(A paper comparing MEMSTOR™ with six other methods)

Reverse Osmosis (RO) Element Preservation Study

William Varnava, Mark Silbernagel, Ted Kuepper and Mark Miller

Navel Facilities Engineering Service Center (NFESC), 1100 23rd Avenue, Port Hueneme, California

Proceedings of 1996 Biennial Conference and Exposition of the American Desalting Association, August 4-8, 1996, Monterey, California

Reverse Osmosis (RO) Element Preservation Study

William Varnava, Mark Silbernagel, Ted Kuepper, and Mark Miller

Naval Facilities Engineering Service Center (NFESC), 1100 23rd Avenue Port Hueneme, California

Abstract

The Naval Facilities Engineering Service Center (NFESC) located in Port Hueneme, California has operated the Seawater Desalination Test Facility (SDTF) since 1983 to evaluate and test military and commercial water equipment. A three year test program was conducted at the SDTF to evaluate the effectiveness of seven chemical preservation methods for seawater thin film composite membranes. The Filmtec model FT-30 membrane (DOW Chemical) was used in this evaluation. The results of this study indicate that a variety of preservative solutions offer good overall performance in terms of maintaining product water salt rejection and flux. The factors used to evaluate the membrane preservatives included their effect on salt rejection, product flux, and reduction of microbiological growth.

Introduction

The U.S. military currently lacks a reliable and effective method for preserving and storing reverse osmosis (RO) membranes. Many of the RO membranes used by the military are subject to periods of long term storage due to the nature of combat excursions and training exercises. It has been observed that this storage period between uses has resulted in a degradation in the ability of a membrane to reject salt and produce potable water. The U.S. military has used a 600 gallon per hour (GPH) mobile desalination system known as the reverse osmosis water purification unit (ROWPU) to produce potable water for almost twenty years. The high cost of membrane replacement and the detrimental effect equipment downtime has on military water production require a documented process to preserve the performance of RO elements that are subject to infrequent use and long periods of storage.

This paper discusses a test program sponsored by the U.S. Army Mobility Technology Center, Ft. Belvoir, VA which evaluated seven commercially available preservatives and generic chemical solutions between November 1992 and August 1995 at the SDTF located in Port Hueneme, CA. A set of four 6-inch diameter by 40-inch long Filmtec model FT-30 membranes were tested for each preservation method. These elements were new at the start of the testing program and were not replaced. They were typically operated between 250 to 300 hours on natural seawater using the ROWPU before a preservation cycle occurred. After this test cycle, two Filmtec elements were stored in a preservative solution for a period of 16 to 20 weeks. During the storage period, samples of the preservative solution were taken periodically and microbiological plate counts were performed. The other two elements were not preserved in any way and served as a control group. The initial test established baseline data for the RO elements. After the storage period, the elements were retested and performance between the preserved and control groups was compared.

ROWPU Operation and RO Data Collection

RO elements were loaded into the ROWPU's high pressure vessels in the same order during each test cycle and were identified with a manufacturer's serial number. Blind interconnectors were used to isolate the product water produced by each individual element.

The ROWPU test unit was operated as continuously as possible to determine element performance by running 24 hours a day, 7 days a week during the testing cycle. Seawater was pumped from an open ocean intake at the entrance to the Port Hueneme harbor to the SDTF and provided feedwater to the ROWPU at a rate of approximately 33 gallons per minute (gpm). The seawater intake line extended about 120 ft. out into the water and was 5 ft. above the seafloor. The prefiltration system on the ROWPU consists of a multimedia filter (MMF) and cartridge filter (CF). The MMF, which contains layers of anthracite, sand, garnet, and gravel, operates at a loading rate of 6.7 gpm per ft^2. The CF uses eight wound 40-inch long polypropylene cartridges rated at a nominal 5 microns. It operates at a filtration rate of 1 gpm per 10- inch length. Seawater was filtered through the MMF and CF before entering a positive displacement high pressure pump which then fed the RO elements. The RO elements were operated at 900 psi feed pressure.

The ROWPU was only shut down for performing routine maintenance items such as backwashing the MMF, changing cartridge filters, and changing oil in the high pressure pump. Sodium hexametaphosphate (SHMP), an antiscalant, and CATFLOC-T (Calgon Corporation), a cationic polymer coagulant, were injected at the appropriate locations into the ROWPU's feedwater resulting in a polymer concentration of approximately 0.9 mg/L and an antiscalant concentration of 1.9 mg/L.

A water purification laboratory in the SDTF was used to monitor and record various feed water quality parameters such as turbidity, conductivity, pH, and silt density index (SDI). Before any data were collected, the RO feed pressure was adjusted to approximately 900 psi and all sample lines were thoroughly flushed. RO product water, RO feed, multimedia filter effulent, and raw seawater turbidities were recorded daily. The overall product conductivity, RO feed water conductivity, RO feed pH and individual element flow rates and conductivities were measured daily. Other parameters recorded included the operating time, product water temperature, product water outlet pressure, RO feed pressure, RO vessel differential pressure, and brine flow rate.
Flow and conductivity meters were calibrated for each test cycle.

Chemical Preservation Methods

After each set of elements was tested for 250 to 300 hours by operating in a ROWPU, a preservation cycle was performed. The residual water was drained from the elements before they were placed into 6-inch-diameter PVC pipes which simulated the continued storage inside ROWPU pressure vessels. The Filmtec elements located in positions 2 and 7 were **not** preserved in any way and served as the control group during the evaluation while elements in positions 3 and 6 were preserved with the particular chemical solution being evaluated for each set. The preserved elements remained immersed in the chemical solution during the storage period which was typically 16 to 20 weeks between operational cycles. The particular pattern of operation and storage periods used throughout this test program simulated a typical training scenario at a military base.

Seven commercially available preservatives and generic chemical solutions, designated Methods A through H, were chosen for study:

1. Method A- 1 percent by weight citric acid buffered to pH=3.5 with ammonium citrate, and 20 percent by volume propylene glycol solution.

