Treatment of Produced Water with an Ultra-Filtration Membrane – a Field Trial
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I. Introduction and Background

An oil producer in West Texas would like to reduce the future costs for disposal of produced water via reinjection. To meet this objective, substantial improvements in the quality of water to be reinjected would be required. One option is to process the produced water through an ultra-filtration (UF) membrane with a pore size of 0.01 microns.

To test this option, a small skid mounted UF membrane with associated pretreatment equipment was constructed and field tested from May to September of 2004. The spiral wound UF membrane with a hydrophilic surface was operated in a cross-flow mode to maintain surface cleanliness. To reduce the potential for fouling, MicroSpin™ 12 mm desanding hydrocyclones and Oilspin™ AV deoiling cyclones were used to remove fine oil-coated solids and to reduce oil and grease concentrations from the produced water ahead of the UF membranes.

This paper discusses the pretreatment equipment and membrane test results. Design criteria and estimated operating cost for a full scale facility are also presented.

II. Pilot Testing Objectives

The major objectives for the pilot test were to

- Assess the performance of an UF membrane over an extended time period at operating conditions that are relevant to full scale operation
- Evaluate effectiveness of MicroSpin desanding cyclones and Deoiling cyclones as pretreatment equipment for the produced water
- Define cleaning frequency and effectiveness for the UF membrane
- Determine overall recovery possible through the UF membrane
- Define the sizing criteria for a facility that produces 25,000 BPD of clean water
- Provide data required to define capital and operating costs

III. Simplified Process Flow Diagram (PFD) for the Pilot Unit

The simplified PFD for the pilot unit is shown in Fig. 1. Produced water from a skim tank is pumped to the field for re-injection through the transfer pumps and 0.45 micron cartridge filters. A slip stream from the transfer pump is taken and introduced to the pilot unit feed pump. The purpose of desanding cyclone is to remove solids greater than 6 to 10 microns from the produced water. The deoiling cyclone, installed downstream of the desanding cyclone, could further remove oil coated fine solids and oil droplets. The deoiling cyclone underflow goes through the membrane pre-filter and then to the UF membrane modules. A membrane concentrate re-circulation pump is used to maintain the required cross-flow fluid velocity over the membrane. The permeate stream is introduced to a 0.45 micron cartridge filter to monitor the cleanliness of the permeate stream.

IV. Pilot Plant Operations – Pretreatment Equipment Performance

A. Feed Conditions

The measured oil and grease concentrations from the skim tank to the pilot test skid during the test are shown in Figure 2. The concentrations varied from about 100 ppm to 1000 ppm. The measured total suspended solid (TSS) concentrations to the desanding cyclone inlet are shown in Table 1.

Table 1 Millipore Test Results – Total Suspended Solid Concentration (PPM)

Date	Desanding Cyclone Inlet	Deoiling Cyclone Inlet	Membrane Prefilter Inlet	Feed to Membrane	Pretreatment Equipment
13-May	25.6	7.7		6.4	Desander + 25 Micron Nominal Filter
26-May	6.1	3.0			Desander + 10 Micron Nominal Filter
10-Aug	13.1	12.8	6.1		Desander + Deoiler + 5 Micron Abs. Filter
17-Aug	32.1	41.9	18.0	4.5	Desander + Deoiler + 5 Micron Abs. Filter
24-Aug	5.9	10.6	5.4	3.0	Desander + Deoiler + 5 Micron Abs. Filter
3-Sep	158.0	96.1	12.7	27.6	Desander + Deoiler + 10 Micron Abs. Filter

B. MicroSpin Desanding Hydrocyclone (12 mm) Performance

The purpose of the MicronSpin desanding cyclone was to remove solid particle sizes greater than 6 to 10 microns. The desanding cyclone solid removal effectiveness can be determined either by a Millipore filtration test or by the change out frequency of the downstream membrane prefilter. The downstream prefilter change out frequency during the time when the desanding cyclone was in and out of service is shown in Table 2. The data indicate that the pre-filter service life was increased if the desanding cyclone was in service. The data also indicate that a significant fraction of solids were in the 5 to 10 micron range and the desanding cyclone could remove some solids in this range.

