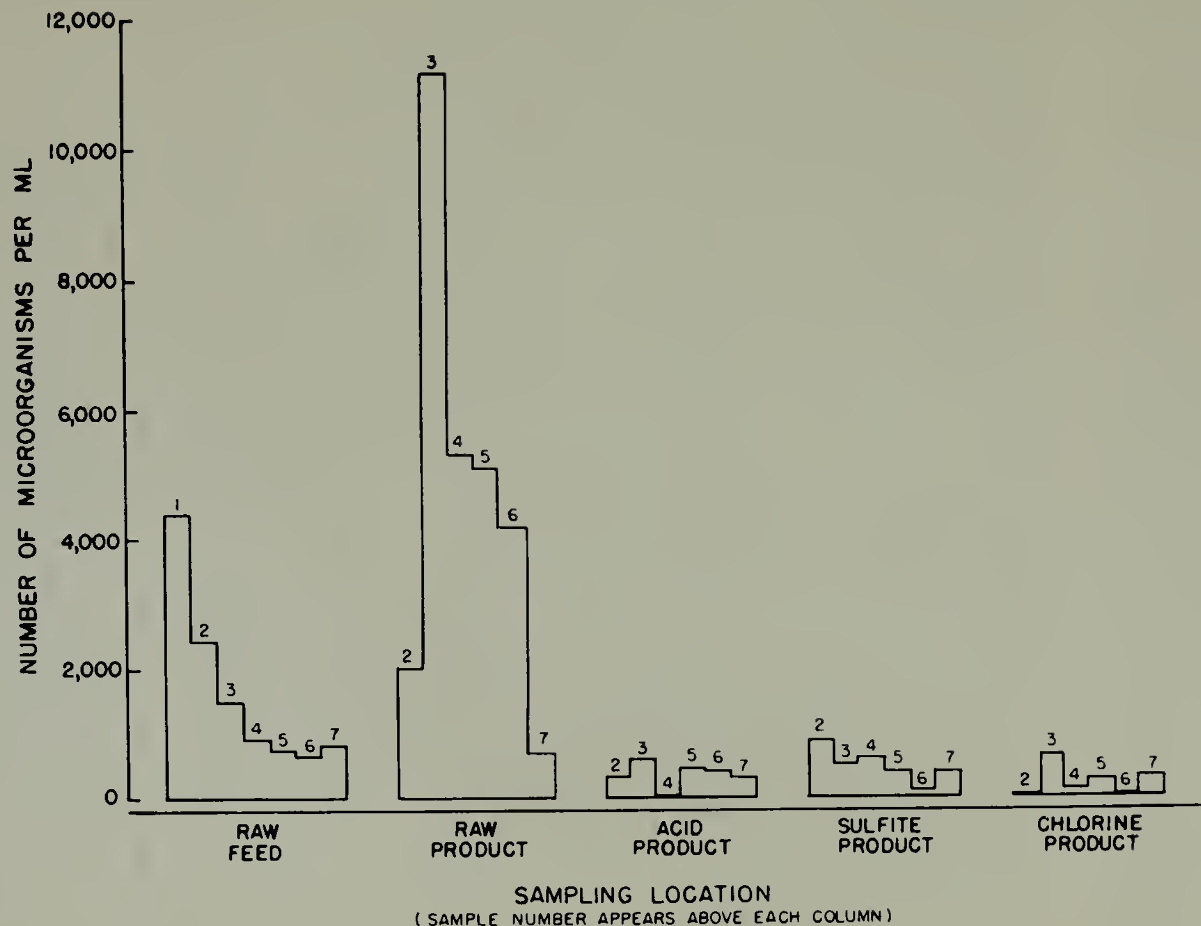


FIGURE 7. PRODUCT WATER PLATE COUNTS



1435 and 69, respectively. These values were expressed as a percentage of the bacteria per area value obtained in the Raw unit in order to determine the overall anti-bacterial effectiveness of the pretreatment chemical. Sulfite treatment reduced the number of bacteria in the slime layer to 65 percent of that observed in the untreated unit. Acid treatment reduced this number to 12 percent of that observed in the untreated unit while treatment with chlorine reduced this number to three percent.

The results obtained for the R_3 tube in the Raw unit are particularly interesting. This tube was similar to the second tube in the Raw unit except that the R_3 tube was not periodically spongeball cleaned. After 71 days of operation, both the second tube and the R_3 tubes failed due to extensive biodeterioration. Examination at that time revealed 3544 bacteria per mm^2 of membrane surface in the second tube (periodically cleaned) and 3330 in the R_3 tube (not cleaned). As already mentioned, periodical cleaning of the RO membranes by the spongeball technique does not appreciably affect the biodeterioration rate of the RO membranes. However, spongeball cleaning does remove a large number of the bacteria from the membrane surface. Microscopic examination of membranes removed from the RO unit immediately after spongeball cleaning revealed very little material and few bacteria remaining on the surface of the membrane. It appears that bacteria on the surface of the RO membranes are able to "regrow", after spongeball cleaning, sufficiently fast to attain a relatively constant number in the slime. This maximum density is in part determined by the pretreatment techniques utilized for the feedwater and, in part, by the shear forces set up inside the RO tubes by the flow of feedwater through the tube. The density of microorganisms within this slime layer is most probably dependent on the type of bacteria present and the activities of these bacteria, whether it be growth and reproduction of other bacteria or the biosynthesis of copious amounts of extracellular slime, either as a cellular reserve material or as a protective coating for the bacteria during times of physiological stress.