2. Method B- Product Water Flush (200 gallons).

3. Method C- 3 percent by weight MEMSTOR (King Lee Technologies) solution.

4. Method D- 20 percent by volume PROGARD (ARGO Scientific) solution.

5. Method E- 1 percent by weight sodium bisulfite/18 percent by volume propylene glycol solution. (Normal preservative recommended by many RO element manufacturers)

6. Method G- 1 percent by weight proprietary chemical solution, adjusted to pH=5.

7. Method H- 10 percent by volume BIOCLEAN 882 (ARGO Scientific) solution.

The buffered citric acid solution used in method A was recirculated for 45 minutes and then drained from the storage vessels prior to recirculating the propylene glycol solution. In method B, product water was not recirculated through the elements but flushed to drain. The BIOCLEAN 882 preservative, method H, was added to the test program in August 1994. During the preservation process, approximately 20 gallons of preservative solution were prepared and recirculated through the elements for 45 minutes using a ROWPU raw water pump at a rate of 30 to 35 gpm. All preservative solutions were prepared with RO product water and were thoroughly mixed before recirculating through the elements. The conductivity, pH, and temperature of the preservative solutions were measured before and after recirculation through the elements. Table 1 summarizes the pH and conductivity of the preservative solutions. The pH and conductivity values shown are averages of the readings taken after the preservative solution was recirculated through the RO elements.

Microbiological Plate Count Data

The effectiveness of the various preservative solutions to limit biological growth was examined by using a conventional plate count method.

In this study, three different media were used for plate counts: marine broth (made by Difco, Inc.), Luria, and glucose-phosphate-acid media (GPA). The marine medium is formulated to grow seawater organisms, the Luria medium is nutrient rich for growth of a wide range of organisms, and GPA is a medium for fungi. The number of visible organisms on each media, called a colony forming unit (CFU) were counted.

Note that a plate count number underrepresents the actual microbial population for two reasons: (1) a CFU could arise from one organism or small group of microorganisms, and (2) since any particular media cannot possibly meet all the nutrient and environmental requirements of every microorganism, the petri dish could contain viable microorganisms that did not grow or did not reach a state of growth during the observed time period.

RO Element Performance Parameters

A set of parameters, the water transport coefficient, *a*, and salt transport coefficient, *b*, were used to evaluate and normalize the performance of RO membranes. The water transport coefficient has the units of gpm/psi and is defined by the following equation:

$$a = \frac{Q_{TCF}}{P_{NET}} \qquad (1)$$

where Q_{TCF} is the temperature-corrected flow rate and P_{NET} is the net driving pressure. The larger the water transport coefficient, the greater the amount of flow produced for each psi of driving pressure.

The temperature-corrected flow rate equation for the Filmtec elements, where Q is the measured flow rate and T is the product water temperature in °C, are as follows:

$$Q_{TCF} = 1.03^{(25-T)} * Q \quad (2)$$

The salt transport coefficient measures the amount of salt that passes through the membrane in gpm. It is defined by the equation:

$$b = \left[\frac{C_{PROD} * Q_{TCF}}{C_{AVG} - C_{PROD}} \right] \quad (3)$$

The term C_{PROD} is the product water TDS and C_{AVG} is average feedwater TDS based on the log mean difference of the feed and brine TDS. The smaller the salt transport coefficient the lower the product water TDS will be.

The normalized product flow (NPF) expressed in gallons per day (gpd), and the normalized salt rejection (NSR) expressed as a percentage, incorporate the water and salt transport coefficients as follows:

$$NPF = 1440 * P_{NORM} * a \quad (4)$$

$$NSR = \left[1 - \frac{1}{\left(1 + \frac{a}{b} * P_{NORM}\right)} \right] * 100\ \% \quad (5)$$

where P_{NORM} is the net driving pressure at standard conditions of 800-psi feed pressure, feedwater TDS of 35,000 mg/L, feed temperature of 25°C , a 6-psi RO element pressure drop, an NPF of 2,100 gpd, an NSR of 99.0 percent, a feedwater flow rate of 18.2 gpm, and a recovery rate of 8 percent. The value for P_{NORM} is 388 psi at standard conditions.

The current military specification for the RO elements states the NPF shall range between 1,850 to 2,550 gpd and the NSR shall be greater than or equal to 99.0 percent.

Test Results

The testing period in this study took place between 11/23/92 and 8/9/95. It involved six tests and five complete preservation cycles for Methods A through G. The evaluation of Method H, BIOCLEAN 882 began in August 1994 so only three tests and two preservations could be performed. The NSR and NPF versus total operating time are shown for each preservative method in Figures 1 through 14. The vertical dashed lines on the graphs separate each test run and indicate when a preservation cycle occurred.

Filmtec Element Performance

Method A-Citric Acid/Propylene Glycol

These elements were tested for a total of 1,581.7 hours and remained in storage for 778 days between 11/23/92 and 3/21/95. In Figure 1 the NSR is shown and indicates that preserved elements maintained their salt rejection better than control elements during the test period. The control group had a drop in NSR of 0.20% while the preserved elements had a decline of less than 0.05%. The NPF in Figure 2 shows the preserved elements also had a more stable flux than the control elements between tests 1 and 6. Control elements 2 and 7 had increases of 400 and 800 gpd respectively and remained above 2550 gpd for most of the test.

Method B-Product Water Flush

These elements were tested for a total of 1,588.9 hours and remained in storage for 779 days between 12/14/92 and 4/11/95. The salt rejection is shown in Figure 3 and product flux in Figure 4. All elements had noticeable declines in NSR during the test period. The preserved group showed an NSR decline between 0.15 to 0.20% and the control a drop of 0.25% between test 1 and 6. The control elements and preserved element 3 had large increases in NPF during the test period while preserved element 6 maintained a fairly stable flux.

Method C-MEMSTOR

These elements were tested for a total of 1,750.0 hours and remained in storage for 754 days between 1/4/93 and 4/25/95. Method C was quite effective in maintaining stable salt rejection during the test period with the preserved elements showing a decline of less than 0.05% as seen in Figure 5. The control elements had a drop in NSR of about 0.25%. In Figure 6 the NPF is shown and indicates the preserved elements remained in specification and had little change. Both control elements showed large increases in flux and remained well above 2550 gpd during most of the test period.

