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NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20034

EVALUATION OF SEA-WATER REVERSE OSMOSIS MODULES FOR SINGLE-PASS SHIPBOARD DESALINATION SYSTEMS

by

J. F. Pizzino and W. L. Adamson

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PROPULSION AND AUXILIARY SYSTEMS DEPARTMENT
Annapolis
RESEARCH AND DEVELOPMENT REPORT

March 1974

Report 27-717

Evaluation of Sea-Water Reverse Osmosis Modules for Single-Pass Shipboard Desalination Systems

Report 27-717

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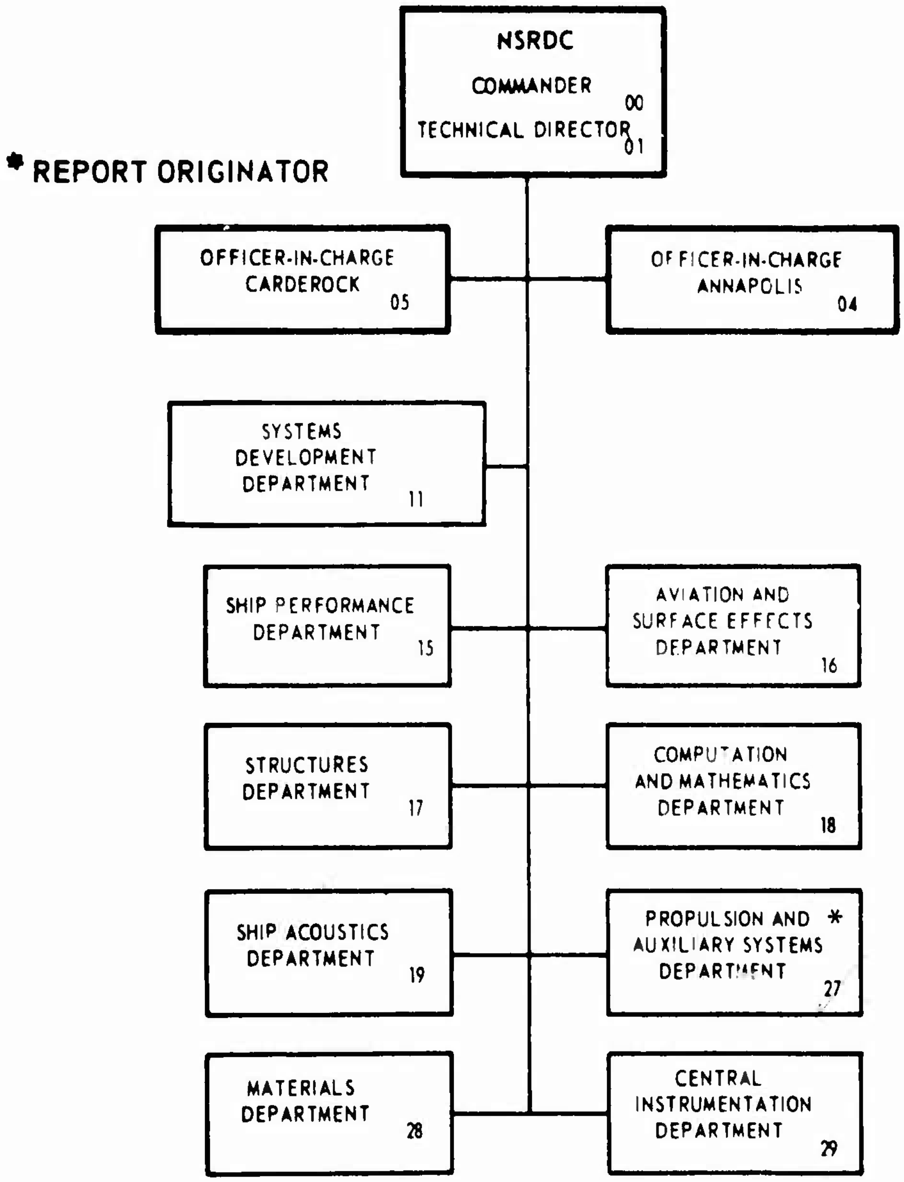

DEPARTMENT OF THE NAVY
NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER
BETHESDA, MD. 20034

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(10) J. F. Pizzino ~~and~~ W. L. Adamson

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ABSTRACT

Experimental evaluations were made on two single-pass sea-water reverse osmosis modules. One was evaluated on synthetic sea water for 1100 hours and the other evaluated on natural sea water for 1500 hours. Both modules initially performed well, producing water of less than 150 parts per million total dissolved solids. It was found that iron fouling from system piping and components reduced product rate and that bacterial attack on the membrane material seriously reduced the product water rate and quality. Further investigations will be conducted on similar reverse osmosis equipment in which the materials of construction are selected to minimize iron fouling, and various methods of pretreating the sea-water feed to kill or remove undesirable microorganisms are used. It is recommended that in future evaluations, in-depth studies of the product water be made to determine its fitness for human consumption.

ADMINISTRATIVE INFORMATION

This report was completed as part of NAVSHIPS Task 15157, Task Area SF43 432 70 304, Work Unit 1-2761-158. The program manager is Mr. L. Benen, NAVSHIPS (SHIPS 03413)

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INTRODUCTION

BACKGROUND

Reverse osmosis (RO) is emerging as a viable process for desalting brackish water, waste water, and sea water. The Center has been evaluating RO for single-pass membrane desalination for surface ships. Under the current RO sea-water desalination program, membranes composed of various materials were first evaluated in small laboratory test cells to determine their ability to produce potable water from a sea-water solution. The results, reflecting sea-salt rejection, product water rate, and product water rate decline, demonstrated the feasibility of RO as a viable process for desalting sea water in a single pass. These membranes were evaluated at pressures between 1000 to 1500 lb/in^2* and exhibited relatively low product flux rates and high product water rate decline.[1]

The Department of Interior, Office of Saline Water (OSW), has been working to develop RO as a practical means of desalting sea water and has successfully demonstrated RO modules with high membrane surface area density (minimizing volume requirements) that operate at lower pressures (800 to 1000 lb/in^2). This report covers operating data and results obtained by using RO modules procured from OSW and operated on synthetic and natural sea water.