The reductions in the bacterial density on the RO membrane surfaces are quite important as the ability of the microorganisms originating in the untreated feedwater to colonize the RO membrane surface at least in part determines whether biodeterioration or membrane fouling will occur. Oxygen removal by the use of catalyzed sodium sulfite appears to reduce the colonization of the membrane surface somewhat whereas acidification or chlorination appear to significantly reduce the occurrence of bacteria on the membrane surfaces. Since membrane biodeterioration occurred only in the Raw unit, each of the pretreatment chemicals must have prevented microbial attack of the membranes. In acid and chlorine pretreatments, this protection may have resulted from the inability of microorganisms to colonize the membrane surface. For the sulfite pretreatment, this protection from bioattack probably was not associated with the overall reduction of the number of microorganisms on the membrane surface but rather on some other factors.

The bacterial counts for the product water samples from the various pretreatment units are graphically illustrated in Figure 7. The untreated feedwater counts are included in this figure for comparison with the RO process product water. Several important points are apparent. Each of the pretreatment units yielded product water of quite low bacterial count in comparison with the input feedwater. However, the untreated unit produced product water of a higher bacterial count than the input feedwater.

Slime Formation

The results of the residue analyses and the volatile solids determinations are presented in Table 2. Here, the dry weight of the residue formed in each pretreatment unit is expressed in grams of residue per one RO tube. The values for slime production ranged from 0.278 to 2.400 grams in the Raw unit, 0.011 to 2.050 grams in the Acid unit, 0 to 2.125 grams in the Sulfite unit, and 0.019 to 0.635 grams in the Chlorine unit (dry weight).

In general, slimes are highly hydrated and normally consist of from 90 to 99 percent water (14,15,16). Separation of the slime material from the feedwater by filtration could not be accomplished so that the exact degree of hydration of the slimes formed in the pretreatment units could not be ascertained. However, if the above values for the percentage of water in slime material is used, then the wet weight of residue due to slime formation in the Bio-test unit would be from 10 to 100 times that reported. For the Raw unit this would be a maximum of from 24 to 240 grams of slime material per one RO tube for each two weeks of operation. The production of fouling material which must be removed from the RO system and disposed of, particularly in a large unit, could become a significant problem.

The amount of slime formed in each pretreatment section varied considerably over time. However, if the values obtained for the residue from each pretreatment unit are normalized to the untreated unit, much of this variation is reduced. These normalized values are presented in Figure 8. Here, the weight of residue formed in each unit is expressed as a percentage of the residue which formed in the Raw (untreated) unit during the same time period.

The average residue formation compared to the Raw unit for the Acid, Sulfite and Chlorine pretreated units was 158.2%, 67.1% and 26.5% respectively. These values were subject to considerably variation on a sample by sample basis and cannot be stated with statistical confidence; however, the trends in slime formation in each of the units due to the pretreatment chemical are important.

In general, the adjustment of the feedwater pH to between 4 and 5 resulted in increased slime formation along the RO tube walls. The addition