Table 2 Membrane Pre-filter Change Out Frequency

Testing Date	Filter Pore Size Used (microns)	Average Filter Service Life (hrs)	Pretreatment Equipment Used
6/16 – 7/6	10 micron nominal	220	deoiling cyclone
7/6 – 7/27	10 micron nominal	244	desanding + deoiling cyclones
8/27 – 9/2	5 micron absolute	62	deoiling cyclone
8/19 – 8/27	5 micron absolute	82	desanding + deoiling cyclones

The total suspended solids measured by Millipore tests are shown in Table 1. According to the Millipore data on May 13, May 26 and September 3, the solid removal efficiencies for the desanding cyclone were 70%, 51% and 39% respectively. For the period from July 31 to August 24, the measured solid removal efficiencies were essentially zero. The inconsistency of the data may be due to the fact that the inlet and outlet samples were not taken at the same time during unsteady state conditions. Millipore data show that a significant fraction of the fine particles that were not removed by the desanding cyclone were removed by the deoiling cyclones and membrane pre-filter.

C. Deoiling Cyclone Performance

The measured oil concentrations in the underflow from the deoiling cyclone are shown in Figure 3. The deoiling cyclone oil removal efficiency can be correlated to the oil concentrations in the inlet to the deoiling cyclone. Figure 4 shows the oil removal efficiency increases from 20% to approaching 80% when the deoiling cyclone inlet oil concentrations increase from 100 ppm to 1200 ppm. These data indicate that the oil droplets to the deoiling cyclone were very fine. Therefore, it would be difficult to reduce the oil concentration to less than 50 ppm by using a de-oiling hydrocyclone alone.

The total suspended solids measured by Millipore tests are shown in Table 1. According to the Millipore data on August 10, 17 , 24 and Sept 3, the solids removal efficiencies for the deoiling cyclone were 52%, 57%, 49% and 86% respectively.

V. Pilot Plant Operations – Membrane Performance

The test data shows that membrane performance is dependent on the membrane inlet oil and solids concentrations and the effectiveness of membrane cleaning. Key parameters used for evaluating membrane performance are membrane flux (gallons/day per square foot of membrane surface area), the required membrane washing frequency, and membrane service life.

A. New Membrane Performance

Based on the pilot test results, the design membrane flux should be at 8 GFD (gallons/day per ft^2) and the recommended design trans-membrane pressure should be 50 psi. The trans-membrane pressure is defined as the average pressure on the concentrate side minus the permeate outlet pressure.

In the field test, the new membrane ran for 7 to 11 days without washing. However, the washing intervals were shortened to 2 - 5 days after 6 to 22 washing cycles during the 30 to 50 days of running with membrane element tested.

It should be noted that the washing intervals are dependent on the oil and solids concentration to the membrane unit, permeate flow rate, effectiveness of washing by detergent, and long term membrane degradation. The new membrane surface had been treated by the manufacturer to be water wet (hydrophilic). However, it appears that some components of oil and/or chemicals in the produced fluid can adhere to the surface and change the wettability of the surface. As a result, the membrane performance degraded over time.

Permeate Flow Rate vs Run Hours

Two UF membrane configurations were tested at the field site. Both used the same membrane material, but have different feed spacer designs. The feed spacer design used for the first two sets of membrane tested was the parallel feed spacer type with 47 mil (1.2 mm) spacing. The third set of membrane tested had the diamond feed spacer type design with 34 mil (0.86 mm) spacing. The membrane with the diamond spacer design has 85 ft^2 (4" OD x 40" long) surface areas per each membrane element, whereas the parallel type feed spacer has only 75 ft^2 (4" OD x 40" long). Since two membrane elements connected in series were used for the testing, the total membrane surface area would therefore be either 150 ft^2 or 170 ft^2 depending on which type of membrane was tested.

Fig. 5 shows the permeate flow rate vs run hours for the new membrane with parallel and diamond feed spacing. The membrane with parallel feed spacer was tested on line for a total of 267 hrs (11.1 days) before the membrane became fouled and required washing. This is discussed further in the next section.

The membrane with the diamond feed spacer was tested for a total of 183 hrs (7.6 days) before the membrane became fouled and required washing.