SCOPE

The purpose of this program is to develop a single-pass RO sea-water desalination system that can serve surface ship requirements. In this connection, two sea-water RO modules, identified as S-52 and S-53, were fabricated under OSW contract 14-30-2799 and initially evaluated at the San Diego Aquarium for short-term runs. The San Diego Aquarium results are available.[2] Under the NSRDC program, the modules were evaluated on synthetic and natural sea water, respectively. The results of these evaluations were used in assessing the characteristics and feasibility of these RO modules for single-stage desalination for shipboard application.

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*Abbreviations used in this text are from the GPO Style Manual, 1973, unless otherwise noted.

[1] Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

A 400 gal/d test unit has since been procured for further and more extensive evaluation on natural sea water.

This report covers the results of the evaluations of RO modulues S-52 and S-53.

DESCRIPTION OF REVERSE OSMOSIS MODULE

MEMBRANE-MODULE CONFIGURATION

Figure 1 is a photograph of one of the two identical RO modules and figure 2 is a photograph of the components which make up the module. The modules are approximately 16 inches long by 4 inches in diameter and were designed to produce 100 gal/d of product water (permeate).

The two RO modules are of the hollow fiber configuration. In this configuration the membrane polymer is extruded into hair-like fibers, with hollow channels running down their centers. (These particular modules have fibers of 30 μm ID and 105 μm OD.) The fibers are wound in a bundle and their ends are collected and "potted" in an epoxy tube sheet. The configuration is similar to that of U-bent tubes rolled into the tube sheet of a heat exchanger. The membrane fibers employed in these modules are made of cellulose triacetate, a fully acetylated cellulose acetate polymer. Cellulose triacetate is more highly resistant to degradation from chlorine and high pH than other cellulose acetate polymers of lower degrees of acetylation and is therefore, a prime candidate for sea water use.

WATER FLOW PATH THROUGH THE MODULE

Figure 3 is a cross-sectional view of the RO modules. Pressurized sea water enters at the right, flows longitudinally along the outside of the bundle and then radially inward through the bundle of fibers to the slotted plastic core where it collects as brine (concentrate). The brine is then pumped overboard. Product water permeates the fibers and flows along the inner fiber channels to the permeate header where it is collected.

METHOD OF EVALUATION

OPERATION OF MODULE S-52 ON SYNTHETIC SEA WATER

Figure 4 is a schematic of the test apparatus employed in evaluating module S-52 on synthetic sea water. The synthetic sea water, made with sea-salt, ASTM D-1141-52, was maintained at a concentration of 35,000 p/m total dissolved solids (TDS) in the feed tank. It was fed by a low-pressure feed pump to a 5 μm filter and then passed through a heat exchanger which controlled the feedwater temperature. The water was then pumped to an operating pressure of 900 lb/in^2 and passed through the RO module. The brine pressure was regulated by a back-pressure valve. The product water (permeate) from the RO module and the brine were returned to the feed tank for mixing and recirculation through the system. Brine and product water samples could be taken via the 3-way valves located in the return lines.

An auxiliary feed tank was kept full of fresh water to flush the RO module whenever it was shut down. This was necessary to prevent possible scaling of the membrane surfaces by sea salts concentrating in the module.

To prevent biological contamination of the test system, a 2 p/m dosage of copper sulfate was maintained in the feed tank. It had been found in previous testing that the recirculation mode of operation enhances bacterial growth on the tank walls if some precaution is not taken.

No attempt was made to run the RO system continuously. The unit was occasionally turned off for maintenance or when the unit could not be properly attended over weekends.

OPERATION OF MODULE S-53 ON NATURAL SEA WATER

Figure 5 is a schematic and figure 6 is a photograph of the test system used to evaluate RO module S-53 on natural sea water at Wrightsville Beach, North Carolina. Sand-filtered sea water was directed through a sand trap, which served as a settling tank, and was then fed through 10 and 5 μm filters, respectively. Filter life was monitored by a differential pressure gage. The sea water was then pumped to 800 lb/in^2 using a positive displacement diaphragm pump. A back-pressure valve was used to adjust the system operating pressure. Both the product water and the brine were dumped overboard. Water samples could be taken via the 3-way valves located in the drain lines.

At approximately 475 hours operating time it was found that the accumulator was contributing a large amount of iron oxide to the system. Since iron oxide can foul the membrane and seriously reduce the product rate, the accumulator was removed from the position shown in figure 5 and placed between the RO module and the back-pressure regulator. With this scheme, corrosion products from the accumulator could not pass through the module. No change in the attenuation of pump pressure fluctuations was apparent as a result of the repiping of the accumulator.

The system was operated 24 hours a day during the working week and turned off on weekends. Again, no attempt was made to assure uninterrupted operation. For maintenance periods, the unit was shutdown as necessary.

Any time the system was shutdown, the drain valve was opened to vent the system pressure. In this way, there was no residual pressure in the module that could cause the sea-water solution to concentrate and foul the membrane. However, the module was not flushed with freshwater.

RESULTS

The tabulation below gives general operating data for both synthetic and natural sea-water test system.