TABLE 2. TOTAL RESIDUE AND VOLATILE MATERIAL IN THE SLIMES WHICH DEVELOPED DURING OPERATION OF THE BIO-TEST UNIT

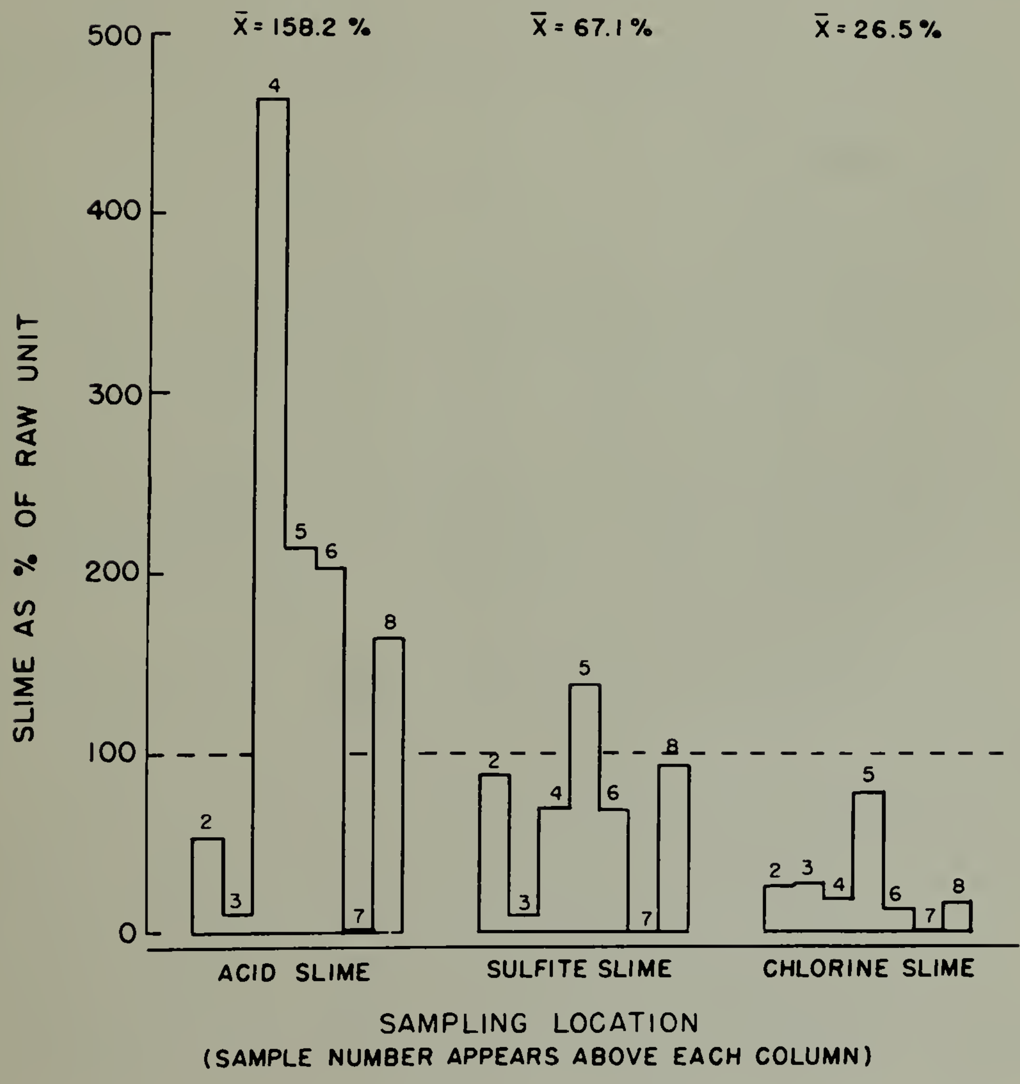
Unit	Type of Residue	Sample 2	3	4	5	6	7	8	9
Raw Feed	Total Residue[1]	5.267	5.497	5.220	4.994	4.336	3.359	3.952	5.694
	% Volatile	8.27	10.11	6.19	6.99	7.00	9.14	8.63	6.77
Raw Slime	Total Residue[2]	2.400	1.500	0.447	0.707	0.775	0.986	0.278	0.475
	% Volatile	7.22	10.13	8.14	7.90	7.90	8.16	10.20	9.29
R_3 Slime	Total Residue	-[3]	-	-	-	0.616	0.404	0.265	1.190
	% Volatile	-	-	-	-	9.45	9.55	10.04	6.53
Acid Slime	Total Residue	1.250	0.151	2.050	1.521	1.524	0.011	0.454	1.326
	% Volatile	6.82	9.94	6.34	8.48	6.47	7.83	7.78	8.04
Sulfite Slime	Total Residue	2.125	0.151	0.316	0.992	0.509	0	0.262	1.704
	% Volatile	6.52	9.96	4.49	8.37	10.05	5.38	9.44	7.07
Chlorine Slime	Total Residue	0.635	0.427	0.081	0.560	0.113	0.019	0.049	0.259
	% Volatile	7.25	9.54	6.18	7.58	8.38	8.02	8.44	8.10

[1]Total residue in untreated feed water in gm/l.

[2]Total residue in slimes which developed during operation (see text) in gm per one RO tube.

[3]This RO tube was not cleaned until sample 6.

FIGURE 8. SLIME FORMATION NORMALIZED TO THE RAW (UNTREATED) UNIT



of sodium sulfite as an oxygen scavenger to the RO feedwater resulted in only a small reduction in slime formation. The use of an 0.1 to 0.2 mg/l total residual chlorine solution in contact with the RO membranes resulted in a marked decrease in slime formation.

The R_3 tube, not periodically spongeball cleaned, contained approximately the same amount of fouling material at the end of the 12 weeks of operation as was formed every two weeks in the first and second tubes in the Raw unit. This again indicates that there is a maximum thickness or density of fouling material which can build-up along an RO tube wall during operation. This amount of material is probably determined by shear forces of the fluid movement within the RO tube and the adhesive nature of the fouling material itself.

Specific Bacteria Involved

One important point discovered in our previous work with slime formation and membrane biofailure (5) was that the microorganisms involved in membrane failure were capable of utilizing nitrate-nitrogen as a sole source of nitrogen for growth while the microorganisms involved in slime formation were less able to use nitrate. The microorganisms in the slime layer were somewhat dependent on the accumulation of organic debris on the RO membrane surface for growth. Microorganisms must be provided with the necessary precursor materials for growth, and any biological complications arising in the RO process will be dependent on the availability of these precursor materials. These microbial nutrients include carbon, nitrogen, phosphorus, hydrogen, oxygen and potassium as major components, comprising 95 percent of the dry weight of the cell, while many others are required in lesser amounts. These include sodium, calcium, chlorine, iron, manganese and several other trace substances (17).

The above discussion is important in terms of the biological problems that have been observed in the desalination operations at Firebaugh, California. Chemical constituents of the drainage water available in the Firebaugh area have been shown to provide a suitable microbiological medium for growth (5). The feedwater contains soluble phosphorus and both forms of nitrogen, organic and inorganic. The membrane material itself may be utilized as a source of carbon and energy by the biodegrading bacteria whereas concentrated organic debris, both soluble and particulate, appears to serve as the carbon and energy source for slime formation and subsequent biofouling. Membrane biofailure may occur in RO systems where the feedwater contains suitable chemical constituents for bacterial growth, such as nitrate-nitrogen, and the appropriate environment, such as the presence of oxygen and the proper pH.