Since the membrane with the narrower diamond feed spacer has about 13% more surface area than the membrane with parallel feed spacer, the initial permeate flow rate was set higher at about 0.9 gpm for the first 134 hrs and then increased to 1.2 gpm. Based on the sharp increase of trans-membrane pressure, the membrane was considered to be fouled at 183 run hrs and then was washed.

Based on the membrane surface area of 170 ft^2 for the membrane with the diamond feed spacer, the calculated membrane flux are 7.6 GFD and 10.2 GFD for the permeate flow rate of 0.9 gpm and 1.2 gpm respectively.

Trans-Membrane Pressure (TMP) vs Run Hours

The trans-membrane pressure is defined as the average pressure on the concentrate side minus the permeate outlet pressure. It is the driving force required to force the fluid through the membrane from the concentrate side into the clean permeate stream.

The trans-membrane pressure (TMP) will increase for two major reasons. When the permeate flux is set at a higher flux, it will require a higher TMP to force additional fluid through the membrane. When the membrane is fouled, it will also require a higher TMP in order to maintain the same flux. When the feed water contains higher oil and solid concentrations, the membrane fouls at a faster rate.

The trans-membrane pressure vs run hours is shown in Fig. 6. Two observations are worth mentioning. When the membrane was fouled at the end of the run (at 250 run hrs for the membrane with parallel feed spacer and at 160 run hrs for the membrane with diamond feed spacer), the TMP increased sharply. When the permeate rate was increased (at 134 hrs and 139 hrs respectively for the two different membranes as shown in Fig. 5), the TMP also increased somewhat. At close to the end of the run, the permeate flow rate was increased to about 1.2 gpm for both membranes, which also contributed to the sharp increase in TMP. Based on these data, the optimal permeate flux is between 7 GFD to 8 GFD with the water quality that was available during the test period.

B. Membrane Fouling Mechanism

When the membrane is fouled, it must be washed to restore its permeation rate and to reduce trans-membrane pressure.

Fouling is the most frequently encountered problem with membrane processes. There are several strategies which can be employed to ameliorate the effect of fouling. They are:

- Use pretreatment to reduce solids, oil and gels in the feed
- Maintaining the high cross flow velocities on the feed side of the membrane
- The use of an in-place cleaning cycle.
- The use of blowback or a reverse flow washing of the membrane
- Operating the membrane at a higher temperature

Oil and/or solids can cause membranes to foul. Because the solid concentration in the feed water to the membrane unit was quite low, it is believed that the membrane fouling was mainly due to oil and/or some component of chemicals in the produced fluid.

C. Cleaned Membrane Performance

The permeate flow vs run hours for the cleaned membrane is shown in Fig. 7.

The membranes with parallel feed spacer was washed 8 times during the first 567 hrs of run time. After 567 run hrs, the membrane was backflushed by hot water at 150 F. The permeate flow was initially set at 0.8 gpm, but it gradually declined from 0.8 gpm to about 0.6 gpm at 63 hrs after the membrane was last washed and then to 0.55 gpm at 87 run hrs. At 87 hrs, the membrane was again washed. The permeate flow was maintained at between 0.8 and 0.6 gpm for about 63 hrs (2.6 days). These data can be compared to performance of the new membrane where the permeate flow could be maintained between 0.7 to 1.0 gpm for about 11 days without washing.

The permeate flow vs run hours for the membrane with diamond feed spacer is also shown in Fig. 7. During the first 590 run hrs, the membrane was washed 6 times. After 590 run hrs, the membrane was washed by detergent. The permeate flow was then maintained at between 0.9 to about 0.8 gpm for a total of 51 hrs (2.1 days). When the diamond feed spacer membrane was new, the permeate flow was maintained at between 0.9 to 1.2 gpm for a total of 7.6 days without washing.

D. The Effect of Oil Concentration on Cleaned Membrane Performance

Based upon the operating data, we observed that the required membrane washing intervals decreased from about 4.6 days to about 2 days when the oil concentration in the produced water to the membrane inlet increased from 95 ppm to 187 ppm.

In order for ultra-filtration to be an operationally viable process, the manufacturer recommends that the oil and grease concentration in the produced water to the membrane unit needs be less than 50 ppm. The operational field data from this test would support this recommendation.