Method D-PROGARD

These elements were tested for a total of 1,696.4 hours and remained in storage for 763 days between 1/26/93 and 5/18/95. The preserved elements had a NSR decline between 0.10 and 0.15 % between tests 1 and 6 as shown in Figure 7. On the other hand elements in the control group, showed a drop in salt rejection between 0.25% and 0.30% with a corresponding increase in flux of 500 to 700 gpd. As shown in Figure 8, the preserved group maintained stable flux values during the test with only a slight increase of product water flow.

Method E-Sodium Bisulfite/Propylene Glycol

These elements were tested for a total of 1,598.9 hours and remained in storage for 773 days between 2/19/93 and 6/15/95. Method E had a detrimental effect on salt rejection as seen in Figure 9. The preserved elements had a drop in NSR greater than 0.30% whilie the control group had a decline of about 0.25%. In Figure 10, the NPF is shown and indicates successive increases for all elements during the test period. Control element 7, in particular, experienced a sharp rise in flux and remained well above 2550 gpd.

Method G-Proprietary Chemical

These elements were tested for a total of 1,857.5 hours and remained in storage for 784 days between 3/8/93 and 7/24/95. This preservative was modified prior to the last test cycle. The NSR is shown in Figure 11. Preserved element 6 remained below or at 99.0% during the test period. This element went out of specification during the baseline test run and can not be considered representative of a typical Filmtec membrane. The change in salt rejection for preserved element 3 was less than 0.05% while the control group had a decline of 0.20%. The NPF for all elements was quite stable with the control group having a larger increase in flux as seen in Figure 12.

Method H-BIOCLEAN 882

These elements were tested for a total of 1,010.9 hours and remained in storage for 405 days between 7/7/94 and 8/9/95. The salt rejection for all the elements was very stable during the three test runs with a drop in NSR of less than 0.05% recorded as seen in Figure 13. As seen in Figure 14, the two preserved elements had a slight decline in product flux while the control group exhibited a slight increase in product flux. Additional test cycles are required for this preservative solution to further evaluate the long term effects of preservation.

Microbiological Plate Count Data

During the element storage period, two samples of the preservative solution were taken at periodic intervals. Samples of preservative were taken at 1 week, 8 weeks, and prior to retesting. Three replicates were performed for each sample on the three growth media: marine, Luria, and GPA. An average number of CFUs per mL was determined for each media. No samples were taken for Method B, the product water flush, but plate counts were performed on the RO product water used to batch all the chemical preservatives.

The majority of the growth detected occurred on the marine and Luria media. The GPA media used for fungi usually had none detected and was discontinued in April 1995 toward the end of the test program. The plate counts for the marine and Luria media were almost the same in many cases. The marine media plate counts were used to evaluate preservative effectiveness in terms of microbiological growth because of its ability to support the growth of microorganisms present on seawater operated elements.

The plate count numbers for each method, shown in Table 2, a range of values observed for the marine growth media during the storage period. The range of plate count numbers for the product water used to batch the preservative solutions are also shown. These values were considered a baseline on which to evaluate the other preservatives. Methods D and E had the best results with plate count numbers typically below 10 CFUs per mL. Methods A, C, and H had plate counts between 10 and 100 CFUs per mL. Method G had the highest counts among the preservatives tested with values typically between 100 and 1000 CFU's/ml. Prior to the last test cycle, Method G was modified which reduced plate count numbers to between 10 to 100 CFU's/ml. The plate count values for the product water used in preparing the chemical solutions were usually greater than 1000 CFU's/ml.

Overall Performance

A summary of preservative performance is shown in Table 3. In terms of element performance parameters, salt rejection is the most important because it is related to the ability of the membrane to produce potable water. It is desired that the NSR remain as high as possible. The most effective at maintaining a stable salt rejection appear to be methods A, C, G, and H. The preserved elements for these methods had smaller declines in salt rejection (<0.05%) than elements preserved by methods B, D, and E. Method E was particularly detrimental to salt rejection performance. While the salt rejection was above 99.0 percent for all of the control elements, they tended to have a larger drop in NSR over the testing period than the preserved elements. This decline in salt rejection is undesirable and could eventually lead to an element falling below the 99.0 percent NSR military specification.

The starting and ending flux values in Table 3 shows the range of flux values for preserved elements 3 and 6. The preserved elements were better at maintaining a stable NPF and had smaller increases of flux than the control groups. The larger increases in NPF and subsequent drop in NSR seen for the control elements throughout the test program are an indication of membrane degradation.

Conclusions

The pattern of usage for the ROWPU during this evaluation was operating 250 to 300 hours on an open seawater intake with an RO element storage period of 16 to 20 weeks. This pattern was repeated six times during the test program. While both preserved and control elements maintained normalized salt rejections above the specification of 99.0 percent, the control group typically had larger declines during the test period. There was an observable benefit to preserving elements with methods A, C, G, and H. The elements preserved by these four methods had an overall change in NSR of less than 0.05% during the test period while the control elements typically exhibited a decline in NSR between 0.25 and 0.30%. The control elements also had a larger increase in product flux than the preserved elements. However the differences between the preserved elements and control elements, in terms of salt rejection and product water flux, were not as dramatic as expected.

Recommendations

The decision to perform a chemical preservation for RO elements used by mobile military desalination equipment depends on the length of storage and type of water source that the equipment is operating on. Table 4 summarizes our recommendations to the military. A chemical preservation should be performed for RO elements operated on low to moderate biologically active waters, such as cold seawater when the storage period is greater than four months. For shorter storage periods from 24 hours to 4 months, a product water flush should be performed on the ROWPU system to remove corrosive brine from the piping.

We are also recommending that elements operated on a microbiologically active feedwater, such as surface freshwater, should be chemically preserved if the storage period is 2 weeks or greater. A product water flush should also be performed for shorter storage periods.

Table 1
Characteristics of RO Element Preservatives

Method	Preservative	Average Solution pH[1]	Average Solution Conductivity[1] micromhos/cm
A	Citric Acid/Propylene Glycol	3.72	1265
B	Product water flush	6.34	534
C	MEMSTOR	4.78	3758
D	PROGARD	6.37	1032
E	Sodium Bisulfite/Propylene Glycol	3.17	6117
G	Proprietary solution	4.93	7883
G[2]	Proprietary solution	2.92	7695
H	BIOCLEAN 882	2.15	4193

Notes:
1. Values shown were measured after recirculation through the elements.
2. Method G was modified prior to the last test cycle.

