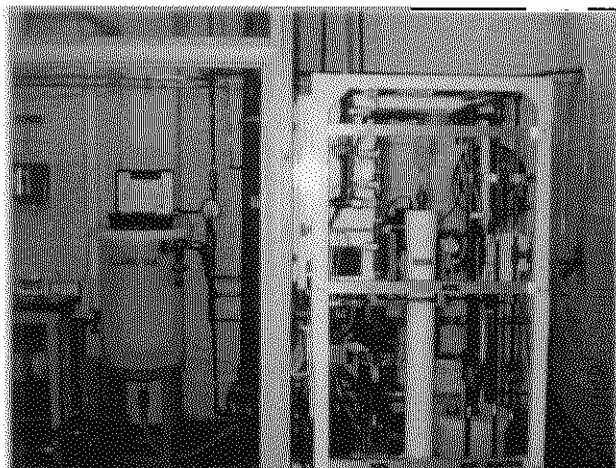
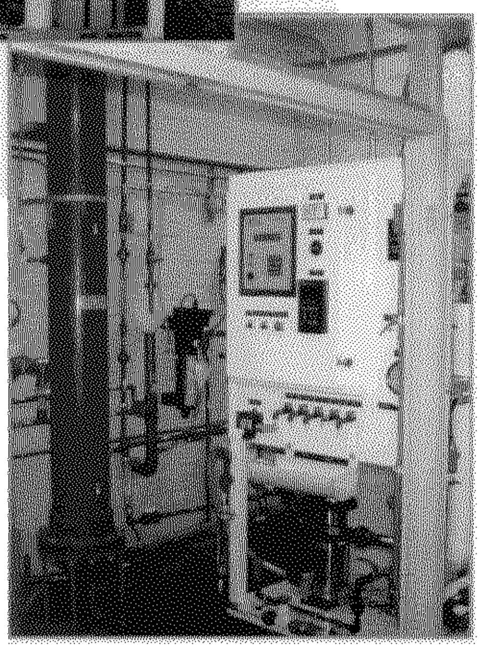
Final Report

Information Collection Rule (ICR)

Membrane Treatment Study





Prepared for

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July 14, 1999

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ICR Membrane Treatment Study - Final Report

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Background Information

The City of Norfolk, Virginia, owns and operates two water treatment plants that provide drinking water to the City, as well as to several consecutive systems, including the U.S. Navy. The 37th Street and Moores Bridges Water Treatment Plants (WTPs) treat 28 and 108 million gallons per day of surface water, respectively. The source waters for both plants are essentially the same series of reservoirs. While the Moores Bridges WTP primarily treats water from Lake Prince, Lake Western Branch and Lake

Wright, the 37th Street WTP treats water exclusively from Lake Western Branch. Both plants provide alum coagulation, sedimentation, granular media filtration with pre-filter chlorination.

The Information Collection Rule (ICR) required that the City conduct bench-scale treatment studies, using either membranes or granular activated carbon (GAC) for disinfection by-product precursor reduction. Since earlier studies had been conducted on the City's water using GAC, the City opted to study membranes. The ICR offered two options for membrane bench-scale testing: the Rapid Bench-Scale Membrane Test (RBSMT) and the Single-Element Bench-Scale Test (SEBST). The SEBST could be conducted in quarterly runs, or as a continuous, long-term test. The nine-month (6,600-hour), Long-Term SEBST (LTSEBST) was selected to provide the City with representative data on membrane performance, reflecting seasonal water quality variations.

Given similar source water quality for both treatment plants, defined by the ICR as source waters with TOC levels within ten percent of the mean for the two plants, only one treatment study was required. It was conducted at the 37th Street WTP.

Project Objectives

The primary objective of the membrane study was to satisfy the requirements of the ICR. The purpose of the ICR treatment studies is to generate cost and performance data for membrane processes used to meet proposed maximum contaminant levels (MCLs) of the Stage 2 Disinfectants/Disinfection By-Products Rule (D/DBPR), when free chlorine is used as a disinfectant. Nanofiltration (NF) membranes with sufficiently low molecular weight cutoff (MWCO • 1,000 Daltons) can achieve significant DBP precursor rejection. NF is also very effective at controlling pathogens.

Because the City of Norfolk periodically experiences elevated manganese levels in the raw water, chlorine is applied ahead of the granular media filters to catalytically oxidize and remove dissolved manganese on the filter media. Elimination of filter pre-chlorination to reduce DBP formation would require that manganese removal be provided. Therefore, a secondary objective of the project was to determine if the selected NF membranes could remove dissolved manganese as needed to meet the secondary MCL of 0.05 mg/L when manganese levels are elevated in the raw water.

The City was also interested in obtaining data on the characteristics of the membrane concentrate to enable a meaningful evaluation of possible future concentrate disposal options. In addition, the City was interested in minimizing concentrate flowrate to maximize their available yield. Toxicity studies and other potential discharge permit parameters were evaluated on the concentrate stream while operating the LTSEBST at maximum anticipated system recovery of 90 percent. However, to obtain permeate water quality representative of full-scale NF system operation, the SEBST (which employs concentrate recycle) was routinely operated at the minimum recovery of 75 percent recommended under the ICR. DBP and water quality samples were collected during both 75 and 90 percent recovery operations. The distinction between operating conditions to obtain representative permeate water quality and those required to obtain representative concentrate water quality is further described below.

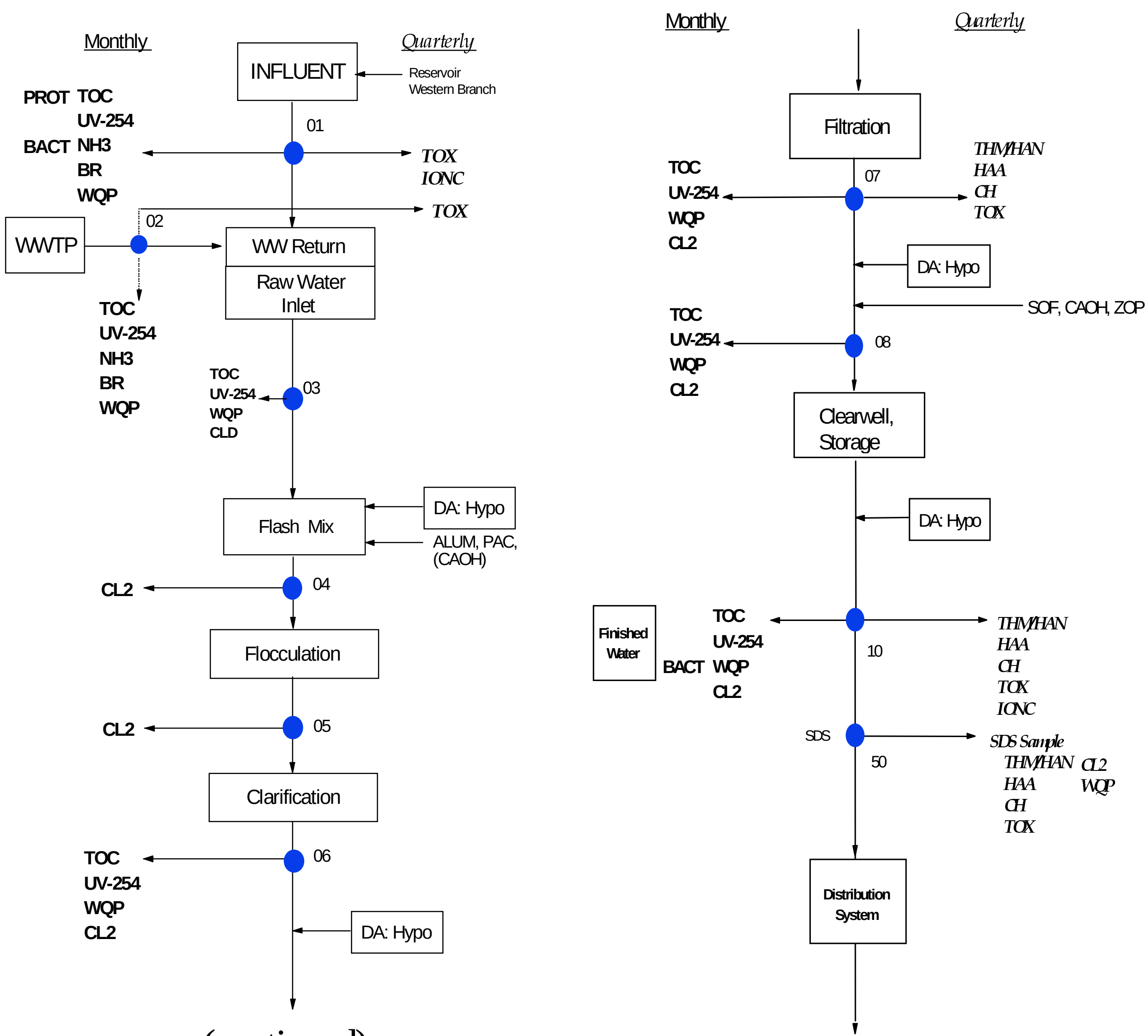
Treatment Plant Description

Both of the City's WTPs employ conventional treatment technologies. However, the Moores Bridges plant has recently installed high rate plate settlers into the existing sedimentation basins. As a result, polymer is fed at Moores Bridges, whereas it is not fed at the 37th Street WTP where the SEBST was conducted. In addition, lime is routinely fed to the rapid mix at Moores Bridges. Under normal operating conditions, lime is not fed at the 37th Street plant unless additional alkalinity is required for the coagulation process.