A determination of the types of microorganisms that predominated in each of the pretreatment units was performed midway through the study at a time when membrane biofailure was evident. The isolated microorganisms were classed into one of ten isolate groups previously shown to be important in the RO process (5). Briefly, these groups were (1) small gram negative rods or cocci, (2) long, slender gram negative rods, (3) large, pleomorphic gram negative rods, (4) gram negative "vibrio" type rods, (5) gram positive non-sporing rods, (6) gram positive endospore forming rods,(Bacillus), (7) gram variable pleomorphic rods displaying a typical life cycle of the genus Arthrobacter, (8) most fungi, (9) those fungi similar to Penicillium, and (10) all actinomycetes. Sketches of these isolate groups are presented in Figure 9.

The incidence of the various isolate groups in the pretreatment units is indicated in Figure 10. Isolate diversity histograms show the relative proportions of each of the ten main groups of microorganisms evaluated in our initial study (5) that occurred in the samples. It must be remembered when viewing the isolate diversity histograms that they indicate nothing about the number of microorganisms involved, but only the relative distribution of the types present.

As indicated in Figure 10, the untreated agricultural drainage water contained a diversity of types of microorganisms. Gram positive rods (Group 5) and actinomycetes (Group 10) were present while the arthrobacters (Group 7) and Gram negative rods (Group 1) were predominant.

The microorganisms isolated from the Raw unit slime sample were predominantly of the arthrobacter group. Gram negative rods were also prevalent in this sample. The Raw unit product water sample contained both the arthrobacter group and Gram negative rods in the same proportions. The R_3 slime sample contained a predominance of the arthrobacter group.

The high incidence of the arthrobacter group in the Raw unit, at a time when membranes failed due to biological attack, again demonstrated the possible role that these microorganisms play in the biodeterioration process.

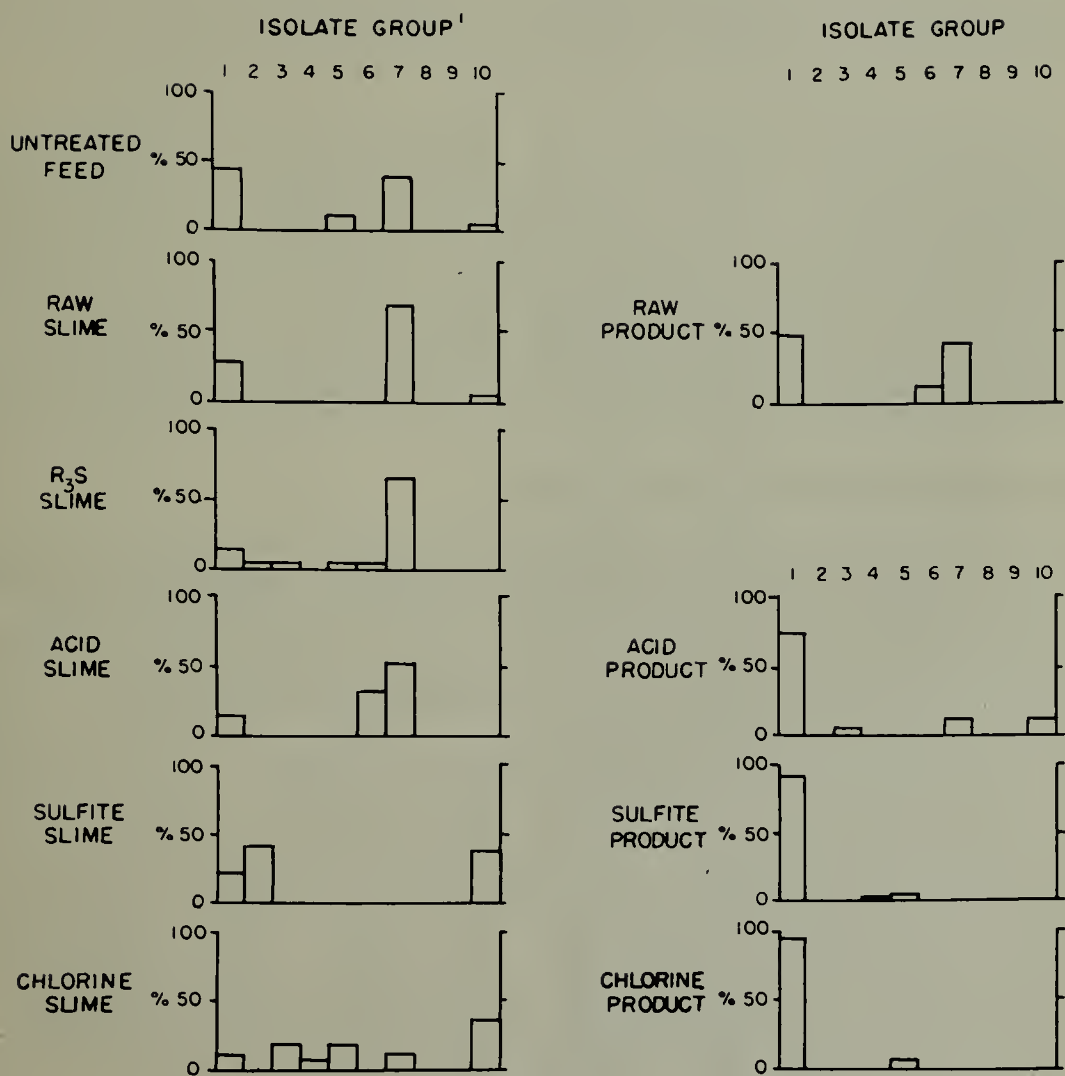
The microorganisms isolated from the Acid unit slime sample were somewhat similar to the Raw unit except that the bacillus group increased considerably. This is important as this bacterial group has been identified as being involved in the membrane fouling process (5). The Acid unit product water, on the other hand, shows a shift of microbial groups from the arthrobacter and bacillus groups to Gram negative rods. Acid pretreatment of the RO unit appears to reduce the colonization of the product water side of the membrane by the arthrobacter group. Several species of Arthrobacter, involved in the initiation of membrane biofailure, have been shown to not grow well below a pH of about 5. This is probably the reason for the shift away from the arthrobacter group in the microorganisms isolated from the product water of the Acid unit.