OPERATING DATA OF RO SEA-WATER MODULES

	Module S-52 on Synthetic Sea Water	Module S-53 on Natural Sea Water
Feed rate (gal/d)	400	400
Operating pressure (lb/in^2)	900	800
Biocide used	Copper sulfate	None
TDS (p/m)	35,000	Variable 31,000-33,000

DISCUSSION OF MATERIALS

During the operation of RO module S-52 on synthetic sea water, it was found that iron oxide particles from stainless steel piping fouled the RO membrane and reduced the product rate significantly. Since the iron oxide could accumulate in the system, due to the recirculation mode of operation, the sea-water solution was periodically changed. The degree to which corrosion did occur is demonstrated in figure 7 which shows the 316 stainless steel permeate header with deep pitting on the sealing faces. The faces, which were sealed with a gasket material, were in contact with product water containing only 100 to 200 p/m TDS. Apparently the amount of chlorides in this water was high enough to cause crevice attack after the water had permeated the gasket.

PERFORMANCE OF MODULE S-52 ON SYNTHETIC SEA WATER

Figure 8 shows the performance of RO module S-52 on synthetic sea water. As can be seen from the top curve in the graph, product quality varied between 100 and 200 p/m. On the lower portion of the graph is a plot of the product rate (gal/d) versus operating time (hours). It was noticed after 373 hours of operation that the product rate had declined markedly. It was suspected that this decrease was caused by iron fouling on the membrane surface and not membrane compaction caused by water pressure. Therefore, the membrane was cleaned by back flushing the module with a 1.0% citric acid solution, which had been found effective by other investigators in cleaning iron fouled membranes. Backflushing was accomplished by feeding the cleaning solution to the module brine discharge port for 2 hours as shown in item (a) of figure 9. The solution being circulated took on a deep yellow color, an indication of dissolved iron. This was followed by a 0.2% citric acid solution fed through the module in the normal flow direction, item (b) of figure 9. Finally, the module was flushed with distilled water for 15 minutes. It can be seen from figure 8 that the product rate was partially restored by the cleaning procedure.

Again, after 728 hours of operation, the RO module was backflushed in the manner previously described. In this instance, the backflush procedure was less successful since the product rate improved only very slightly. The cleaning procedure was attempted again after 1050 hours of operation but again only a small improvement in the module product rate was noted after cleaning.

After each cleaning, at 400, 728, and 1050 hours of operation, the temperature of the feedwater to the RO module was varied between approximately 50° to 82° F to determine the effect of feedwater temperature on performance. Curves were generated which showed product rate versus feedwater temperature. If the citric acid thoroughly cleaned the membrane surfaces each time the module was flushed, it was theorized, then, that the relative change in these product-rate/feedwater-temperature curves should be an indication of the degree of membrane compaction with time (assuming no membrane hydrolysis occurred). Figure 10 shows the three curves generated after each module-cleaning operation. No definite conclusion can be drawn to relate membrane compaction and total operating time because the curves show no definite trend. Apparently either the cleaning procedure at 1050 hours of operation was incomplete and partially ineffective or considerable compaction occurred. The latter seems unlikely in view of the fact that almost no measurable reduction in product rate occurred between 400 and 728 hours.

It is apparent from figure 10 that the product rate is a strong function of the feedwater temperature, which fact is well known among other RO investigators. It appears that the citric acid cleaning of RO iron-fouled membranes was only partially effective in restoring membrane surfaces.

EVALUATION OF RO MODULE S-53 ON NATURAL SEA WATER

Figure 11 is a graph of the performance of RO module S-53 on natural sea water. As seen in the figure, performance was satisfactory for 1200 hours until the product quality began to drop precipitously. The product rate showed a steady decline throughout the test period. A combination of several influencing factors including membrane compaction, hydraulic oil fouling, iron fouling, and bacterial action are suspected to have caused the flux and product quality declines.

At 490 hours of operation, one of the diaphragms in the duplex high-pressure pump ruptured, allowing hydraulic oil to seep from the pump into the sea-water system. When the rupture was discovered, the unit was secured and the module disassembled for visual inspection, figure 2. The actual membrane fibers were not visible because of a nonremovable fabric covering around the fiber bundle. However, the pressure case was found to have a thin coating of oil on its inside walls. Also, the water remaining in the case had a high concentration of iron oxide particles. The fabric covering the fiber bundle had a brown hue, indicating that the membrane fibers had been exposed to a large amount of iron oxide, found previously to be detrimental to RO operation.

The module was reassembled and flushed out (in a manner similar to the flushing procedure previously described with module S-52) with a 0.5% citric acid solution to clean out the iron oxide and a 0.5% Biz home-laundry presoak solution to dissolve any remaining oil from the module.

The module was reassembled and the accumulator (found to be a source of iron oxide) was moved to a position downstream from the RO module. The system was restarted, but after a short operating time, the newly replaced diaphragm again broke. A subsequent inspection revealed no oil contamination. It was again flushed and reinstalled for testing. As can be seen in figure 11, the product water quality dropped abruptly from 60 to 120 p/m. The drop in product water quality was evidently due to membrane damage by either oil or cleaning solution (in this case, citric acid or Biz presoak). However, the permeate quality was still at a highly acceptable value. (500 p/m TDS is the acceptable Public Health Standard limit for drinking water.)

At the termination of the evaluation of RO module S-53 on natural sea water, the accumulator was cut open for inspection. Supposedly, it was constructed of carbon steel with a phenolic finish on the interior walls to prevent corrosion. The inspection revealed that the accumulator was badly corroded and the phenolic finish had almost completely peeled off. Other parts supposedly constructed of 304 stainless steel appeared to be of regular carbon steel. Because of these findings there is good reason to suspect that prior to 475 hours of operation, the RO module was exposed to high levels of iron oxide and other corrosion products.