Treatment Plant Schematic

Figure 1 is the 37 WTP plant schematic developed under the ICR for determining monitoring point sample locations.

Figure 1. ICR Treatment Plant Schematic for 37th Street WTP



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Treatment Plant Design Information

Following are the component unit processes at the 37th Street WTP:

Flash Mixer

- Mechanical mixer
- Unbaffled
- Liquid volume: 4,189 gals
- Mean Velocity Gradient: 78 sec^{-1}

Flocculation Basins

- Mechanical
- Unbaffled
- Liquid volume: 2,345,132 gals
- 4-trains
- 4-stages/train

  Stage 1:
  - Liquid volume: 122,582 gals
  - Mean Velocity Gradient: 30 sec^{-1}

  Stage 2:
  - Liquid volume: 154,567 gals
  - Mean Velocity Gradient: 29 sec^{-1}

  Stage 3:
  - Liquid volume: 154,567 gals
  - Mean Velocity Gradient: 29 sec^{-1}

  Stage 4:
  - Liquid volume: 154,567 gals
  - Mean Velocity Gradient: 27 sec^{-1}

Sedimentation Basins

- Surface Area: 59,134 ft^2
- Liquid volume: 3,980,826 gals

Filters

- Number: 24
- Surface Area: 469,512 ft^2
- Total Media Depth: 35 in.
- Media Type: Dual
- Minimum Water Depth to Top of Media: 3.5 ft
- Depth from Top of Media to Top of Backwash Trough: 2.5 ft

Finished Water Clearwells

- Number: 2
- Surface Area: 73,381 ft^2
- Liquid Volume: 6,586,678 gals
- Covered

Treatment Plant Chemical Feed

Typical chemical feed dosages at the 37th Street WTP are as follows:

Flash Mix

- Aluminum sulfate: 31 mg/L
- Powdered activated carbon: 6.6 mg/L
- Calcium hydroxide (if needed): 1.8 mg/L

Note that calcium hydroxide was not fed to the rapid mix during most of the ICR treatment study.

Settled Water (just upstream of Filtration)

- Sodium hypochlorite: 3.3 mg/L

Filtered Water (just upstream of Finished Water Clearwell storage)

- Sodium hypochlorite: 1.9 mg/L
- Zinc orthophosphate: 2.6 mg/L
- Calcium hydroxide: 8.3 mg/L

Finished Water (just before entry to distribution system)

- Sodium hypochlorite: 0.5 mg/L

Treatment Challenges Facing Plant

The 37th Street WTP meets all current drinking water regulatory standards. To meet the Stage 1 D/DBP Rule and Interim Enhanced Surface Water Treatment Rule (ESWTR), the City will provide primary disinfection using free chlorine and secondary/residual disinfection with chloramines. It is unlikely, however, that this strategy will suffice in meeting the Stage 2 D/DBP Rule and Long Term 2 ESWTR. An advanced treatment process to remove organic material or an alternative disinfectant will be required to meet the combined objectives of these future regulations.

Historical Source and Finished Water Quality

A summary of raw water quality characteristics for both the 37th Street and Moores Bridges WTPs is provided in Table 1.

Table 1. Raw Water Quality, January 1996- January 1999

PARAMETER	37th Street WTP			Moores Bridges WTP		
	AVERAGE	MAX	MIN	AVERAGE	MAX	MIN
Temperature (degrees Centigrade)	20	32	9	20	30	6
pH	6.9	7.6	6.4	7.1	7.7	6.0
Turbidity (NTU)	4.2	15.7	7.6	4.2	15.8	1.5
Alkalinity (mg/L as $CaCO_3$)	19	29	10	28	70	11

Table 1. Raw Water Quality, January 1996- January 1999

PARAMETER	37th Street WTP			Moores Bridges WTP		
	AVERAGE	MAX	MIN	AVERAGE	MAX	MIN
Total Hardness (mg/L as $CaCO_3$)	37	58	28	45	79	21
TOC (mg/L)	6.6	13.0	5.6	7.0	9.3	5.4
Color	36	55	15	43	100	15
Iron	0.37	0.75	<0.03	0.45	1.17	<0.03
Manganese	0.048	0.36	<0.14	0.061	0.78	<0.014

Materials and Methods

This section describes the materials and methods employed in conducting the Long-Term SEBST, ICR Treatment Study.

Pretreatment Processes

A schematic of the ICR Membrane Study system is provided in Figure 2. Alum-coagulated, settled water was pumped from the full-scale plant at a rate of 1.67 gpm to a 10-inch diameter, dual media, pressure, pilot filter (filter loading rate of 3.3 gpm/sf). The filter media was based on the future filter design for 37th Street WTP when the plant filter system is upgraded. The plant's practice of chlorine addition prior to filtration required that a pilot filter be used to process unchlorinated settled water for membrane treatment, in accordance with ICR requirements.

Pilot-filtered water was collected in a 500-gallon clearwell and pumped through a cartridge filter. Initially, only scale inhibitor (King Lee PreTreat Plus 0100) was added prior to cartridge filtration. This is a phosphonate-based scale inhibitor. Its use minimizes the organic carbon contribution in comparison with a polymer-based scale inhibitor.

Advanced Treatment Process Information

Process Equipment

The test membrane was contained in a Single Element Pilot Unit manufactured by Harn R/O Systems, Inc. Flow, pressure, pH, conductivity, temperature, and run time were automatically monitored and recorded using a RODI Membrane Monitor system. These parameters were monitored at selected points in the NF process train, as indicated in Figure 3. Permeate was collected in a cleaning tank and was used as cleaning solution makeup water. Pilot-filtered water was used to prepare scale inhibitor feed stock solutions.