The Sulfite unit is quite interesting in that members of the

FIGURE 9.

SKETCHES OF ISOLATE GROUPS FROM FIREBAUGH AGRICULTURAL DRAINAGE WATER

FIGURE 10. ISOLATE DIVERSITY HISTOGRAMS



[1] SEE FIGURE 9 FOR SKETCHES OF THE ISOLATE GROUPS

arthrobacter group were not isolated from this unit. The microorganisms isolated were mainly Gram negative rods and actinomycetes. This is important as both the growth of the arthrobacter group and the membrane biodeterioration process have been shown to occur only under aerobic conditions. Removal of the dissolved oxygen from the RO unit resulted in the elimination of the biofailure-initiating population of microorganisms.

The Chlorine unit slime sample isolates varied, with no one group predominating. Gram negative rods were observed to predominate in the Chlorine unit product water. Apparently, there is some selection for this microbial group on the product water side of the membrane.

The results of this analysis for the predominant microbial groups in the pretreatment units were essentially the same as observed in our previous study (5). Bacteria of the arthrobacter group were observed to predominate in both the slime and product water samples from units undergoing biofailure. Acid treatment reduced the occurrence of the arthrobacter group and increased the occurrence of other groups, notably the bacillus group known to be involved in slime formation in the RO process. The use of sulfite as an oxygen scavenger resulted in the complete removal of the arthrobacter group from the RO unit. Chlorine treatment appeared to reduce most microbial groups.

Operational Parameters and Biofailure

The effects of operating pressure and product recovery rates have not been investigated in these studies. However, a summary of membrane biofailure which has been observed in the RO process at Firebaugh, presented in Table 3, sheds some light on this area. Membrane biodeterioration has been observed at operating pressures of 200, 400 and 600 psi. The time necessary for biological attack of the RO membranes is comparable at each of these pressures. The effects of the operating pressure on the physiological activities of the responsible bacteria, however, still remain unknown. The effects of various product water recovery rates on biological problems have not been examined. It might be expected, though, that increased product water recovery, perhaps at the 90 percent or greater figure, might reduce biological problems. This would be due to increased salinity within the RO tubes which would effectively inhibit many of the bacteria shown to be involved in biofailure of the membranes. The sensitivity of membrane-deteriorating bacteria to increasing salt concentrations was previously shown to occur at approximately two-to-three percent salt concentration (5) and may account for the absence of these bacteria from seawater and brackish water desalination operations.

Laboratory Studies

Sections of cellulose acetate membranes provided by UCLA were

TABLE 3. BIODEGRADATION OF RO MEMBRANES AT FIREBAUGH

Unit	Period of Operation	Pretreatment	Operating Pressure psi	Average % Recovery of Feed Water	Days to Biological Failure	Notes
24- tube unit[1]	July through August, 1971	Spun cotton Prefilter	600	16	25 - 98	range for various membranes in unit
1 tube-test unit[2]	March through October, 1973	none	200	5	79, 137	two membranes
Bio-test unit[3]	June through October, 1974	none	400	5	21 - 71	range for various membranes

[1]Information from State of California Department of Water Resources Desalination Reports, 1971 - 1974.

[2]Biodeterioration and Slime Formation in Reverse Osmosis Systems, a study performed for the Department of Water Resources by the University of California, Berkeley, California.

[3]Current report.

innoculated with material from a laboratory enrichment culture that had the ability to degrade cellulose acetate rapidly. The compositions of membranes tested are listed in Table 4. The innoculated membrane sections were allowed to incubate at 30 C until biodeterioration of the membranes could be determined by visual examination. The number of days that the membrane sections resisted biodeterioration in the test system are also listed in Table 4.

The results of this experiment indicate that the acetyl percentage in the cellulose acetate, within the range 39.4 to 40.0 percent acetyl content, does not appreciably affect the biodeterioration rate. However, increasing viscosity of the parent material appears to confer increased resistance to microbial attack. Apparently the most critical parameter of the cellulose acetate material with respect to biodeterioration is the temperature at which the cast RO membrane is annealed. Unannealed membranes, regardless of the percent acetyl content or viscosity, within the range tested, had the longest life in the laboratory tests. The 84 C-cured membranes were degraded faster than the uncured membranes and the 94 C-cured membranes failed the fastest. The effect of increased viscosity of the parent material was significant in the 84 C- and 94 C-cured membranes. These results are shown in Figure 11.