Table 2
Summary of Microbiological Plate Count Data

Method	Preservative Plate Counts[1] CFU's/ml	Product Water Plate Counts[2] CFU's/ml
A	10 to 100	10,000 to 100,000
B	NM	1000 to 10,000
C	10 to 100	1000 to 10,000
D	< 10	100 to 1000
E	< 10	1000 to 10,000
G	100 to 1000	10,000 to 100,000
G[3]	10 to 100	10,000 to 100,000
H	10 to 100	100 to 1000

Notes:
1. This data is the range of plate counts for marine growth media during the 16 to 20 week storage period. Colony forming units per ml.
2. The data shown is for the product water used to batch the chemical solutions.
3. Method G was modified prior to last test cycle.

Table 3
Summary of RO Element Performance

Method	Start NPF[1] El. 3	Finish NPF El. 3	Start NPF El. 6	Finish NPF EL. 6	Overall Change in NSR[2] Preserved Elements (%)
A	1820	1960	1710	1825	<0.05
B	1630	1900	1550	1605	0.15 to 0.20
C	1885	1760	2075	2105	<0.05
D	1810	1950	1870	2200	0.10 to 0.15
E	1780	2360	1775	2260	>0.30
G	2140	1875	2270	2010	<0.05
G[3]	1875	1850	2010	1990	<0.05
H	1380	1330	1560	1400	<0.05

Notes:
1. Normalized product flow, (gallons per day). Values shown are an average.
2. Normalized salt rejection. This is the difference between start and finish.
3. Method G was modified prior to last test cycle. This is for one test run only.

Table 4
Recommended Preservation Schedule for Military ROWPU's

Storage Period	Seawater Operation	Surface Freshwater Operation
24 hrs to 2 weeks	PWF[1]	PWF
2 weeks to 4 months	PWF	CP[2]
> 4 months	CP	CP

Notes:

1. PWF is product water flush using unchlorinated product water.
2. CP is a chemical preservative.

FIGURE 1
NORMALIZED SALT REJECTION (NSR)- FILMTEC ELEMENTS - SET A
PRESERVATIVE: CITRIC ACID/PROPYLENE GLYCOL

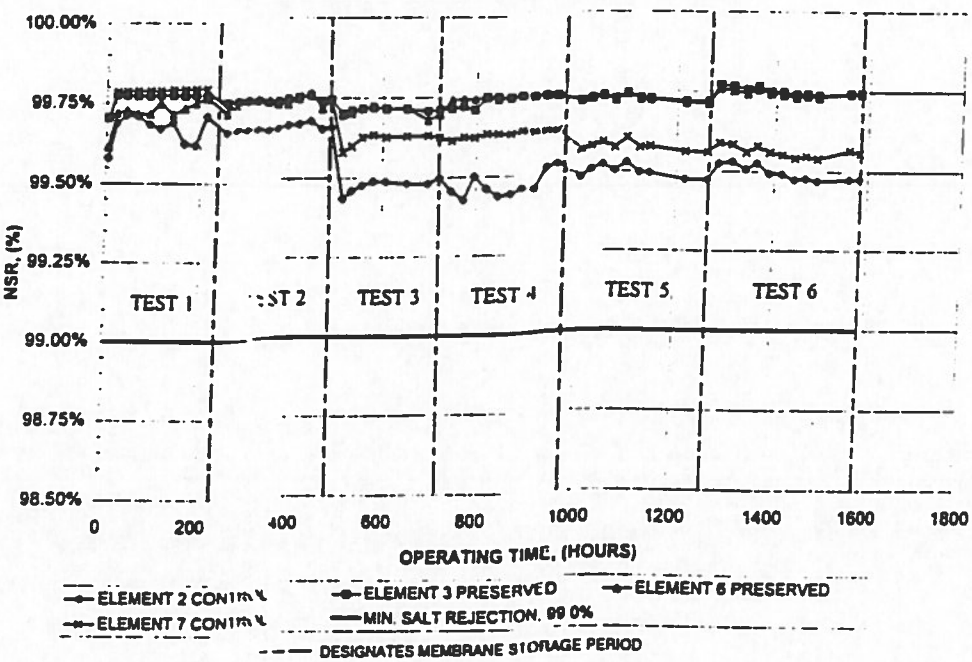

FIGURE 2
NORMALIZED PRODUCT FLOW (NPF)- FILMTEC ELEMENTS - SET A
PRESERVATIVE: CITRIC ACID/PROPYLENE GLYCOL

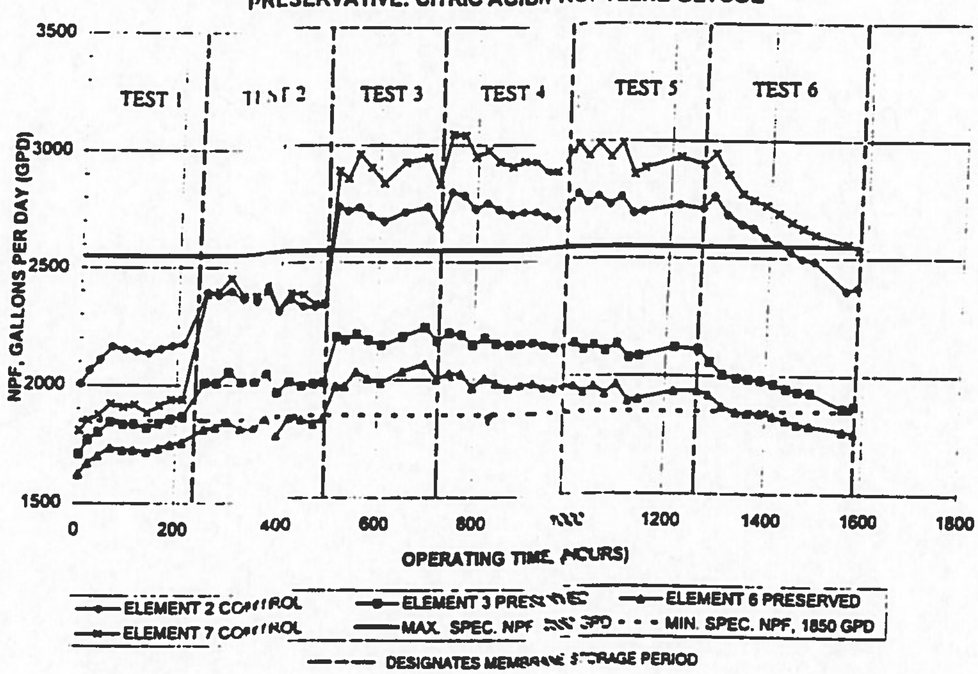

FIGURE 3
NORMALIZED SALT REJECTION- (NSR)- FILMTEC ELEMENTS - SET B
PRESERVATIVE: PRODUCT WATER FLUSH