Figure 2. ICR Membrane Study System Schematic

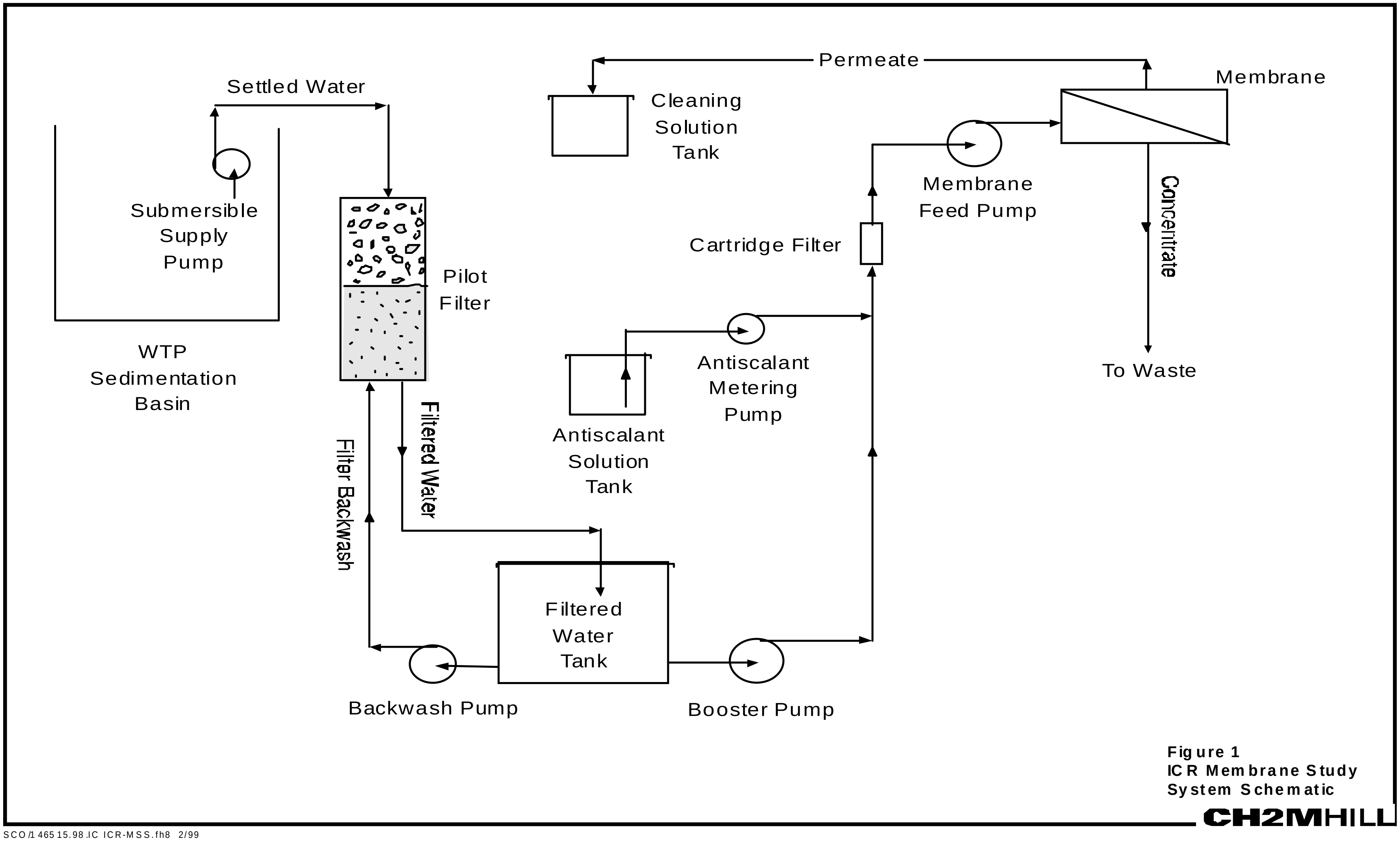
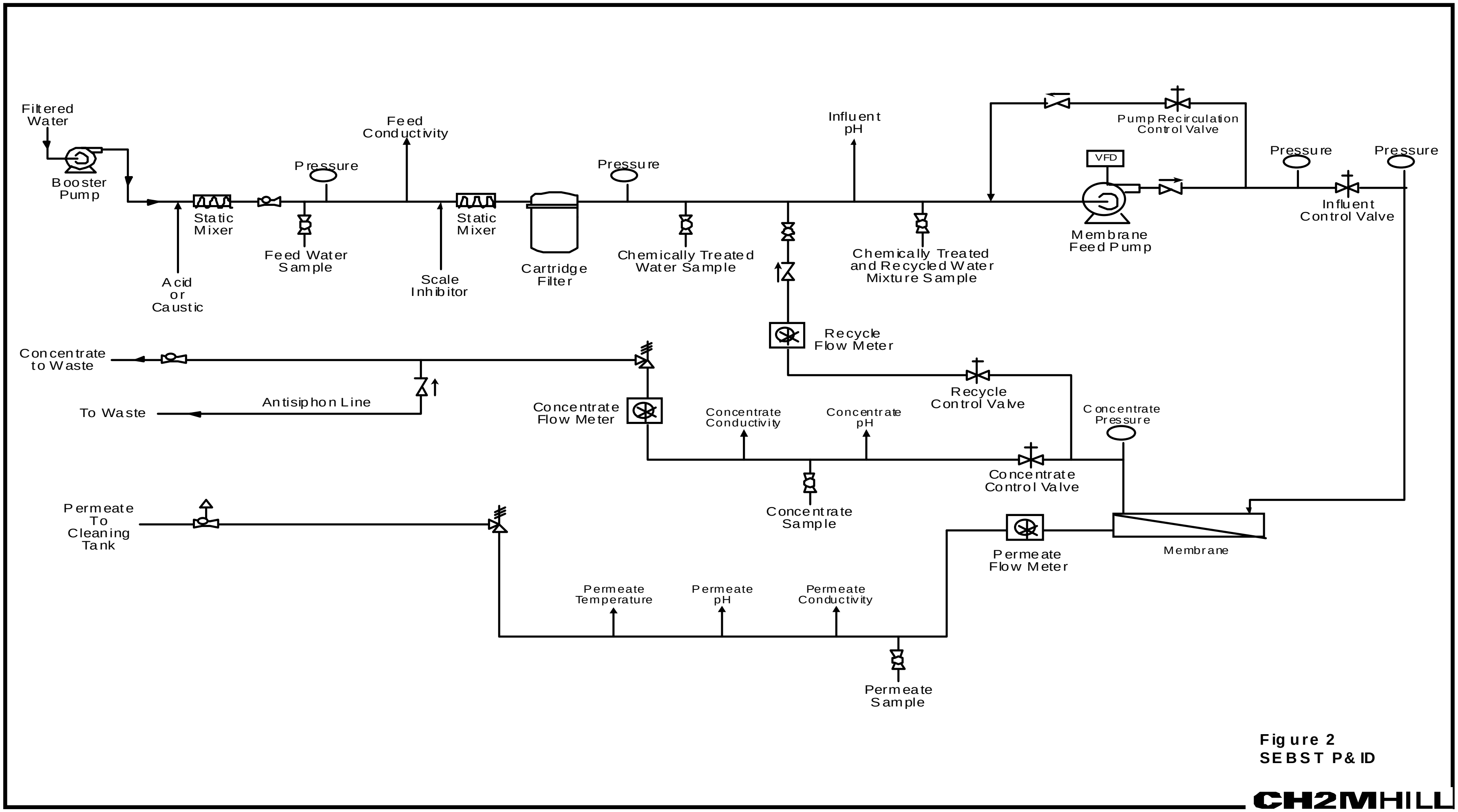


Figure 3. SEBST Monitoring Points



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Experimental Design

ICR Membrane Study System Description

To obtain the target operating recoveries, a portion of the membrane concentrate was recycled to the suction side of the NF feed pump. The pilot-filtered stream is referred to as “Feed” and mixture of Feed and recycled concentrate as “Influent.” The impact on water quality of using this recycle stream is described below.

SEBST Design and Operation

To enhance NF cost effectiveness, it is desirable to operate the process at a high feedwater recovery rate to reduce feedwater pretreatment costs and to minimize the amount of treated water discarded as waste (concentrate). Based on the chemistry of the filtered water from the 37th St. WTP, a recovery of 90 percent was projected to be feasible based on scaling indices for the filtered water.

The SEBST contains a single element in a single pressure vessel. The element is operated to produce the same permeate flow as the average permeate flow for the full-scale system or 0.7 gpm. Proper hydraulic operation for a single element requires that element recovery be $\leq$15%. This requires the element feed flow to be 4.7 gpm, resulting in a concentrate flow of 4.0 gpm. To achieve 90% feedwater recovery, the feedwater flow must be 0.78 gpm with a concentrate flow 0.078 gpm. However, to maintain a maximum element recovery of 15%, it is necessary to recirculate a relatively large flow (4.7 –0.78 = 3.95 gpm) across the element in a concentrate recycle loop.

Concentrate recycle permits the desired element recovery (15%) and the desired system recovery (90%), however it penalizes permeate quality. The concentrate stream that is recycled back to the element feed side contains a very high solute concentration. When 3.95 gpm of concentrate flow (containing high solute concentration) is blended with 0.78 gpm of incoming filtered water (at a lower solute concentration), the solute concentration to the single element is greater than a full-scale system would experience.

In a full-scale system the first stage produces the most permeate flow; conversely, the final stage produces the least permeate flow. Because the flow contribution of the first stage to the total system permeate (sum of all system stages) is greater than that of the other stages, its permeate solute concentration dominates the composite permeate solute concentration.

In contrast, the permeate solute concentration of the SEBST unit is greater compared to the composite solute concentration of a full-scale system because the single element is fed a higher average feedwater solute concentration than other stages of the full-scale system. The higher feed concentration results in a significantly higher solute concentration in the permeate of the SEBST unit than the permeate from a full-scale design.