A possible mechanism for the bacterial degradation of cellulose acetate has already been provided. This hypothesis is that an initial group of bacteria modify the membrane, possibly through deacetylation of the membrane, and make it possible for heretofore inhibited cellulytic microorganisms to hydrolyse the cellulose portion of the membrane. Fully acetylated cellulose, the triacetate, has been shown to be resistant to biological attack (7, 8). This presumably is due to the inability of the degradation-initiating enzymes, secreted by the responsible bacteria, to act upon the triacetate, probably due to steric hindrance of the enzyme(s). Cellulose acetate containing less than three acetyl groups per cellulose molecule is attacked by bacteria. If the initial step in degradation is deacetylation, then the amount of available acetate, as the limiting substrate, should decide the deterioration rate, howeever, over the range of acetyl content used in these tests, 39.4 to 40.0 percent, no apparent difference in the deterioration rate was observed. Much larger differences in acetyl content probably need to be used to see a change in the rate of attack due to this parameter.

The viscosity of the parent material presumably applies to the molecular arrangement of acetate-substituted cellulose-to-cellulose bonding. More bonding would produce a membrane that was more viscous and thus would have a tighter molecular arrangement. As the membrane molecular structure becomes denser, bacterial attack slows down. This is probably due to less of the substituted acetyl groups being exposed to the action of the bacteria.

TABLE 4. MEMBRANE COMPOSITION AND RESISTANCE TO BIODETERIORATION

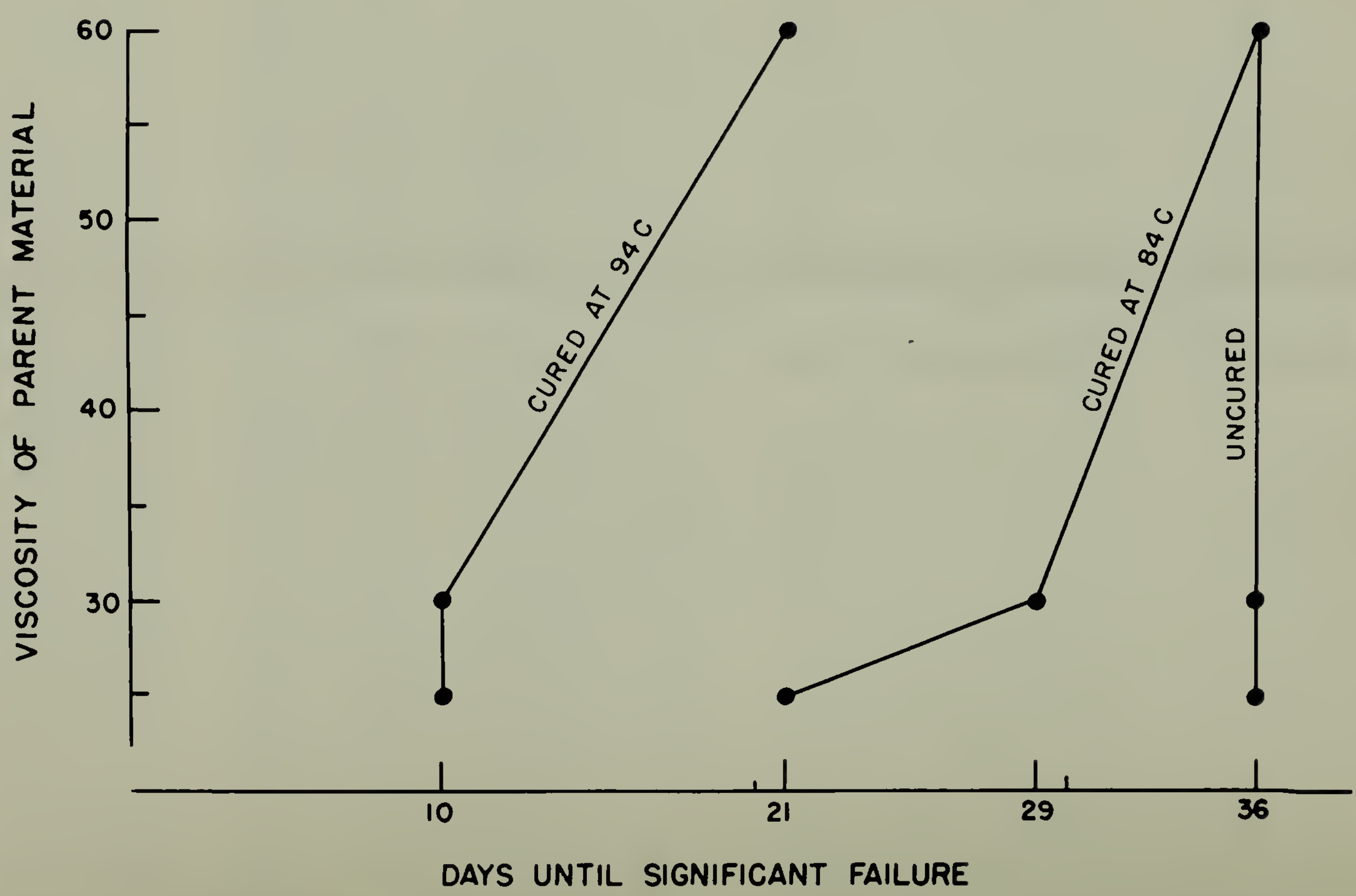
Membrane Composition[1]	Days till Failure[2]	% Increase in Life[3]
400 - 25 - 94 C	10	-
394 - 30 - 94 C	10	0
394 - 60 - 94 C	21	110
400 - 25 - 84 C	21	110
394 - 30 - 84 C	29	190
394 - 60 - 84 C	36	260
400 - 25 - uncured	36	260
394 - 30 - uncured	36	260
394 - 60 - uncured	36	260