There was also concern that the membrane used in this RO module, composed of cellulose triacetate, was vulnerable to biological attack. This susceptibility to bacterial attack increases with temperature; hence, bacterial activity would be increased in the spring and summer months. Bacterial matter in the sea-water channel where water was drawn for use in these tests, would also be expected to increase due to the influx of tourists in the area during this period.

Checks of the feedwater, upstream of the RO module, revealed that bacterial activity increased substantially during the later stages of the test. The product water quality decline beginning at 1200 hours of operation is suspected of being attributable to holes in the membrane caused by increasing bacterial attack.

If holes were to develop in the membrane, a concommitant increase in product rate and decrease in product quality would follow. This unusually steady decrease in product rate is attributed to membrane fouling from slime given off as bacterial waste products. This effect may have caused the channeling of feedwaters through the fiber bundles resulting in further poor performance. Attempts to clean the RO module with a biocide (copper sulfate), citric acid, and Biz presoak in the flushing procedure resulted in only partially restoring product water rate and quality.

In summarizing the performance of RO module S-53 on natural sea water, performance declined noticeably at 350 and 1200 hours of operation. The product water quality decline at 350 hours was attributed to hydraulic oil or cleaning solution effects on the membrane. The drastic product water quality decline beginning at 1200 hours of operation was attributed to biological attack on the cellulose triacetate membrane. The steady decrease in product water rate was probably a result of several factors: hydraulic oil fouling, bacterial waste product fouling, and membrane compaction.

CONCLUSIONS AND RECOMMENDATIONS

Both RO modules operating on synthetic and natural sea water performed well in the initial stages of these evaluations. Both modules displayed the capability of producing water having a TDS content far below the U. S. Public Health standard of 500 p/m TDS. However, neither module produced potable water at its designed rate of 100 gal/d; both modules exhibited large declines in product water rate and one module, S-53, appeared to have suffered from biological attack.

The fact that neither module produced water at its designed product rate is not felt to be of great importance. This can be easily corrected by installing membranes with improved higher productivity such as have since been developed by the company, or by increasing the membrane area.

Of prime concern are the significant declines in product water rate exhibited by both RO modules. It is difficult to separate the effect of membrane compaction on product water decline from the other contributing factors. If this contribution is, in fact nil, then significant gains could be achieved by reducing the external sources of decline in product water rate such as iron fouling and bacterial fouling.

It was found in the evaluation of RO module S-52 that by operating in a recirculation mode, iron from stainless steel piping and the accumulator can build up and ultimately reduce the product water capacity of a hollow fiber RO module of cellulose triacetate. Further testing of module S-53 on natural sea water illustrated the same effect when an accumulator of carbon steel was allowed to operate upstream of the RO module. The use of a citric acid solution for removing iron fouling from RO membranes is considered to be only partially effective. In future work every effort will be made to eliminate possible sources of iron oxide upstream of any RO module. It seems at this point to be more feasible to prevent iron fouling than to attempt to remove it after fouling has occurred.

Another area of future study will be the investigation of various methods for controlling bacterial matter in feedwaters. RO modules with membranes of cellulose triacetate are potential breeding grounds for many types of bacteria. Bacterial waste matter is thought to be one cause of the product rate flux decline and the cause for the ultimate failure of the S-53 RO module. Also, and more important, this could affect the sanitary quality of the product water. Various methods will be evaluated for treating RO feedwater. The most feasible method appears to be injection of hypochlorite solution into the RO feed stream. In this scheme it has been found by other investigators that hypochlorite ions permeate the RO membrane almost completely. This would ensure intimate contact between the membrane and hypochlorite ions on both the feed and permeate sides. The evaluation of an ultraviolet purifier in the feed line operating simultaneously with hypochlorite injection downstream will also be pursued. Further, an in-depth study will be made of the product water to assure that it is medically safe to drink.

From a comparison of the data taken with synthetic and natural sea waters, it is concluded that salt separation and water permeation performance are initially comparable for synthetic and natural sea water, but that only natural sea water can be used to correctly assess long-term membrane reliability.

TECHNICAL REFERENCES

1 - Pizzino, J. F., and W. L. Adamson, "Investigation of Sea-Water Reverse Osmosis Membranes for Single-Pass Shipboard Desalination Systems," NSRDC Rept 27-54 (June 1972)

2 - Dept. of Interior, Office of Saline Water," Membrane Digest," Vol. 1, No. 1 (Apr 1972)

Figure 1
External View of Reverse Osmosis Module S-53

1 - Gasket
2 - Sea-Water RO Module
3 - Module Pressure Vessel
4 - Permeate Header
5 - Internal Snap Ring