Therefore, it is evident that the permeate TOC level from the SEBST unit would be greater than that from the full-scale system when operated at the same feedwater recovery. Because of this, it is necessary to operate the single-stage unit at a lower recovery rate to simulate a full-scale system.

Using a solution-diffusion solute passage model that accounts for the concentration of TOC through each stage and the permeate flow of each, a log-mean average feedwater TOC concentration was estimated. The log-mean average concentration was then compared with the average feedwater TOC concentration achieved in the SEBST to determine the respective SEBST recovery. Use of this model for the filtered water at 37th St. WTP predicts an SEBST recovery of approximately 66 percent.

The ICR recommends a minimum SEBST recovery of 75 percent. This is greater than the projected 66 percent that would be needed to represent full-scale permeate water quality at 90 percent recovery. As such, the membrane selected for the LTSEBST for ICR operation was run at a recovery of 75 percent, and provided a conservative estimate full scale permeate water quality.

Operation of the SEBST at 90 percent recovery will produce a concentrate that simulates the concentrate from a full-scale system operating at the same recovery rate. During concentrate testing, the SEBST unit was operated at 90 percent recovery to more fully characterize the concentrate waste stream. In addition, bioassay testing was performed with the concentrate to confirm that it is not acutely toxic to indicator organisms.

Membrane Screening Results

The membrane that was used in this study was selected by conducting a series of screening tests using the SEBST apparatus. Seven different thin-film composite membranes were tested prior to initiation of the ICR Treatment Study, with the best performer selected for the LTSEBST. Selection was based on achieving sufficient TOC removal, manganese rejection, and high specific flux. Manganese rejection was required to be a minimum of 88 percent to reach the SMCL of 0.05 mg/L Mn, given a maximum influent concentration of 0.4 mg/L. In addition, concentrate analyses were evaluated for parameters of concern relative to anticipated discharge permit requirements, such as total phosphorus, at both 75 and 90 percent recoveries. The total phosphorus limit of 2 mg/L restricted the use of just one of the membranes screened. The membranes were screened under identical flow conditions. The results are summarized in Table 2, in order of increasing net operating pressures.

Table 2. Summary of Membrane Screening Test

Manufacturer	Membrane	Net Pressure	TOC Rejection	Mn Rejection	Total Phosphorus @ 75% Recovery	Total Phosphorus @ 90% Recovery
Osmonics Desal	HL	36	94.8%	69.1%	0.16	0.55
FilmTec	NF70	46	98.0%	95.0%	0.12	0.30
Hydranautics	ESNA	55	84.5%	99.4%	0.35	0.76
FilmTec	NF90	61	87.5%	99.3%	0.30	0.83
Fluid Systems	TFCULP	64	99.6%	99.6%	1.99	5.86
Osmonics Desal	DL	78	95.2%	85.7%	0.23	0.48
Hydranautics	LFC1	99	95.4%	99.8%	0.19	0.61

All membranes screened achieved adequate TOC removal. Consideration of the best-performing membranes in terms of pressure requirements and manganese rejection performance led to the selection of the Dow FilmTec NF70 membrane for conducting the ICR LTSEBST.

Water Quality Monitoring

The water quality parameters monitored consisted of those required under the ICR, as well as several other key parameters to help characterize potential foulants and concentrate water quality. These parameters are noted below under the discussion of results.

Analytical Methods

The analytical methods, and corresponding method reporting levels, are provided in Appendix A.

Results and Discussion

Process Performance – NF70

Membrane Pretreatment Adjustments and Operational Results

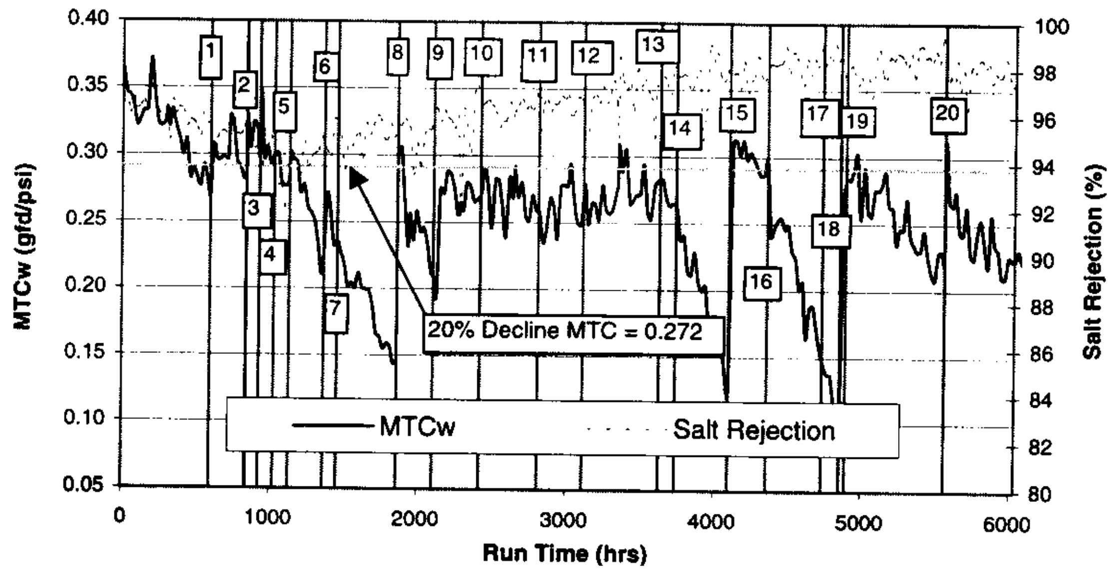
The ICR study with the selected membrane began on May 15, 1998. Initially, the only chemical adjustment made to the membrane feedwater was the addition of a phosphonate-blend scale inhibitor to prevent scaling by sparingly soluble salts. This was followed by a 20-micron cartridge filter.

As the rate of membrane fouling became excessive, pretreatment was adjusted several times in an attempt to alleviate fouling. Cleaning and subsequent pretreatment modifications were triggered by membrane performance degradation. Specific flux, as expressed by the Water Mass Transfer Coefficient (MTC_w) and membrane differential pressure (DP), were the primary indicators of fouling. The graphs in Figure 4 show the MTC_w, Differential Pressure and Temperature with SEBST run time for the NF70 membrane. Key treatment events are noted on the graphs and described below in Table 3.

FilmTec NF70
Norfolk ICR SEBST

NOTES

1 - NaOH Cleaning
2- Citric acid & NaOH Cleaning
3 - H3PO4 & NaOH Cleaning; 1 um CF
4 - 0.2 um CF
5 - Filter nozzle failure
6 - NaOH cleaning; NH2CL startup
7 -Temperature Probe Correction
8 - NaOH & HCl Cleaning
9 - NaOH Extended Cleaning & NaOH Feed Begun
10 - Concentrate conductivity transmitter replaced
11 - Chloramine feed stopped
12 - 90% Recovery Test 1
13- Lime feed at plant begun
14 - Lime feed at plant stopped
15 - HCl & NaOH Cleaning
16 - Probes calibrated
17 - 90% Recovery Test 2
18 - HCl & NaOH Cleaning
19 - Lowered flux to 9 gfd
20 - Cleaning; Drop pH to 4.0