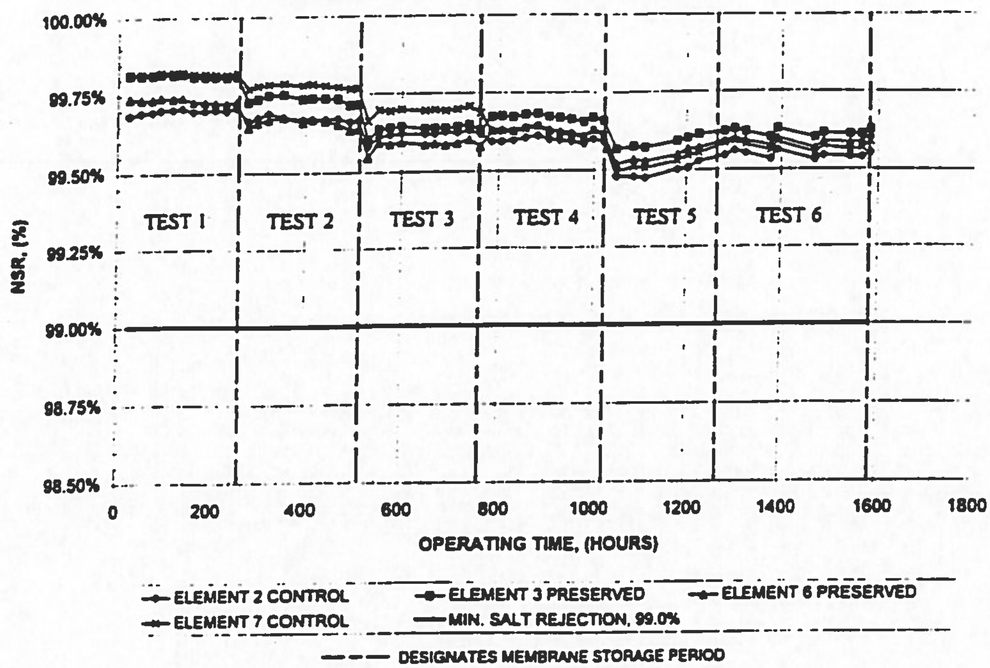

FIGURE 4
NORMALIZED PRODUCT FLOW- (NPF)-FILMTEC ELEMENTS - SET B
PRESERVATIVE: PRODUCT WATER FLUSH

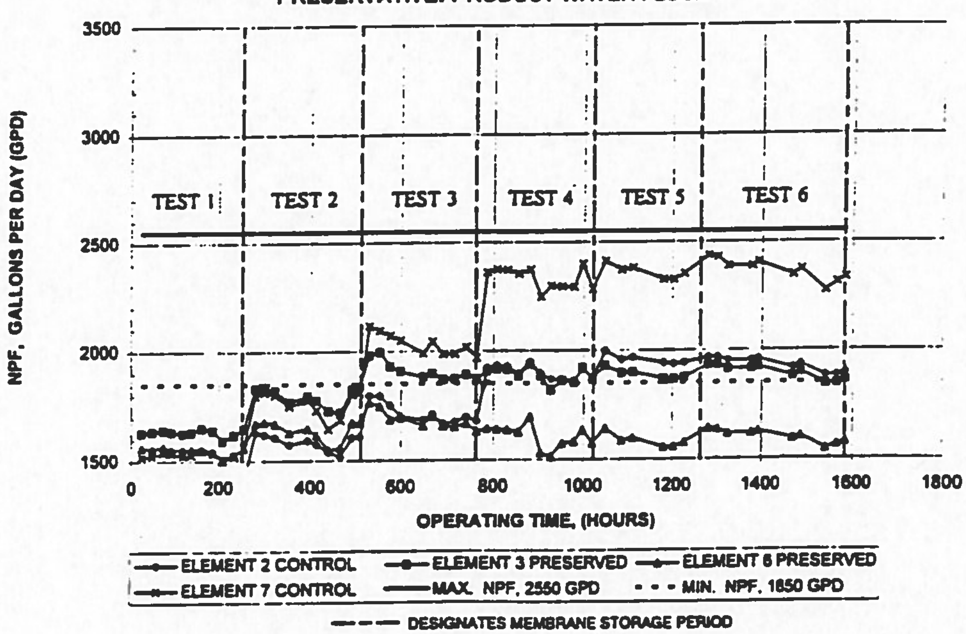

FIGURE 5
NORMALIZED SALT REJECTION- (NSR) FILMTEC ELEMENTS - SET C
PRESERVATIVE: MEMSTOR

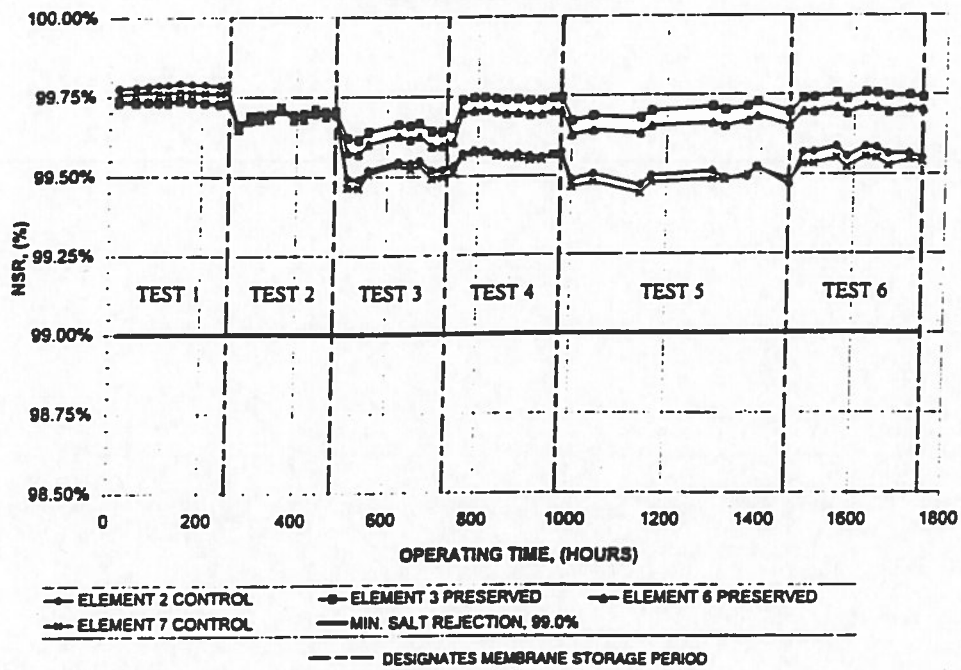

FIGURE 6
NORMALIZED PRODUCT FLOW- (NPF) FILMTEC ELEMENTS - SET C
PRESERVATIVE: MEMSTOR

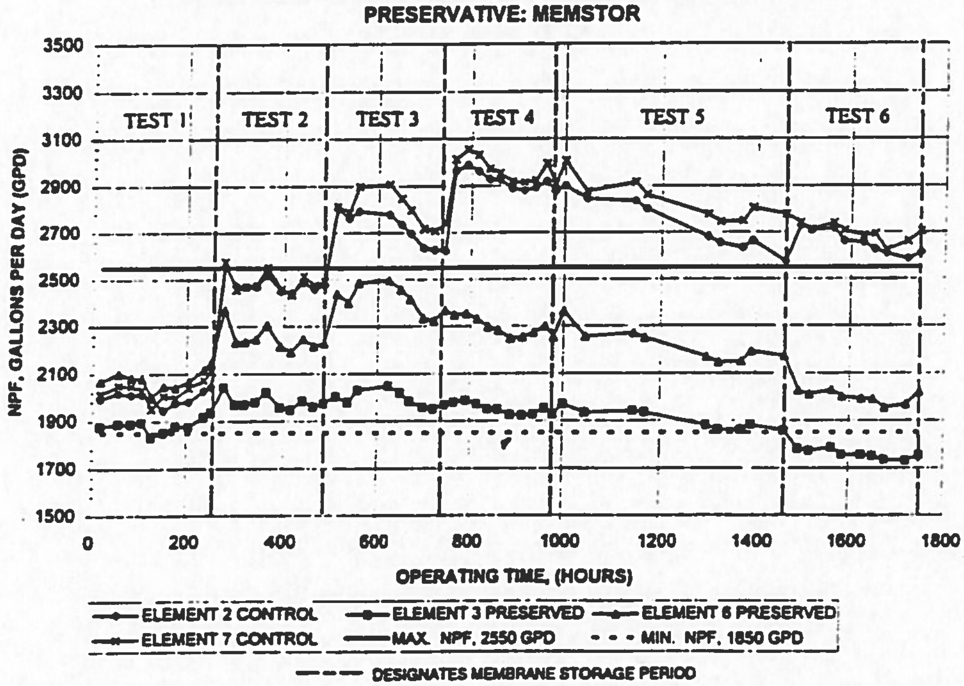

FIGURE 7
NORMALIZED SALT REJECTION- (NSR)- FILMTEC ELEMENTS - SET D