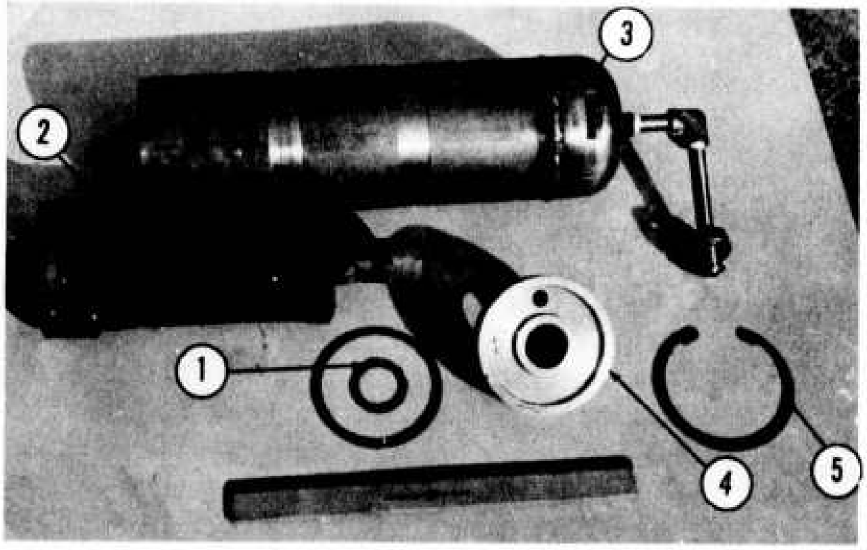


Figure 2
Reverse Osmosis Module Disassembled for Inspection

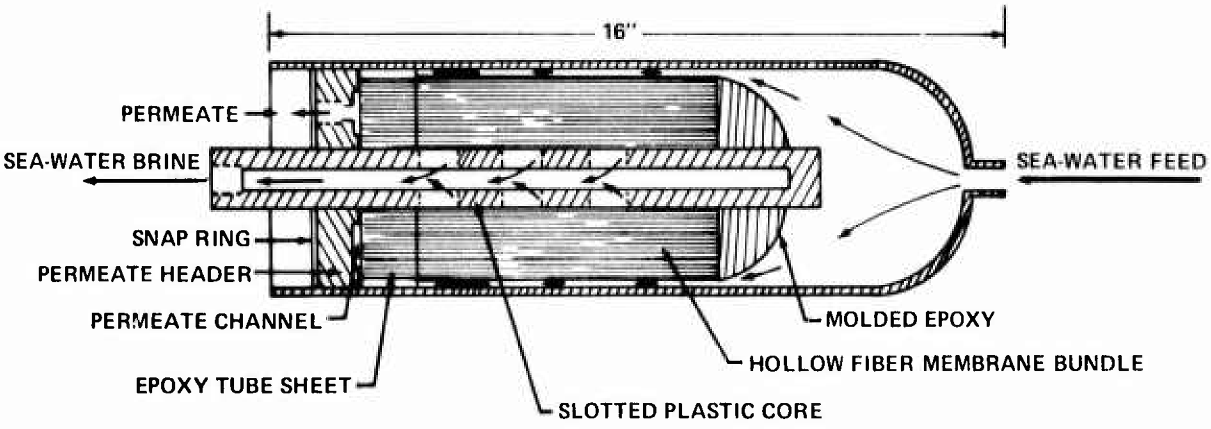


Figure 3
Cross-Sectional View of
Hollow Fiber Sea-Water Reverse Osmosis Module

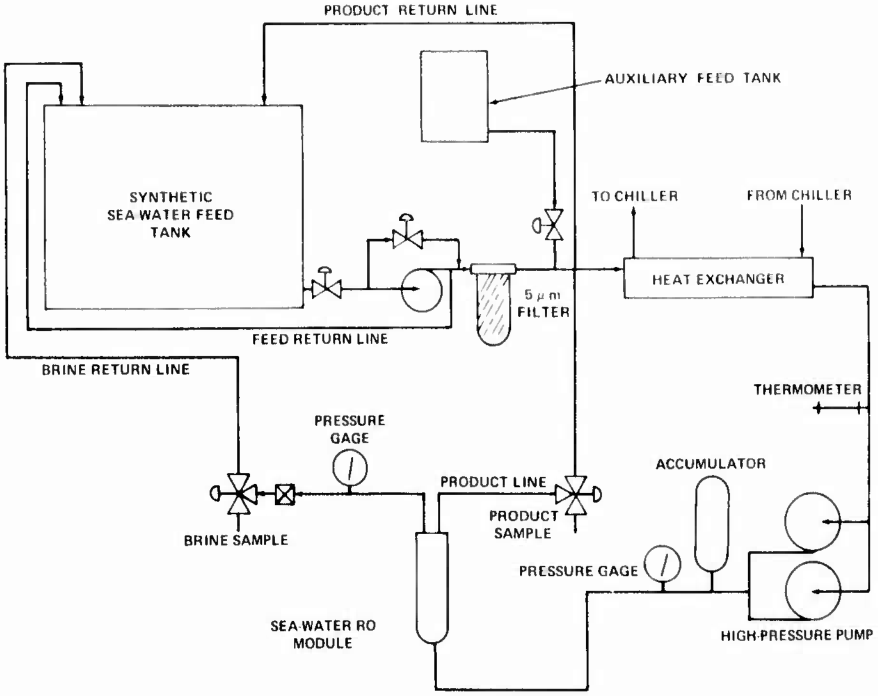


Figure 4 - Reverse Osmosis Synthetic Sea-Water Test System at NSRDC