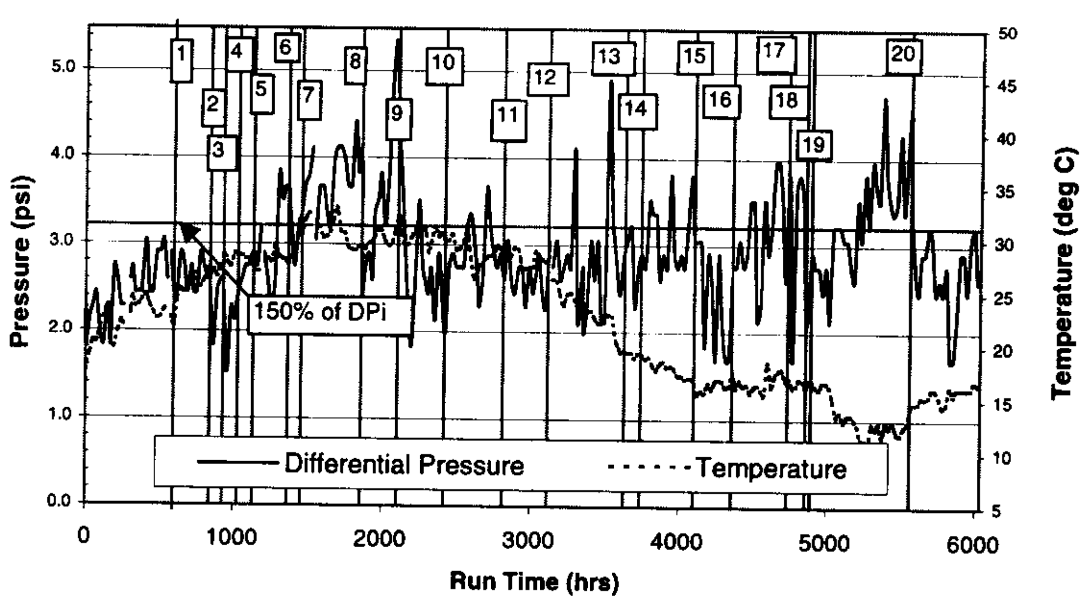


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Figure 4

Table 3. Key ICR SEBST Treatment Events

Event No.	Run Time in hours	Days since previous cleaning	Event	Description	MTCw (Initial = 0.339)
1	594	25	Cleaning	NaOH (0.1% by weight) at 30 deg C	Precleaning: 0.251 Post-cleaning: 0.289
2	837	10	Cleaning	Citric Acid (2% by weight), followed by NaOH (0.1% by weight), at 30 deg C	Precleaning: 0.263 Post-cleaning: 0.308
3	927	4	Cleaning	H3PO4 (0.5% by weight, followed by NaOH (0.1% by weight), at 30 deg C	Precleaning: 0.277 Post-cleaning: 0.326
4			Changed cartridge filtration	Replaced 20-micron cartridge filter with 1-micron cartridge filter	
5	1025	8	Changed cartridge filtration	Replaced 1-micron cartridge filter with 0.2-micron cartridge filter	0.277
6	1364	14	Cleaning	NaOH (0.1% by weight) at 30 deg C	Precleaning: 0.196 Post-cleaning: 0.253
7			Chloramine feed initiated	Chloramines to membrane feed water to maintain 1 mg/L residual at membrane influent (includes concentrate recycle stream)	
8	1860	21	Cleaning	NaOH (0.1% by weight) at 30 deg C Extended duration (overnight soak)	Precleaning: 0.134 Post-cleaning: 0.285
9	2104	10	Cleaning	NaOH (0.1% by weight) at 30 deg C Extended duration (6 hours)	Precleaning: 0.196 Post-cleaning: 0.253
10			pH adjustment	Increase feed pH to 8.0 with NaOH addition (pre-cartridge filter.)	

Table 3. Key ICR SEBST Treatment Events

Event No.	Run Time in hours	Days since previous cleaning	Event	Description	MTCw (Initial = 0.339)
11	2812	34	Chloramine feed stopped		
12	3629 - 3739	64	Lime feed at full-scale plant rapid mix		
13	4098	83	Cleaning	HCl & NaOH	Precleaning: 0.193 Post-cleaning: 0.292
14	4855	32	Cleaning	HCl & NaOH; Recovery reduction to 50 % attempted	Precleaning: 0.100 Post-cleaning: 0.269
15	4893	2	Reduced flux	Changed flux from 14.4 gfd to 9 gfd	
16	5559	29	Cleaning	HCl & NaOH (with overnight soak)	Precleaning: 0.205 Post-cleaning: 0.290
			pH adjustment	Reduced feed pH to 4.0 with HCl addition (pre-cartridge filter). Flux returned to original operating condition (14.4 gfd).	
17	6100 (est.)	23	Replaced membrane	Replaced NF70 with Hydranautics LFC1.	

Cleanings and Cartridge Filter Modification

Event No. 1, membrane cleaning with sodium hydroxide (NaOH), took place after only 25 days of continuous operation. It was suspected that the primary foulants were organic compounds and silts, therefore a high pH cleaning using sodium hydroxide was conducted. The water mass transfer coefficient (MTC_w) recovered to 85 percent of its original condition. During the next cleaning event (Event No. 2), low pH acid cleaning using citric acid was performed prior to caustic cleaning, to address any suspected inorganic salt scaling (iron and aluminum). This cleaning approach appeared to improve the post-cleaning performance of the membrane, bringing the mass transfer coefficient back up to 91 percent of the original condition.

A third cleaning event was required less than 4 days later (Event No. 3) as the MTC_w began to drop. During cleaning Event No. 3, phosphoric acid was used instead of citric acid because it was suspected that the foulant was an inorganic salt or metal oxide such as aluminum hydroxide, that may have formed from reflocculation occurring at the membrane surface. A low pH cleaning preceded a high pH cleaning. The MTC_w recovered to 96 percent of original operation. Cartridge filtration was changed to a nominally rated 1 micron pleated cartridge filter (Event No. 4) to simulate pretreatment using microfiltration to eliminate the effect of particulate loading and better understand the types of foulants present. Shortly thereafter, the 1-micron cartridge filter was replaced with a 0.2-micron filter (Event No. 5) to provide more complete particle removal.

Membrane performance further declined. Pressure drop across the cartridge filter was stable, indicating that it was providing little additional filtration. Water temperature was approximately 25 degrees Centigrade, prompting investigation of biological fouling. A high pH cleaning (Event No. 6) yielded a MTC_w of only 75 percent of original.

To control potential biological fouling, the membrane feedwater was dosed with chloramines, batched at a chlorine to ammonia ratio of 4 to 1 using pilot-filtered water as makeup water. Chloramines were fed (Event No. 7) prior to cartridge filtration at a dose sufficient to maintain a 1 mg/L total chlorine residual in the membrane influent (which included concentrate recycle.) Chloramines were applied continuously for 1448 hours (60 days). There was no apparent benefit from the chloramine feed, and differential pressure continued to increase steadily. Chloramine use was discontinued after 2812 hours of total SEBST run time (Event No. 11).

During the period of chloramination, two additional cleanings were required: Event No. 8 consisted of a high pH cleaning in which the membrane was soaked for an extended period of time (overnight). The MTC_w recovered to 84 percent of the original condition. X-ray diffraction analysis was conducted on the filters of filtered membrane feed and concentrate streams to determine whether aluminum (added during the alum coagulation process) was precipitating out onto the membrane surface. To determine if membrane fouling was caused by the precipitation of aluminum residuals carrying over from the coagulation process, samples of the cartridge filtered feedwater and concentrate were filtered through 0.45-µm disc filters and the surface of the filters analyzed by x-ray diffraction. The results showed a net loss of aluminum of 17 ug/L from the feed to concentrate streams, confirming aluminum precipitation.

The next cleaning event (Event No. 9) consisted of a 6-hour soak in high pH cleaning solution. MTC_w recovered to 75 percent of original operation. Directly following the cleaning, the pH of the feed water was then increased to 8.0 (Event No. 10) to increase aluminum solubility in the membrane feed/concentrate loop. MTC_w was stable for approximately 1500 hours (64 days.)

At hour 3629 of SEBST operation, the full-scale plant began feeding lime to the rapid mix for a period of 110 hours or 4.5 days (Event No. 12.) During this time, MTC_w began to drop, and continued on a steep decline after the lime feed had been stopped. The flux loss was attributed to the precipitation of calcium carbonate that caused the increase in the membrane feedwater calcium concentrate in combination with elevated pH operation. To remove the precipitate, a low pH cleaning (Event No. 13) was conducted with HCl. This was followed by NaOH cleaning with a 3-hour soak to remove any organic foulants present.

MTC_w recovery was 86 percent of original condition. Despite the discontinuance of lime addition, MTC_w declined at approximately the same rate as prior to the cleaning (Event No. 13). Cleaning (Event No. 14) was conducted again using the same cleaning regimen (HCl followed by NaOH), with TOC, Al, Fe, Mn, Ca & total P levels measured in the spent cleaning solution. TOC in the spent NaOH solution was measured at 100 mg/L, while aluminum concentration in the spent HCl was 60 mg/L. All other metals and phosphorus were low in both solutions. The TOC level was not unexpected given the high concentration in the membrane influent, however the high level of aluminum indicated that operation at a feed pH of 8.0 was no longer preventing aluminum precipitation

Following the cleaning at 4855operating hours (Event No. 14), an attempt was made to operate the SEBST at a reduced system recovery of 50 percent. This was not successful as insufficient flow could be processed through pilot granular media filter to maintain the higher SEBST feedwater flow rate. The flux of the NF70 element was reduced to 9 gallons per square foot per day (gfd) beginning at hour 4893 (Event No. 10) in an attempt to reduce membrane fouling. The rate of MTC decline was reduced, but only slightly.