PRESERVATIVE: PROGARD

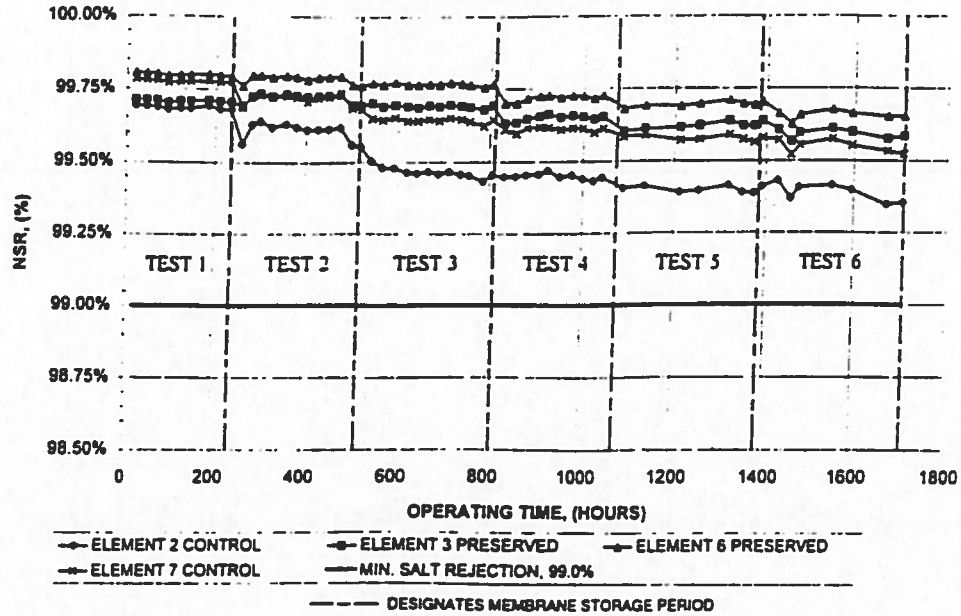

FIGURE 8
NORMALIZED PRODUCT FLOW- (NPF)- FILMTEC ELEMENTS - SET D
PRESERVATIVE: PROGARD

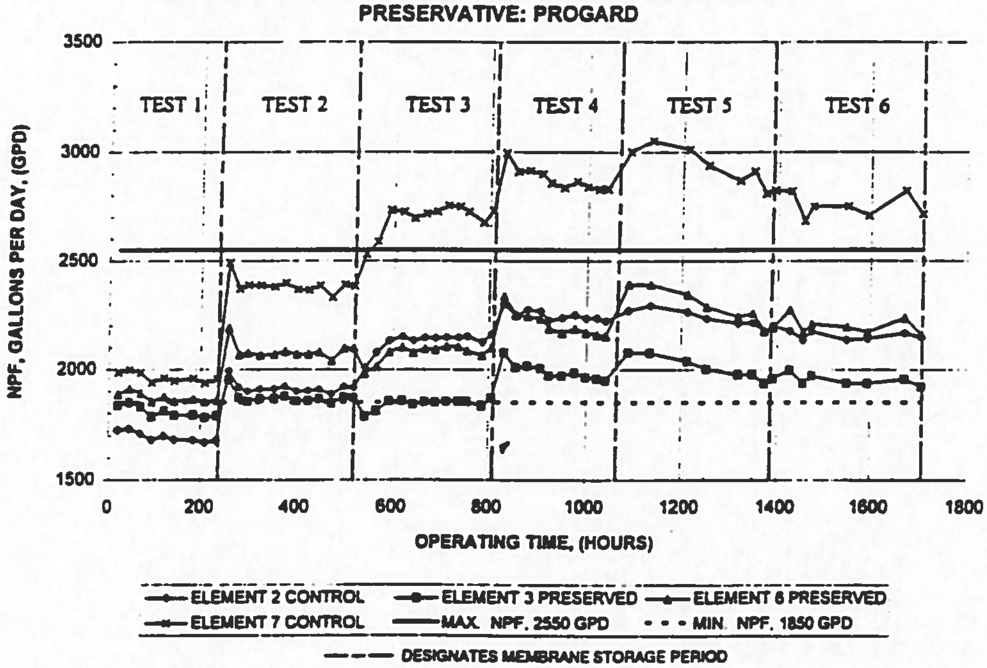

FIGURE 9
NORMALIZED SALT REJECTION- (NSR)- FILMTEC ELEMENTS - SET E
PRESERVATIVE: SODIUM BISULFITE/PROPYLENE GLYCOL

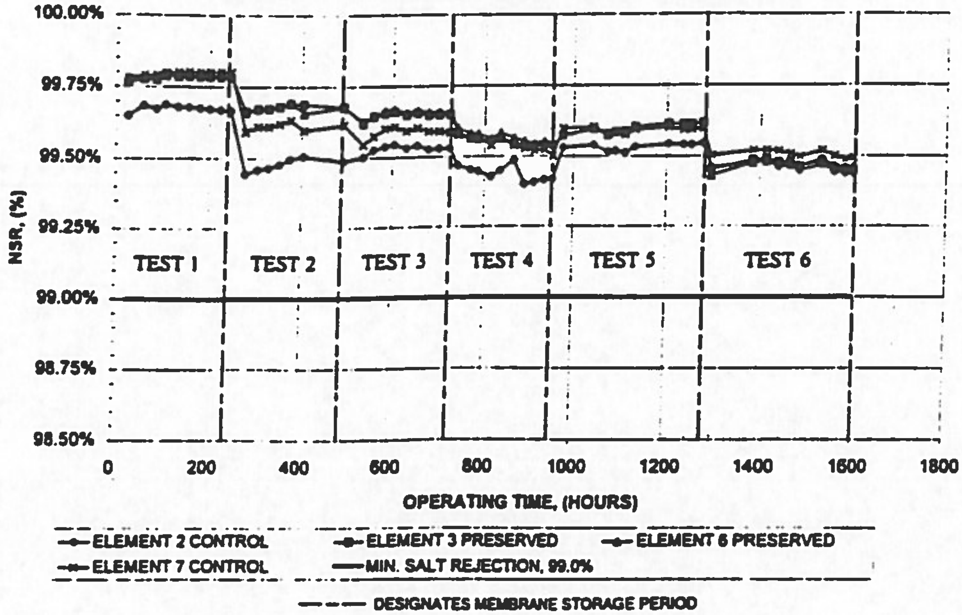

FIGURE 10
NORMALIZED PRODUCT FLOW-(NPF)- FILMTEC ELEMENTS - SET E
PRESERVATIVE: SODIUM BISULFITE/PROPYLENE GLYCOL

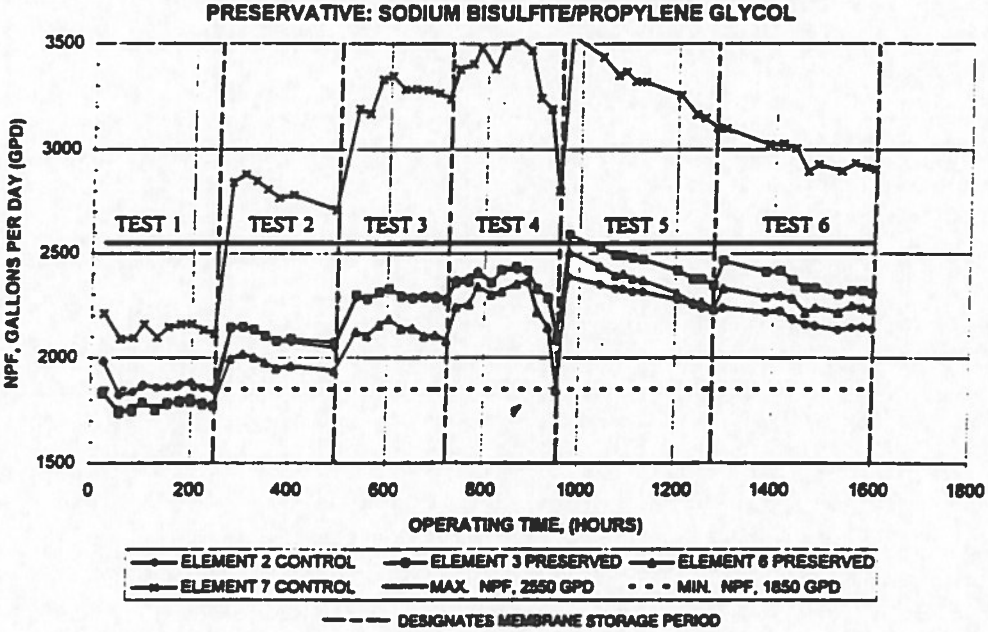

FIGURE 11