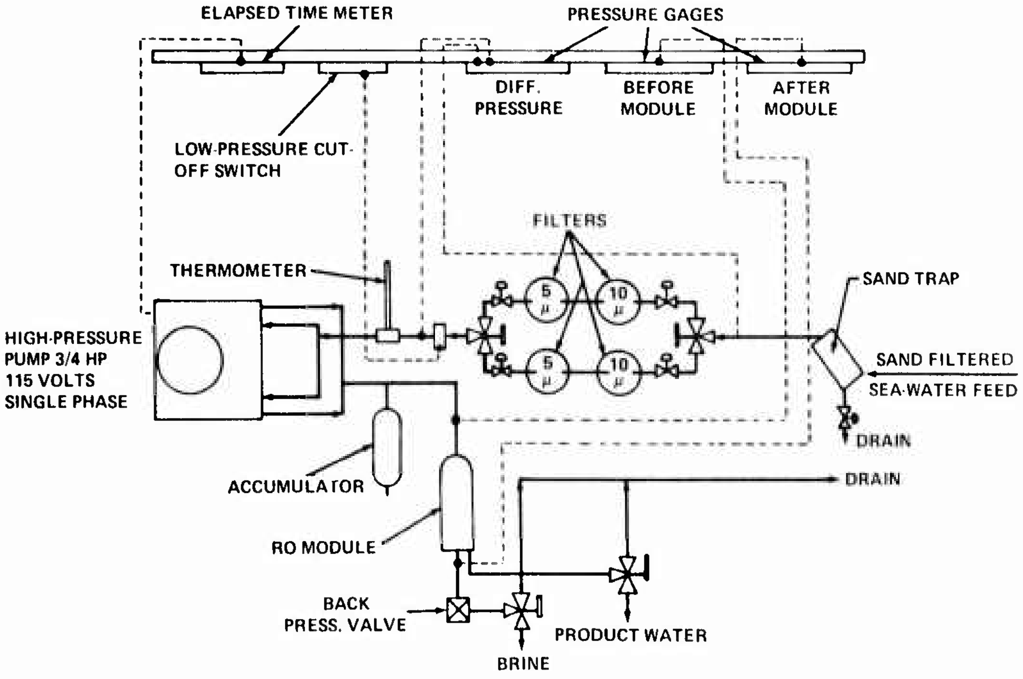


Figure 5 - Natural Sea-Water Reverse Osmosis Desalination Test Loop at Wrightsville Beach, North Carolina

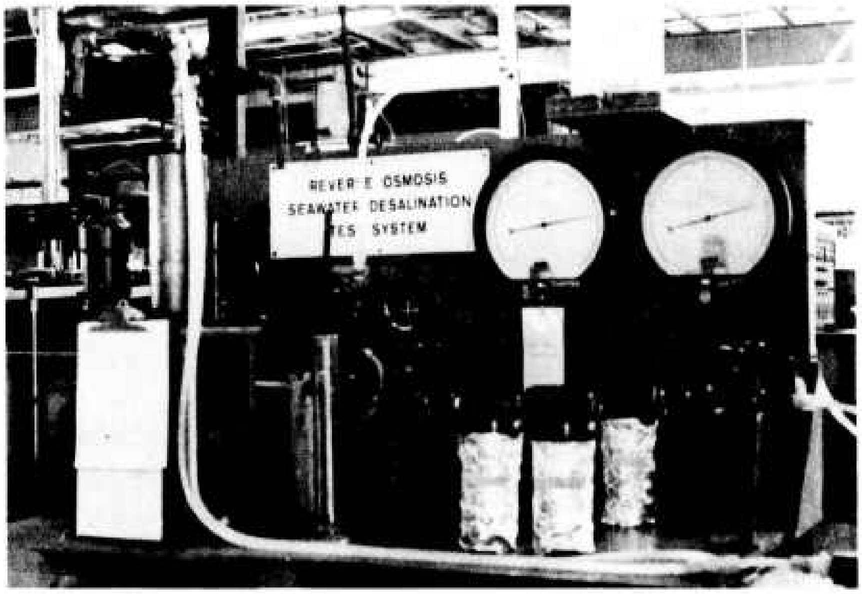


Figure 6
System Used to Evaluate Reverse Osmosis Module
S-53 on Natural Seawater at
Wrightsville Beach, North Carolina