Membrane Autopsy

After 6100 hours of operation, the NF70 was removed from the SEBST and sent out for autopsy. The autopsy results indicated that the primary foulant consisted of organic matter (90%), either from upstream biological activity or raw water TOC. The remaining 10% of the constituents were inorganic ($BaSO_4$ and silicates). Flux was restored by cleaning; it was found that the foulant was removed most effectively with proprietary chemicals that are specifically designed to remove organic polymeric substances.

Since the autopsy was conducted immediately following low pH membrane testing most of the fouling material was organic. However, it is also possible that metal oxides might have predominated during earlier operations at ambient pH. The relatively stable performance achieved with the NF70 under elevated pH conditions could be indicative that the suspect, primary, foulant (aluminum) was effectively controlled by keeping it in its soluble state. A low fouling composite membrane (Hydranautics LFC1) was then installed in the SEBST and tested. This membrane was installed to determine if the rate of membrane fouling is related to membrane surface charge. The LFC1 is reported to have a lesser (negative) surface charge than the NF70 and, as such, should be less susceptible to fouling caused by feedwater/membrane electrostatic interactions. The results of this testing are documented below.

Feedwater Treatment

Three distinct adjustments to feedwater treatment were described in the previous section. These were:

- Chloramine feed to mitigate suspected biofouling;
- pH increase with sodium hydroxide to maintain aluminum solubility;
- pH decrease with hydrochloric acid to maintain aluminum solubility and avoid calcium carbonate scaling if lime were again needed to be fed to rapid mix.

Neither chloramines nor pH reduction proved effective at improving membrane performance with the NF70. Increasing the feedwater pH to 8.0 appeared to improve membrane performance, presumably by preventing aluminum hydroxide precipitation on the membrane surface. However, treatment demands of the full-scale plant prevented adequate control over membrane study pretreatment to fully demonstrate its potential effectiveness. If a source of alkalinity other than lime (e.g., sodium hydroxide), was used at the plant during the treatment period in which alum doses were increased and supplemental alkalinity required, operating at the elevated pH could have remained a effective strategy for membrane pretreatment. Given the constraints of the current plant operations, this could not be determined.

Water Quality Results

A summary of water quality results from testing of the FilmTec NF70 membrane is provided in Table 4. Additional water quality analyses were performed on the concentrate during operation of the NF70 at a 90 percent recovery. Results from these analyses are tabulated in Table 5.

Table 4. LTSEBST Water Quality Results – FilmTec NF70

PARAMETER	FEED			PERMEATE			CONCENTRATE		
	Avg.	Range	Std. Dev.	Avg.	Range	Std. Dev.	Avg.	Range	Std. Dev.
Chlorine Demand (mg/L)	2.95	1.92-3.92	0.53	0.94	0.20 – 1.95	0.47	---	---	---
TTHM (ug/L)	49	26 - 90	16.5	1.5	0.5 - 5.1	1.47	---	---	---
HAA5 (ug/L)	39	29 - 54	7.5	1.3	1.0 - 3.3	0.73	---	---	---
TOX (ug/L)	173	128 – 268	36	38	25 - 61	13	---	---	---
TOC (mg/L)	2.5	2.2 - 2.9	0.22	<0.5	<0.5	---	11	9 - 28	4.4
UV_{254} (cm^{-1})	0.044	0.038 - 0.056	0.005	<0.009	<0.009	---	0.201	0.149 - 0.504	0.082
Bromide (ug/L)	30	20 - 40	10	<20	<20	---	---	---	---
Ammonia (mg/L)	0.06	<0.05 - 0.17	0.03	0.07	<0.05 - 0.15	0.03	0.07	<0.05 - 0.23	0.04
Alkalinity (mg/L as $CaCO_3$)	14	6 - 21	4.6	4	1 - 7	1.7	64	15 - 221*	49
Total Hardness (mg/L as $CaCO_3$)	35	27 - 51	6.8	5	2 - 11	1	136	97 - 308*	53
Calcium Hardness (mg/L as $CaCO_3$)	19	13 - 35	6.5	0	0 - 7	1.6	87	53 - 183*	39
Turbidity (ntu)	0.16	0.07 - 0.44	0.10	0.11	0.06 - 0.28	0.06	0.20	0.10 - 0.42	0.09
Aluminum (ug/L)	92	<8 – 201	80	79	<8 - 254	80	201	<8 - 1,110	24
Manganese (ug/L)	20	<3 - 48	10	9	<3 - 44	10	70	22 - 188	40
Dissolved Oxygen (mg/L)	8.07	5.60 – 10.1	1.27	7.62	5.03 - 10.6	1.40	8.13	5.68 - 10.40	1.37
Barium (mg/L)	0.025	0.016 – 0.037	0.009	0.010	<0.005 – 0.012	0.003	---	---	---

Table 4. LTSEBST Water Quality Results – FilmTec NF70									
PARAMETER	**FEED**			**PERMEATE**			**CONCENTRATE**		
	Avg.	Range	Std. Dev.	Avg.	Range	Std. Dev.	Avg.	Range	Std. Dev.
Sulfate (mg/L)	25	21 - 33	5	<4	<2 - <5	1	---	---	---
Reactive Silica (mg/L)	2	<2 - 2	---	<2	<2	---	---	---	---

* Maximum values occurred during 90% recovery run.

Table 5. Additional Concentrate Water Quality at 90% Recovery		
PARAMETER	**AVERAGE VALUES**	**POTENTIAL DISCHARGE LIMITS**
BOD	<1 mg/L	Discharge limit would be for Dissolved Oxygen: 4 mg/L[1]
COD	<2 mg/L	
Phosphorus	0.16 mg/L	2 mg/L[1]
Metals (Cd, Cr, Pb, Hg, Se, Ag, Zn)	All below detection limits.	Detection limits range from 6 to 60,000 times smaller than the potential discharge limits for these metals.[2] Cd – 86 ug/L Cr(VI) – 2200 ug/L Cu – 5.8 ug/L Pb – 425 ug/L Hg – 1.25 ug/L Se – 200 ug/L Ag – 4.6 ug/L Zn – 190 ug/L
Arsenic	1.5 ug/L	As – 138 ug/L[2] This result is also well below the anticipated drinking water standard of 50 ug/L.

In addition, Silt Density Index (SDI) measurements were obtained on the feedwater both prior to and after 0.2-micron cartridge filtration. Average SDIs were 4.5 and 2.5, respectively, indicating that filtration using a 0.2-um nominal cartridge enhanced NF feedwater quality .

DBPs and DBP Precursor Reduction and Blending

NF permeate contained very low levels of TOC, UV_{254} and DBP precursors throughout the testing period. Simulated distribution system SDS-THM and SDS-HAA levels, measured after 24 hours of free chlorine contact time were mostly below detection. The highest SDS THM(4) and HAA(6) values were 5.1 and 3.3 ug/L, respectively, below the proposed Stage 2 MCLs. Blending ratios calculated using the ICR spreadsheets indicate that up to 50 percent of the NF-treated permeate could be blended with filtered water and still meet the proposed Stage 2 D/DBPR MCLs.

Increasing system recovery had no impact on permeate water quality, even under severely fouled conditions (e.g., at hour 1856.) Recovery did, however, have a significant impact on concentrate water quality, as would be expected.

Manganese

Manganese spiking tests were conducted to determine the rejection capability of the NF70. At feed concentrations ranging from 0.4 to 0.5 mg/L, manganese rejections were consistently better than 98 percent, with permeate concentrations below the minimum reporting limit of 0.014 mg/L.

Concentrate Toxicity

The SEBST on the NF70 was operated at 90 percent recovery on two separate occasions (at 3114 and 3734 hours) for a period of approximately 2 hours to collect concentrate samples for biotoxicity testing.

Chronic definitive bioassay tests using Sheepshead Minnow (*Cyprinodon variegatus*) and the mysid shrimp (*Mysidopsis bahia*) were conducted in accordance with the "*Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms,*"1988, EPA/600/4-87/028. These bioassay tests were selected based on the NPDES permit requirements for concentrate discharge from a nearby membrane plant to a local tributary of the Chesapeake Bay. (It is likely that any concentrate produced at the Norfolk plants would be discharged to a similar water body.) Concentrations tested were 1, 3, 10, 30 and 100 percent effluent (i.e., concentrate). The dilution and control water was prepared using 25 ppt of aged artificial seawater (Forty Fathoms®).