When the oil concentration to the membrane unit was at above 200 ppm, the membrane was washed on a daily basis. With an inlet oil content of 25 – 50 ppm, it is quite possible that the required washing interval would increase to 6-8 days, but this condition could not be tested given the field condition given the water quality that was available during the time of membrane pilot operations.

During the period from June 26 to June 30, the measured oil concentration from the deoiling cyclone outlet to the membrane inlet showed the average concentration of only 80 ppm, which was the lowest measured oil concentration during the entire pilot plant testing period. Since the June 26 to June 30 period was the most stable operation period, a close look at how the membrane performed during this period could definitely provide information as to the value of reducing the oil concentration in order to improve the membrane performance.

Fig. 8 is the plot of permeate flow for the period from June 25 to July 6 for two membrane cleaning cycles.

At 1004 run hrs (on June 25), the membrane was detergent washed. After the wash, the permeate flow was set at 1.6 gpm. It declined to 0.6 gpm at 1116 run hrs and then was maintained at 0.6 gpm until 1142 run hrs. It took about 112 hrs (4.6 days) for the permeate flow to decline from 1.6 gpm to 0.6 gpm. The average of the measured oil concentrations from the deoiling cyclone underflow during this time interval was about 95 ppm.

At 1142 run hrs (on July 1), the membrane was again washed. After the wash, the permeate flow was set at 1.5 gpm. It took only 46 hrs (1.9 days) for the permeate flow to decline from 1.5 gpm to 0.6 gpm at 1187 run hrs. The average of the measured oil concentrations from the deoiling cyclone underflow was about 187 ppm. Once the permeate flow dropped to reached 0.6 gpm, it remained at that rate for about 75 hrs before the membrane was washed again at 1264 run hrs on July 6.

E. Total Oil and Grease (TOG) in Permeate Stream

The measured total oil and grease concentrations in the permeate stream were in the 1 mg/liter range, except during the time when the O-ring broke which caused oil leaking from concentrate side to the permeate side.

VI. Full Scale System and Cost

A. Membrane Unit Design Criteria

Based upon the pilot test data, the membrane design criteria for the commercial membrane unit for producing 25,000 bbl/day of permeate stream are:

- Four modules in parallel
- Chemical-In-Place (CIP) system
- Membrane flux = 8 GFD
- Trans-membrane pressure = 50 psi Maximum
- Membrane Washing Intervals = 4 days Minimun
- Waste generated from membrane washing = 200 bbl/day
- Scale inhibition injection rate = 81 gallons/day
- Permeate outlet Pressure 15 psi.

The simplified membrane system PFD is shown in Fig .9.