[1]Membranes supplied by UCLA. The first digit is the % acetate in the cellulose acetate (decimal point omitted after the first two digits), the second digit is the ASTM viscosity number of the parent material, and the third digit is the curing temperature.

[2]The number of days cultured with a cellulose acetate degrading innoculum until significant biodeterioration was apparent.

[3]Increased operational life or the resistance to biological attack.

FIGURE 11. MEMBRANE COMPOSITION & RESISTANCE TO BIODETERIORATION



It is not clear how variations in the annealing temperature of the cast membrane affects its subsequent biological hydrolyzation. The heat treatment significantly affects the desalination characteristics of the membranes (1). The effect of annealing temperature on biodeterioration is probably due to molecular rearrangement in the cellulose acetate or the thickness of the actual operating membrane surface.

The above observations are based upon only a limited variety of cellulose acetate membrane types. From the information presented, though, it can be said that the cellulose acetate membrane composition can affect the susceptibility of the membrane to biological attack. Membrane fouling in the RO process has also been shown to be related to the type of cellulose acetate membrane used in desalination. Membranes annealed at the lower temperatures have been observed to be more susceptible to membrane fouling than membranes annealed at higher temperatures (4).

IV. SUMMARY

The 12-tube Bio-test unit was operated from March 1974 to January 1975. During this time ten membranes were replaced due to membrane failure. Four of these failures occurred in the acid, sulfite and chlorine pretreated units and were due to mechanical failure (a hole or tear being formed in the membrane). There were no membrane failures in these three units due to bacterial action. Six membranes failed in the Raw (untreated) unit and all were shown to be due to the action of bacteria. Acidification of the RO feedwater or the removal of dissolved oxygen from the feedwater or the maintenance of chlorine residual in contact with the membranes all prevented biofailure of the membranes.

Analysis of the number of bacteria capable of colonizing the membrane surfaces in the various pretreatment units revealed important differences. In summary, the average value for the number of bacteria per square millimeter of membrane surface for the Raw unit, Acid unit, Sulfite unit and Chlorine unit was 2200, 259, 1435 and 69, respectively. These values can be expressed as a percentage of the value obtained in the Raw unit. Sulfite pretreatment reduced the number of bacteria residing on the membrane surface to 65 percent of that observed in the untreated unit. Acid treatment reduced this number to 12 percent while chlorine treatment reduced the number to three percent.

Spongeball cleaning (mechanical) appeared to not appreciably reduce the colonization of the membrane surface by bacteria nor the subsequent biodeterioration of the colonized membranes. Bacteria on the surfaces of the RO membranes appear to be able to "regrow" sufficiently fast after spongeball cleaning so as to maintain a relatively constant number of bacteria in the slime layer. The depth of the slime layer and the number of bacteria that exist on the membrane surface is, to a large extent, determined by shear forces along the RO tubes.

Each of the units that utilized pretreatment chemicals yielded product water of quite low bacterial count in comparison with the input feedwater. The untreated unit, however, contained higher numbers of bacteria in the product water than in the incoming feedwater. This was due to membrane failure (holes in the membrane) and to microbial growth on the product water side of the membrane. It appears that RO feedwater chemical pretreatment is necessary to produce a product water of low bacterial count.

Fouling material that accumulated along the RO tube walls was found to have a maximum concentration of from 24 to 240 grams wet weight of slime material per one RO tube for each two weeks of operation. This slime product could be an important removal and disposal problem in RO units processing large volumes of tile drainage water.

The average slime material formed along the RO tube walls for the Acid, Sulfite and Chlorine units compared to the Raw (untreated) unit was 158.2%, 67.1% and 26.5%, respectively. In general, pH adjustment of the feedwater to between pH 4 and 5 resulted in increased slime formation along the tube wall compared to that observed in the untreated unit. The removal of dissolved oxygen by the addition of sodium sulfite resulted in only a small reduction in slime formation. The use of a solution of chlorine in contact with the membrane surfaces at all times resulted in a marked decrease in slime formation along the RO tube wall. Membrane failure due to brittleness, however, may have resulted from the use of the acid and chlorine pretreatments.

A number of microbiological aspects of membrane biofouling and biofailure were investigated. For the most part, the bacteria involved in membrane biodeterioration could use nitrate nitrogen for growth. The bacteria responsible for slime formation and membrane fouling appeared to require organic nitrogen for growth to a greater extent.

Examination of the types of bacteria isolated from the various units revealed certain important differences. Bacteria of the genus Arthrobacter were observed to predominate in the Raw unit slime and product water samples. The Raw unit experienced numerous biologically mediated membrane failures. Members of the arthrobacter group were observed in the Acid unit slime sample but did not occur to any considerable extent in the product water sample. This unit experienced no biofailures. Members of the arthrobacter group were completely absent from the Sulfite unit and were reduced to low incidence in the Chlorine unit. These two units were free from bacterial attack during the study.