Fifteen gallons of concentrate was collected during the first run at 90 percent recovery (at hour 3114.) The results of the first test (Test 1A) indicated that there was a reduction in growth of the Sheepshead minnows in the 100 percent effluent relative to the control. The IC_{25} value, which expresses the concentration of effluent causing a 25 percent reduction in biological measurement, such as growth), was calculated to be 58 percent. The mysid shrimp, a more sensitive species, showed a significant reduction in survival in the 100 percent effluent when compared to the control. The toxicity effects were attributable to insufficient salinity in the concentrate. To test this theory, a "simulated concentrate" sample was prepared using distilled, deionized water, and reagent grade salts to match the hardness, alkalinity and salinity of the SEBST concentrate. Thirty-and 100-percent simulated concentrates were tested with the mysid test (Test 1B.) Toxicity results using the simulated concentrate matched those for the SEBST concentrate, indicating that the toxicity observed with the SEBST concentrate could have been caused by insufficient salinity.

For the second membrane operation at 90 percent recovery (at hour 3734), the SEBST concentrate salinity was adjusted to 15 ppt, the minimum salinity expected for the water body under consideration for concentrate disposal. The results of this test showed no toxic effects for the salinity-adjusted concentrate on either Sheepshead Minnows or Mysid shrimp.

These results are summarized in Table 7, below.

Table 7. Toxicity Testing Results

	Test 1		Test 2 – SEBST concentrate with salinity adjusted to 15 ppt
	Test 1A – SEBST concentrate without salinity adjustment	Test 1B – "Simulated concentrate"	
Sheepshead Minnows			

Growth – 100% Concentrate	Significant reduction		No significant reduction
NOEC	30%		100%
LOEC	100%		>100%
IC_{25}	57.6%		>100%
Mysid Shrimp			
Survival – 100% Concentrate	Significant reduction	Significant reduction	No significant reduction
NOEC	30%	30%	100%
LOEC	100%	100%	>100%
IC_{25}	47.5%	47.5	>100%

Process Performance – LFC1

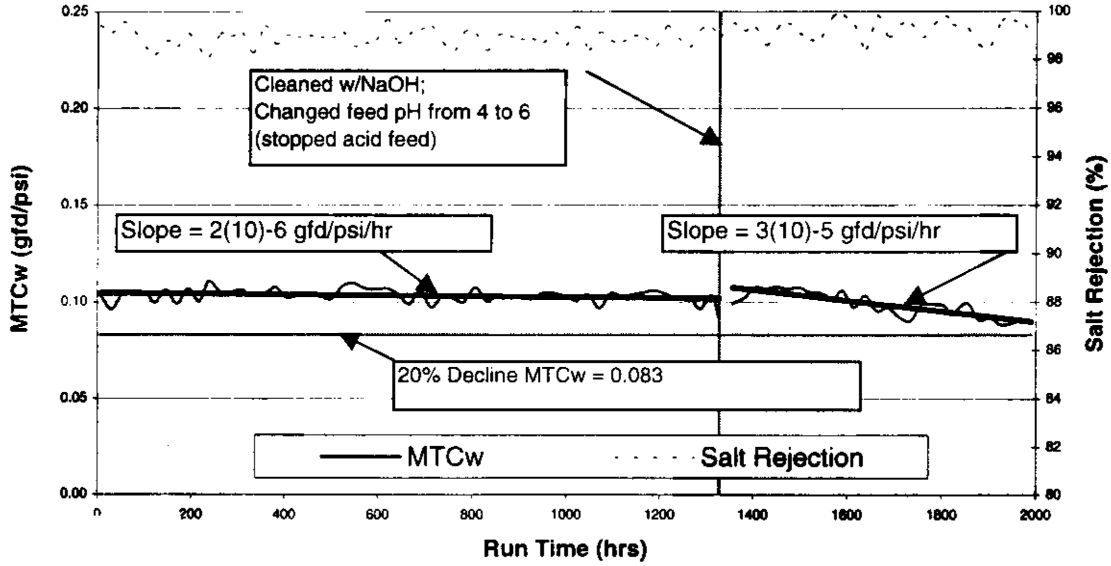
Membrane Pretreatment Adjustments and Operational Results

Testing of the Hydranautics Low Fouling Composite (LFC1), a neutrally-charged, polyamide, low pressure, reverse-osmosis membrane, was initiated on February 9, 1999. Operation continued at the depressed pH (4.0) at which the NF70 had been previously operating prior to test termination. Acidification of the membrane influent was stopped after 1328 hours. Performance, as indicated by the water mass transfer coefficient (MTC_w) and differential pressure, was stable for this entire period.

The membrane was cleaned with NaOH (although there was no apparent performance degradation), and operation was continued at ambient influent pH of 6.0. This is the only pretreatment adjustment made to the LFC1 membrane test. The graphs in Figure 5 show the relationship between MTC_w, Differential Pressure and Temperature and SEBST run time for the LFC1 membrane. The slopes of the MTC_w decline for both the periods of pH depression and ambient pH operation are indicated. Following cessation of acid addition to the membrane feedwater, the rate of flux decline increased by an order of magnitude, i.e., from $2x10^{-6}$ gfd/psi/hr to $3x10^{-5}$ gfd/psi/hr. Testing was terminated after 660 hours of continued operation at ambient pH.

Projecting the slope of the to MTC_w curves to the intersection with the 20 percent decline of MTC_w which triggers membrane cleaning, the expected cleaning frequency at depressed pH would be no more than annually, whereas the expected cleaning frequency at ambient pH would be quarterly.

Hydranautics LFC1
Norfolk ICR SEBST



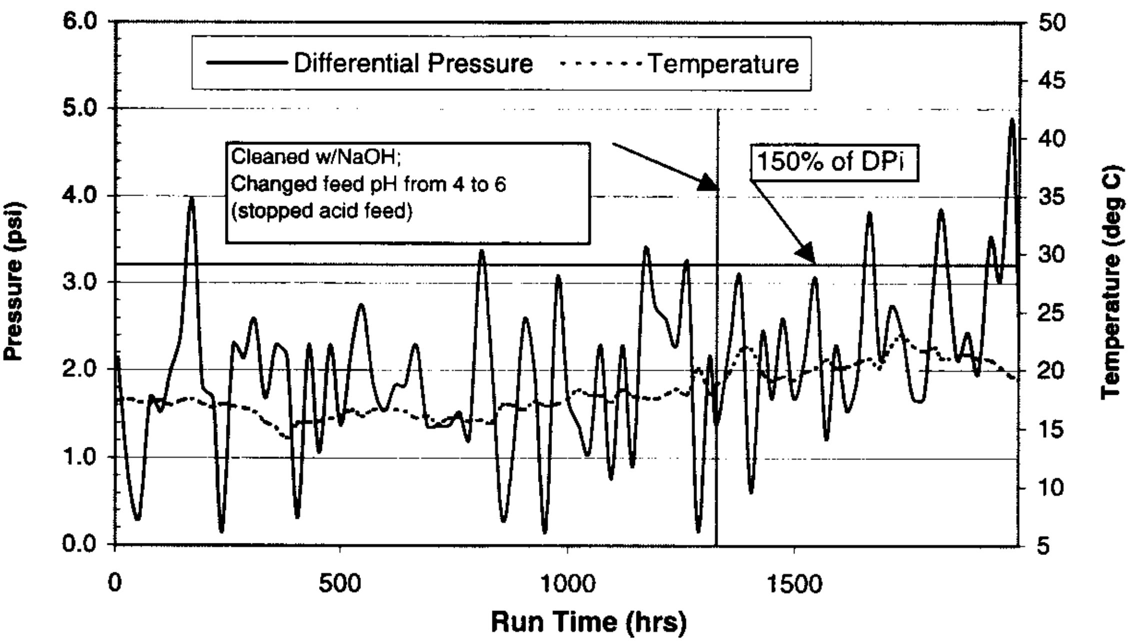


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Figure 5

Water Quality Results

A summary of water quality results for the Hydranautics LFC1 membrane is provided in Table 8.