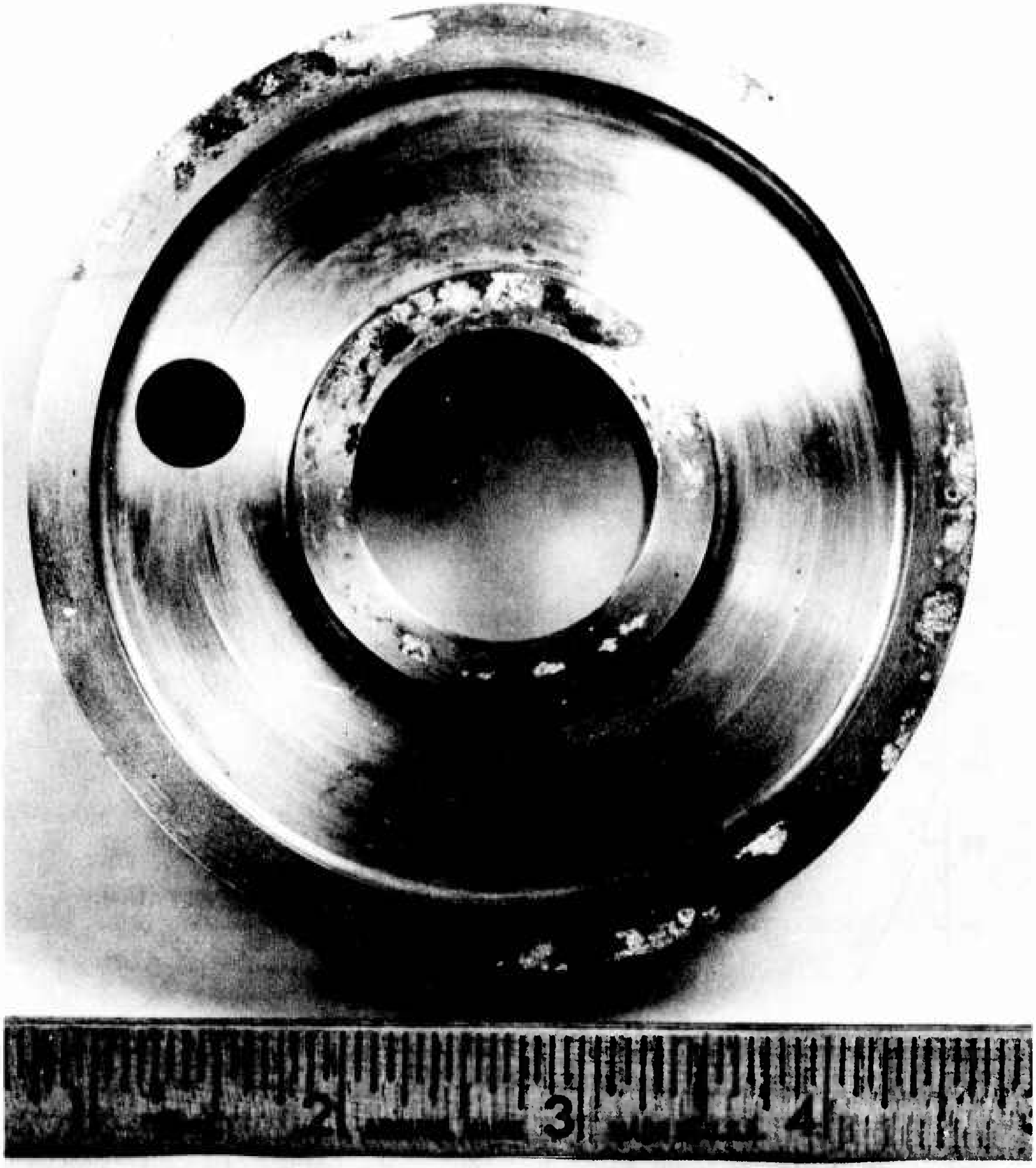


Figure 7
Reverse Osmosis Module Permeate Header
Showing Evidence of Corrosion

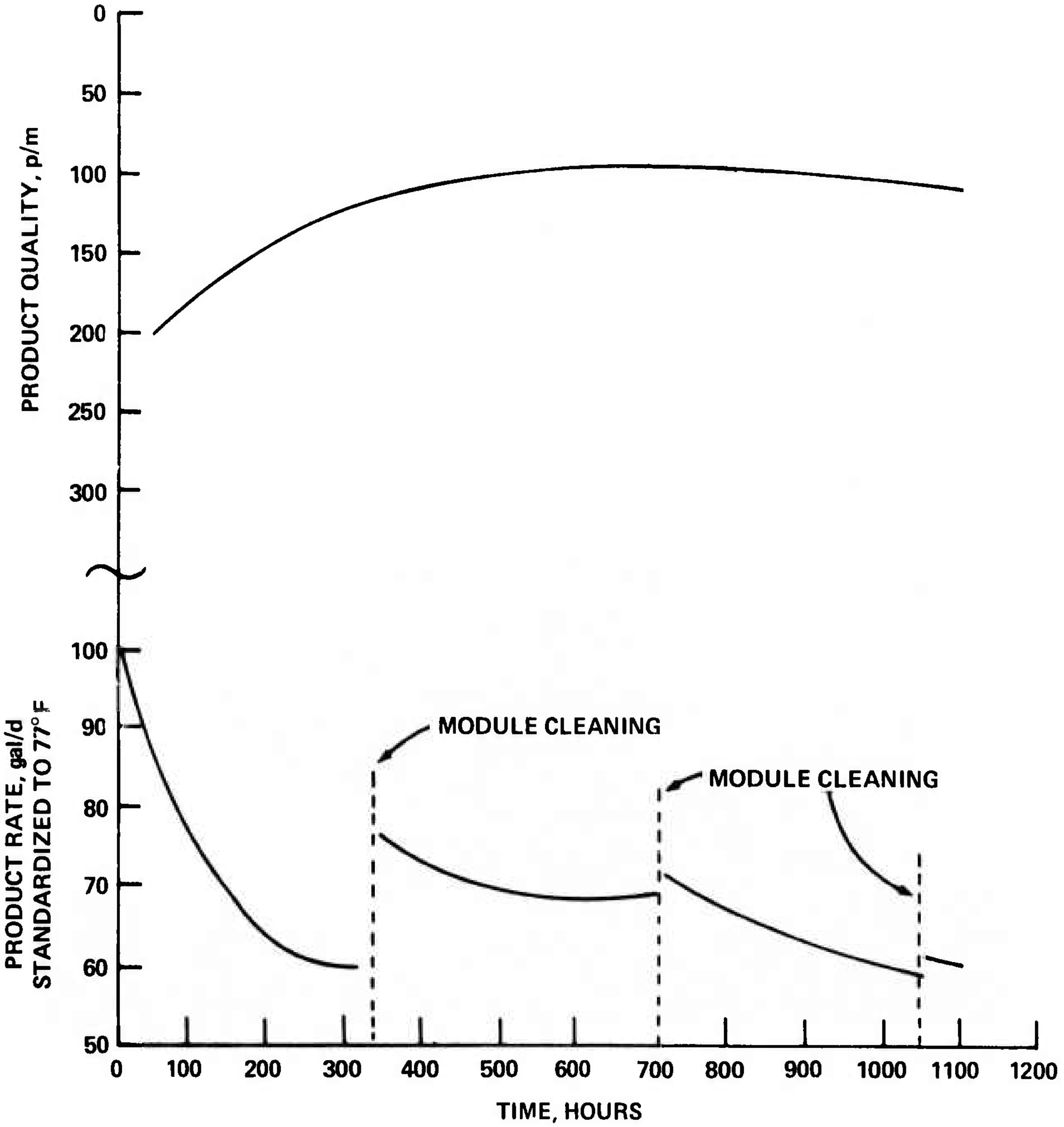
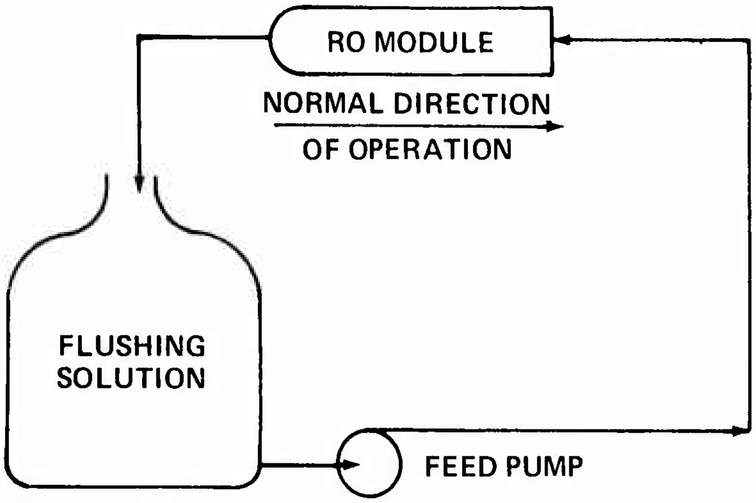