The individual cellulose acetate membrane compositions utilized in desalination by the RO process can affect the susceptibility of the membranes to biological attack. Increases in the precentage acetate and parent material viscosity reduced this susceptibility while increases in the curing temperature of the cast membrane increased susceptibility. This variation in the deterioration rate was observed both in field studies with RO units in operation and in laboratory studies using cellulose acetate-adapted cultures.

Membrane biodeterioration does not appear to be significantly affected by the increased pressure of the RO process. The effect of increased product water recovery rates upon degradation is not known.

Each of the chemical agents used in this study can be characterized by its effects on the overall slime production in the RO unit, on the growth of bacteria in the slime layer, and on the specific target organisms, bacteria of the genus Arthrobacter. This is summarized in Table 5.

Chlorination of the feedwater significantly reduced the occurrence of slime growths and accumulations, the growth of most bacteria, and the occurrence of the arthrobacters. The removal of dissolved oxygen did not appreciably affect slime accumulation or colonization of the membrane surface but did essentially eliminate the arthrobacter group from the RO unit. Acidification reduced the bacterial populations along the RO tube wall and also inhibited the arthrobacter group. However, slime formation may have been increased.

TABLE 5. ACTION AND EFFECTS OF PRETREATMENTS

All Prevented Membrane Biodeterioration

Treatment	Action	Effects on Bacteria in the Slime Layer	Effects on Slime Production	Action on Arthrobacters	Side Effects
Chlorination (0.1 mg/l)	Bacteriocidal	Reduction of all bacterial groups to low numbers (3% of untreated)	Large reduction in slime formation (26% of untreated)	Reduced to low numbers	Membrane weakness
Removal of dissolved oxygen	Bacteriostatic for some bacteria, bacteriocidal for others	Only slight reduction of bacteria. Selection of specific isolate groups (2 and 10) which are able to grow anaerobically	Slight reduction in slime formation (67% of untreated)	Complete elimination	None
Acidification (pH 4.5-5.5)	Bacteriostatic	Reduction of all bacterial groups to low numbers (12% of untreated). Some selective increase in the *Bacillus* group	Increased slime production (158% of untreated)	Reduced to low numbers	Membrane weakness Corrosion

V. CONCLUSIONS

1. Membrane deterioration of the type herein described was caused by microorganisms. These microorganisms originated in the soil and found the particular combination of cellulose acetate membrane material (as a source of carbon and energy) and inorganic constituents of the agricultural drainage water to be suitable for growth.

2. Species of the bacterium *Arthrobacter*, a species of *Bacillus*, an actinomycete tentatively identified as belonging to the genus *Streptomyces*, and a fungus resembling *Penicillium* were isolated from biodeteriorated membranes.

3. A possible mechanism for biodegradation of the membranes is the modification of the cellulose acetate material, possibly by the metabolism of the acetyl groups, which makes it possible for cellulytic microorganisms to act upon the remaining modified material.

4. Slime formation, which causes a reduction of the flux rate and increased operational problems, appears to be a result of accumulation and growth of microorganisms.

5. Chemical pretreatment of the feedwater must be performed in order to protect RO membranes from biodeterioration. Removal of slime accumulations by mechanical means does not appear to inhibit membrane biofailure.

6. A pretreatment method is necessary that will maintain an active residual in the RO unit itself both on the brine and product water sides of the membrane. Acidification to pH 4-6 with sulfuric acid or removal of dissolved oxygen with catalyzed sodium sulfite or chlorination at 0.1-0.2 ppm total residual prevented bacterial attack of the RO membranes.

7. Acidification reduced the colonization of the membrane surface by bacteria but may have resulted in increased slime formation in the RO unit over that observed in an untreated unit and, in addition, posed handling problems, caused corrosion of the system, and may have structurally weakened the membranes. Chlorination reduced the occurrence of bacteria and reduced slime formation significantly but may have structurally weakened the membranes. Oxygen removal by the use of sodium sulfite did not significantly affect membrane colonization by bacteria and slime formation but did eliminate the microbial population involved in initiation of membrane biofailure.

8. Oxygen removal appeared to be the single best method of those tested in preventing biodeterioration of the RO membranes while not increasing slime formation or posing handling problems. An additional asset of this pretreatment is that routine monitoring of the brine and product water flows for the abscence of dissolved oxygen may be a reliable indication of the abscence of membrane-degrading bacteria.

9. Acidification, chlorination, or oxygen removal can be easily maintained while the RO units are not functioning and thus protect the units from microbial damage during this period. Oxygen removal would be particularly valuable in this regard in that the biodeterioration-initiating population is entirely eliminated from the unit while with acid and chlorine treatment this population is only suppressed.

10. A bioassay for potential biodeterioration problems can easily be performed on waters considered for possible desalination by cellulose acetate reverse osmosis. This would indicate the levels of pretreatment necessary prior to initial field trials of the desalination unit.

11. The individual cellulose acetate membrane compositions (parent material composition) utilized in desalination by RO can affect the susceptibility of the membranes to biological attack. Increases in the percentage acetate and increases in the parent material viscosity reduced susceptibility to biological attack. Increases in curing temperatures of the cast membranes increased susceptibility.

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