Table 8. LTSEBST Water Quality Results – Hydranautics LFC1

PARAMETER	FEED			PERMEATE			CONCENTRATE		
	Avg.	Range	Std. Dev.	Avg.	Range	Std. Dev.	Avg.	Range	Std. Dev.
Chlorine Demand (mg/L)	2.12	1.68 - 2.40	0.30	0.48	0.28 – 0.70	0.16	---	---	---
TTHM (ug/L)	39	36 – 46	4.1	2.1	0.9 – 3	1.0	---	---	---
HAA5 (ug/L)	28	25 - 31	2.6	0	0	---	---	---	---
TOX (ug/L)	129	113 – 151	15.5	<25	<25	---	---	---	---
TOC (mg/L)	2.5	2.4 – 2.7	0.12	0.3	<0.5	---	9.23	8.23 – 10.28	0.80
UV_{254} (cm^{-1})	0.036	0.033 – 0.039	0.003	0.001	0.000 – 0.002	0.001	0.144	0.129 – 0.155	0.013
Bromide (ug/L)	30	20 – 30	0	<20	<20	0	---	---	---
Ammonia (mg/L)	<0.05	<0.05	0	<0.05	<0.05	0	0.10	0.05 – 0.23	0.09
Alkalinity (mg/L as $CaCO_3$)	5	1 – 10	3	2	1 - 3	0.8	13	0 - 29	12.7
Total Hardness (mg/L as $CaCO_3$)	28	26 - 33	3.0	1	1 – 2	0.45	99	91 - 106	7.4
Calcium Hardness (mg/L as $CaCO_3$)	15	14 - 16	0.57	0	0	---	61	53 - 71	5.5
Turbidity (ntu)	0.13	0.09 – 0.16	0.02	0.10	0.06 – 0.16	0.03	0.20	0.02 – 0.38	0.1
Aluminum (ug/L)	117	50 – 164	39	74	50 – 90	19	270	155 – 341	60
Manganese (ug/L)	16	14 – 28	5	<14	<14	---	39	14 - 113	40
Barium (mg/L)	0.030	0.025 – 0.032	0.003	<0.005	<0.005	---	---	---	---
Sulfate (mg/L)	22	22 – 23.0	0.7	8	5 - 18	5.8	---	---	---

DBPs and DBP Precursor Reduction and Blending

All of the DBP precursors, as measured by TOC and UV_{254} were below detection limits. Simulated distribution system SDS-THM and SDS-HAA levels, measured after 24 hours of free chlorine contact time, were also extremely low. The HAA values were consistently below detection, while the maximum

THM(4) level measured was 2.9 ug/L. Blending ratios calculated using the ICR spreadsheets indicate that a maximum of 23 percent of the NF-treated permeate would need be blended with filtered water to meet the proposed Stage 2 D/DBPR MCLs.

Summary and Conclusions

Nanofiltration of the City of Norfolk, Virginia's filtered water effectively and consistently produced high quality permeate, as indicated by a reduction in DBP precursors, and manganese. NF reduced TOC and UV_{254} to below detection limits, and DBPs to near detection limits. Permeate water was analyzed while operating the SEBST unit at feedwater recoveries of both 75 percent and 90 percent. The 75 percent recovery operation better represented the permeate water quality that could be expected during a 90 percent recovery full scale system, however, water quality results under both operating conditions were excellent. Blending of up to 50 percent of nanofiltered water or up to 23 percent of low-pressure RO permeate with conventionally treated water would meet Stage 2 DBP limits for TTHM4 and HAA6, and manganese treatment could be provided as needed.

Concentrate water quality, evaluated while operating the SEBST on the NF70 at a recovery of 90 percent to better simulate full-scale system concentrate water quality, was found to be within the anticipated requirements for potential waste disposal options. Toxicity to the saltwater test organisms was found to be attributable to insufficient salinity in the concentrate sample, rather than to the toxicity of the concentrated constituents of the waste stream. This issue would have to be addressed for full-scale implementation.

Testing conducted during the long-term SEBST with the FilmTec NF70, thin film composite membrane indicated that a rapid fouling rate could be expected. Fouling initially occurred on filtered water with minimal additional pretreatment within 25 days of operation. Several strategies to reduce the rate of fouling were tested, including chloramination, pH adjustment, and flux reduction. Although membrane performance with elevated pH was stable for an extended period of time (63 days,) full-scale plant pretreatment changes disrupted this trend and the membrane was unable to recover . It is suspected that the high recycle ratio required to produce a system recovery of 75 percent while maintaining the maximum element recovery of 15 percent may be a contributing factor to the fouling observed. Nevertheless, such a high rate of fouling on the NF70 would render full-scale implementation of this particular membrane cost-prohibitive and operationally intensive.

A membrane autopsy was conducted on the NF70 following low pH operation to determine the primary foulants contributing to the rapid deterioration of membrane performance. Suspected foulants include: organics, possibly from upstream biological activity or from raw water TOC; inorganic salts, barium sulfate and silicates (barium sulfate had originally been projected to be the limiting salt); and aluminum hydroxide, likely from residual aluminum added during the coagulation process. Cleaning fully restored flux, and the foulant was removed most effectively with chemicals specific to removing organic polymeric substances.

The Hydranautics LFC1 low-pressure RO membrane was tested in the SEBST unit for 2000 hours. The first 1300 hours were operated at a depressed pH of 4.0, to maintain the previous feedwater conditions under which the NF70 had been operating. Performance was very stable during this time. However, when acid feed was stopped and operation continued under ambient feedwater pH conditions of 6.0, performance degraded. Projected cleaning intervals dropped from annual to quarterly events.

Although the low-pressure RO LFC1 membrane operates at nearly twice the driving pressure than does the nanofilter NF70 membrane, the trade-off in cleaning intervals could make it a more cost-effective, as well as operationally attractive, treatment option to meet the future Stage 2 D/DBP Rule standards.

Appendices

A – Analytical Methods

B – Treatment Study Summary Report Spreadsheets (TSSUMRPT.XLS)

C – Data Collection Spreadsheets

APPENDIX A

ANALYTICAL METHODS

Norfolk ICR SEBST Analytical Methods

PARAMETER	METHOD	MRL[1]
Alkalinity	SM2320 B	0 mg/L
Aluminum	EPA 200.9	8 ug/L
Ammonia	SM4500-NH3 D	0.05 mg/L
Arsenic	EPA 200.9	1.0 ug/L
Barium	SM3111 D	0.11 mg/L
BOD	EPA 405.1	1 mg/L
Bromide	EPA 300.0	0.020 mg/L
Cadmium	EPA 200.9	1.000 ug/L
Calcium Hardness	SM3500-Ca D	0 mg/L
Chlorine Residual	SM4500	0 mg/L
Chromium VI	EPA 200.7	0.050 ug/L
COD	EPA 410.4	20 mg/L
Copper	SM3111 B	2.5 ug/L
Dissolved Oxygen	SM4500-O G	1 mg/L
HAA	SM6251 B	
MCAA		2.0 ug/L
DCAA		1.0 ug/L
TCAA		1.0 ug/L
MBAA		1.0 ug/L
DBAA		1.0 ug/L
BCAA		1.0 ug/L
TBAA		4.0 ug/L
CDBAA		2.0 ug/L
DCBAA		1.0 ug/L
Lead	EPA 200.9	2.5 ug/L
Manganese	SM3111 B	0.014 mg/L
Mercury	EPA 245.1	0.0002 mg/L

Norfolk ICR SEBST Analytical Methods

PARAMETER	METHOD	MRL[1]
PH	EPA 150.1	
Phosphorus	SM 4500-P F	0.04 mg/L
Reactive Silica	EPA 370.1	2 mg/L
SDS	SM5710 C	
Selenium	EPA 200.9	6 ug/L
Silver	EPA 200.9	1 ug/L
Sulfate	SM 4500-SO_4 B	5 mg/L
Temperature	SM2550 B	
THM	EPA 502.2	
$CHCl_3$		0.5 ug/L
BDCM		0.5 ug/L
DBCM		0.5 ug/L
$CHBr_3$		0.5 ug/L
TOC	SM5310 C	0.5 mg/L
Total Hardness	SM2340 C	0 mg/L
TOX	SM5320 B	25 ug/L
Turbidity	SM2130 B	0.05 NTU
UV_{254}	SM5910	0.009 cm^{-1}
Zinc	SM 3111 B	0.003 ug/L

[1]Method Reporting Level

APPENDIX B

TREATMENT STUDY SUMMARY REPORT SPREADSHEETS (TSSUMRPT.XLS)

APPENDIX C

DATA COLLECTION SPREADSHEETS

FilmTec NF70
Membrane Study Data

Hydranautics LFC1
Membrane Study Data