Figure 8
Evaluation of Reverse Osmosis Module S-52
on Synthetic Sea Water at NSRDC

Item (a)
Back Flushing



Item (b)
Forward Flushing

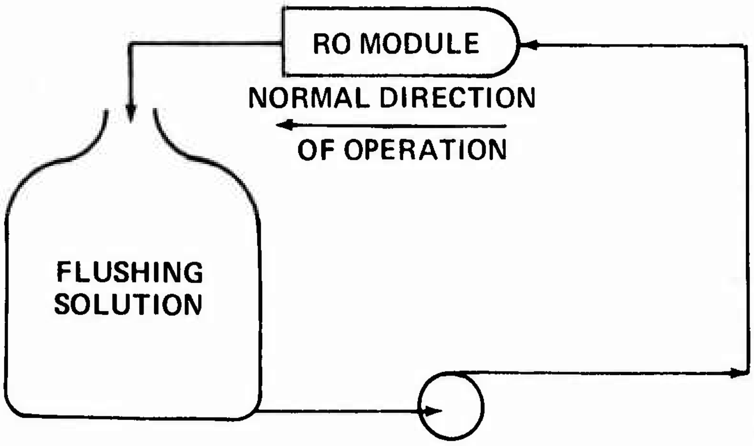


Figure 9
Flushing Modes for Cleaning
Reverse Osmosis Sea-Water Module

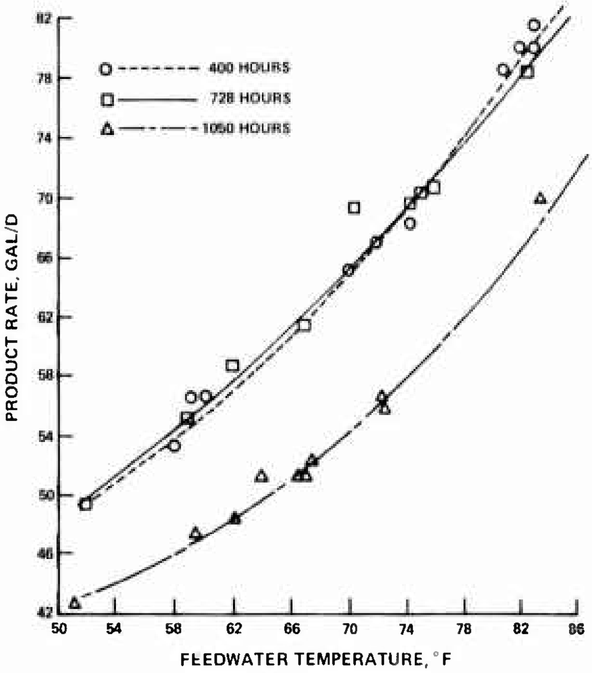


Figure 10 - Product Rate Versus
Feed Water Temperature for Reverse Osmosis
Module S-52 at Three Operating Times

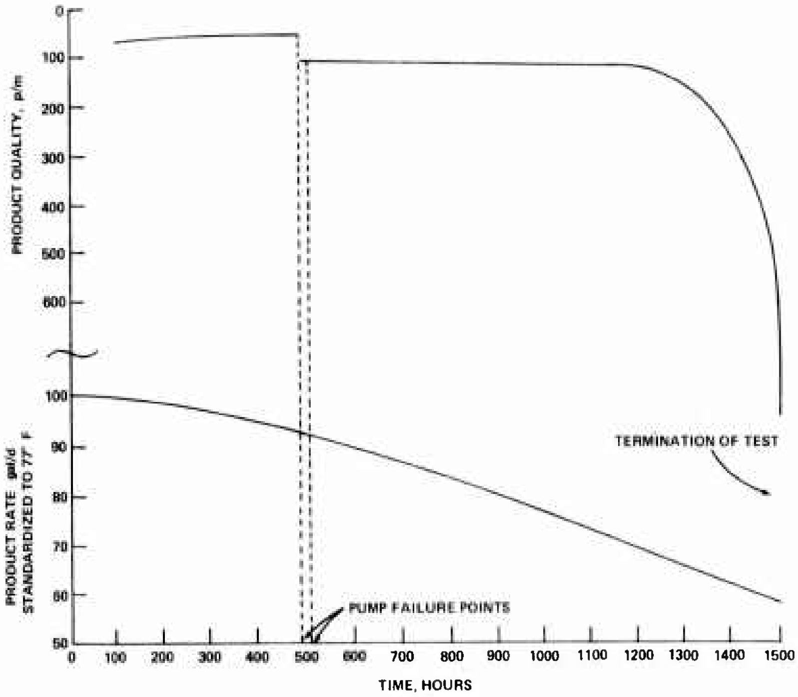


Figure 11 - Evaluation of Reverse Osmosis
Module S-53 on Sea Water at
Wrightsville Beach, North Carolina

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13. ABSTRACT

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Sea water						
Dissolved solids						
Membranes						
Bacterial attack						
Desalination						

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