NORMALIZED SALT REJECTION- (NSR)- FILMTEC ELEMENTS - SET G
PRESERVATIVE: PROPRIETARY CHEMICAL

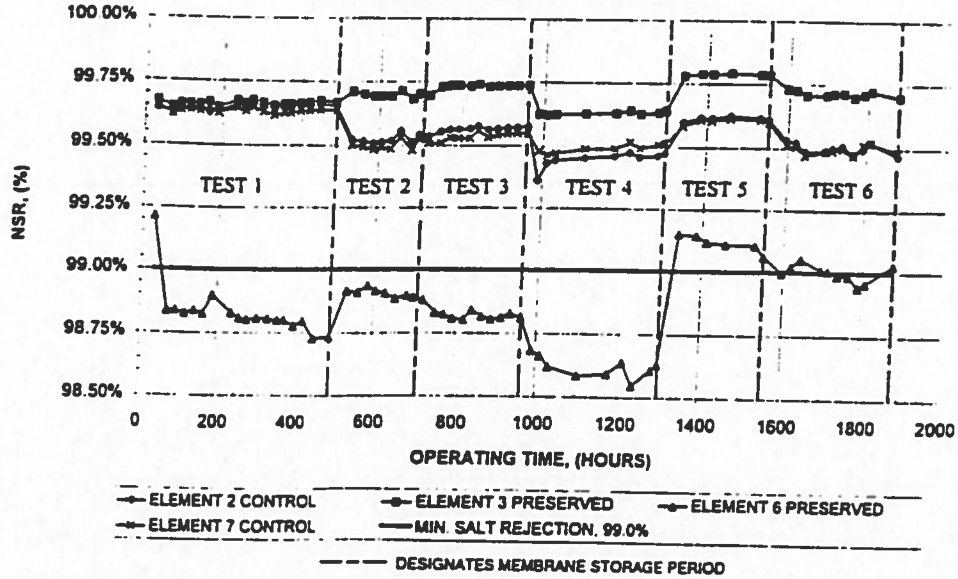

FIGURE 12
NORMALIZED PRODUCT FLOW-(NPF) FILMTEC ELEMENTS - SET G
PRESERVATIVE: PROPRIETARY CHEMICAL

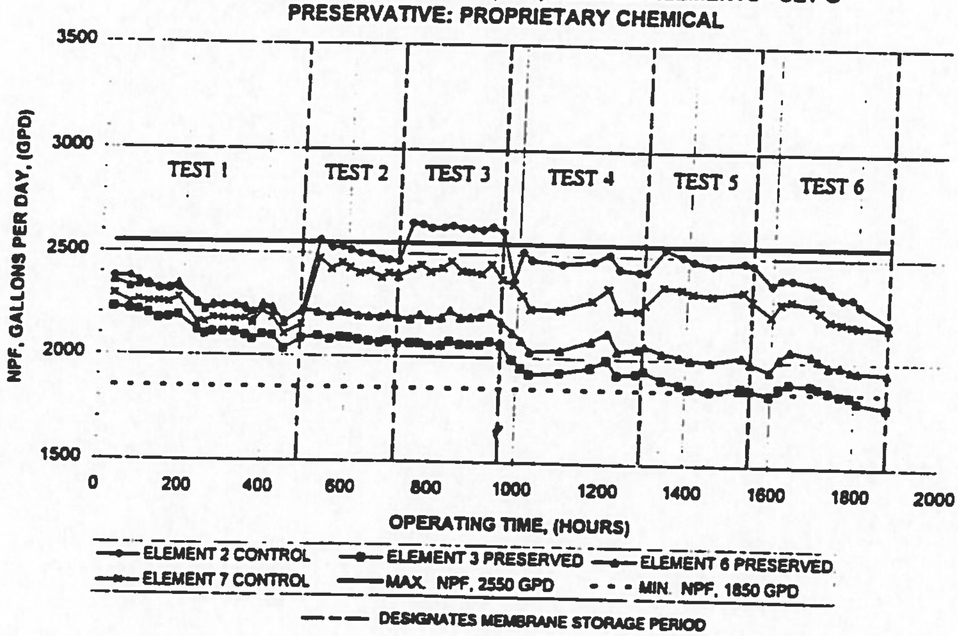

FIGURE 13
NORMALIZED SALT REJECTION-(NSR) -FILMTEC ELEMENTS - SET H
PRESERVATIVE: BIOCLEAN 882

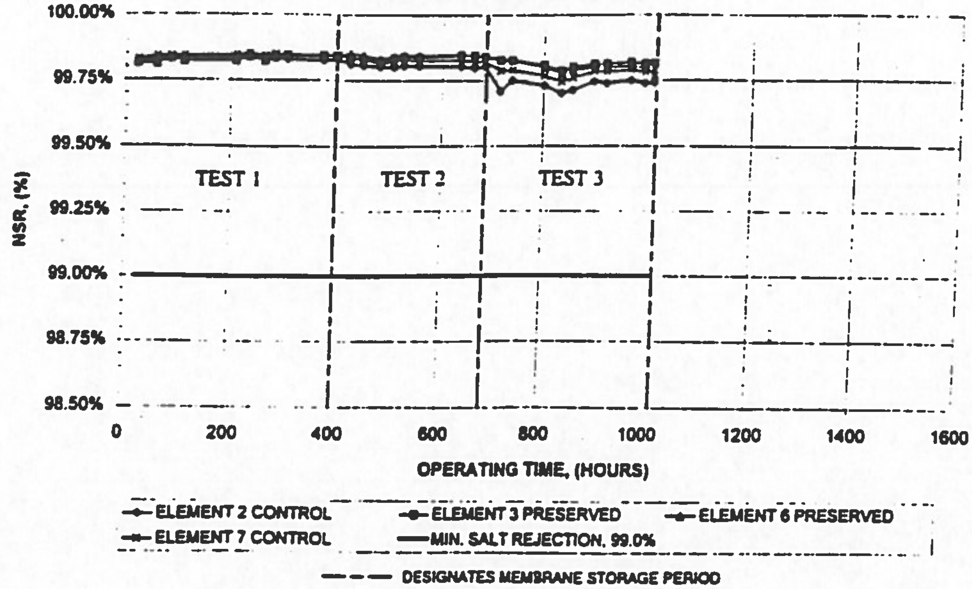

FIGURE 14
NORMALIZED PRODUCT FLOW-(NPF)- FILMTEC ELEMENTS - SET H
PRESERVATIVE: BIOCLEAN 882