B. Operating Cost (25,000 bbl/day case)

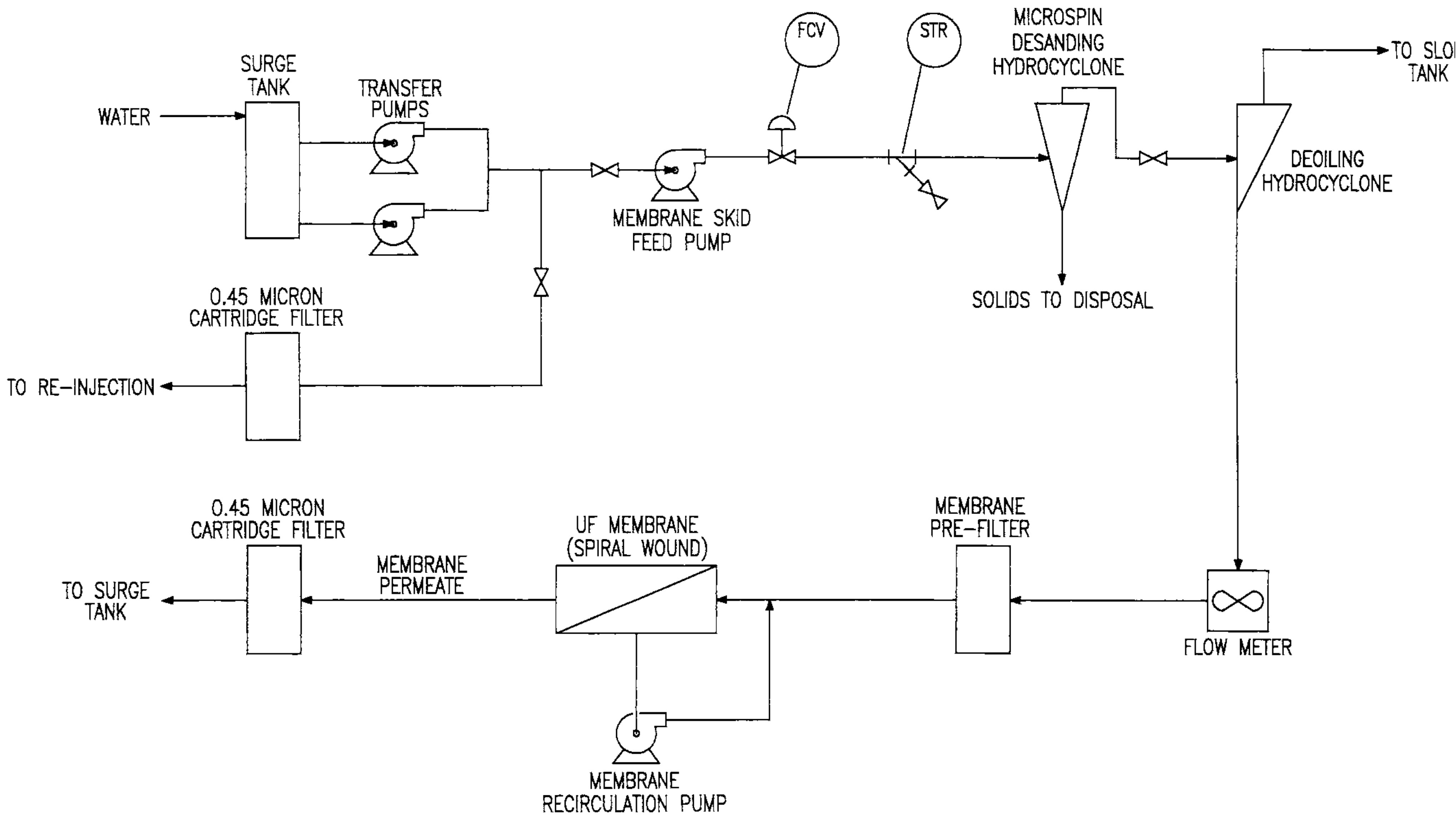
The membrane operating cost is shown below:

	Design Basis	Cost (cents/bbl)
1. Chemical Costs		
• **Detergent for Membrane Washing**	washing every 4 days	2.35
• **Scale Inhibition**		1.46
2. Membrane Replacement @ 2 yr interval	Based on membrane flux of 8 gal/(day-sq ft)	2.3
3. Fresh Water for Washing Membrane		0.68
4. Waste Disposal Cost		0.23
5. Energy Costs		
• **Pumping cost based on 6 cents/kw.hr**	Cyclones and Membrane Feed Pumps, Membrane Recirculation Pumps	2.47
• **Heating cost for washing fluid based on $5/mmbtu**	10 mmbtu/day	0.2
Total		**9.69**

VII. Summary and Conclusions

- Pretreatment of produced water to less than 50 ppm of oil and 15 ppm of solids in the water feed to the membrane unit is recommended.
- Membrane fouling was related to the deposition of ultra-fine oil coated solids on the membrane surface and oil concentration polarization.
- Emulsified oil droplets were shown to be a carrier for ultra-fine solids into the membrane unit.
- The design membrane flux of 8 GFD (gallons/day/ft^2) and trans-membrane pressure of 50 psi are recommended.
- Membrane could be washed at an acceptable frequency to maintain permeability (4 days or longer) if oil concentration to the membrane could be reduced to less than 50 ppm.
- The waste generated from membrane washing was about 0.8% of the total fluid processed.
- Permeate quality was excellent with total oil and grease concentration in the 1 mg/liter range.
- The operating cost for a full scale membrane unit is estimated at 9.7 cents/bbl of fluid processed.

FIG.1 SIMPLIFIED PROCESS FLOW DIAGRAM FOR THE PILOT UNIT



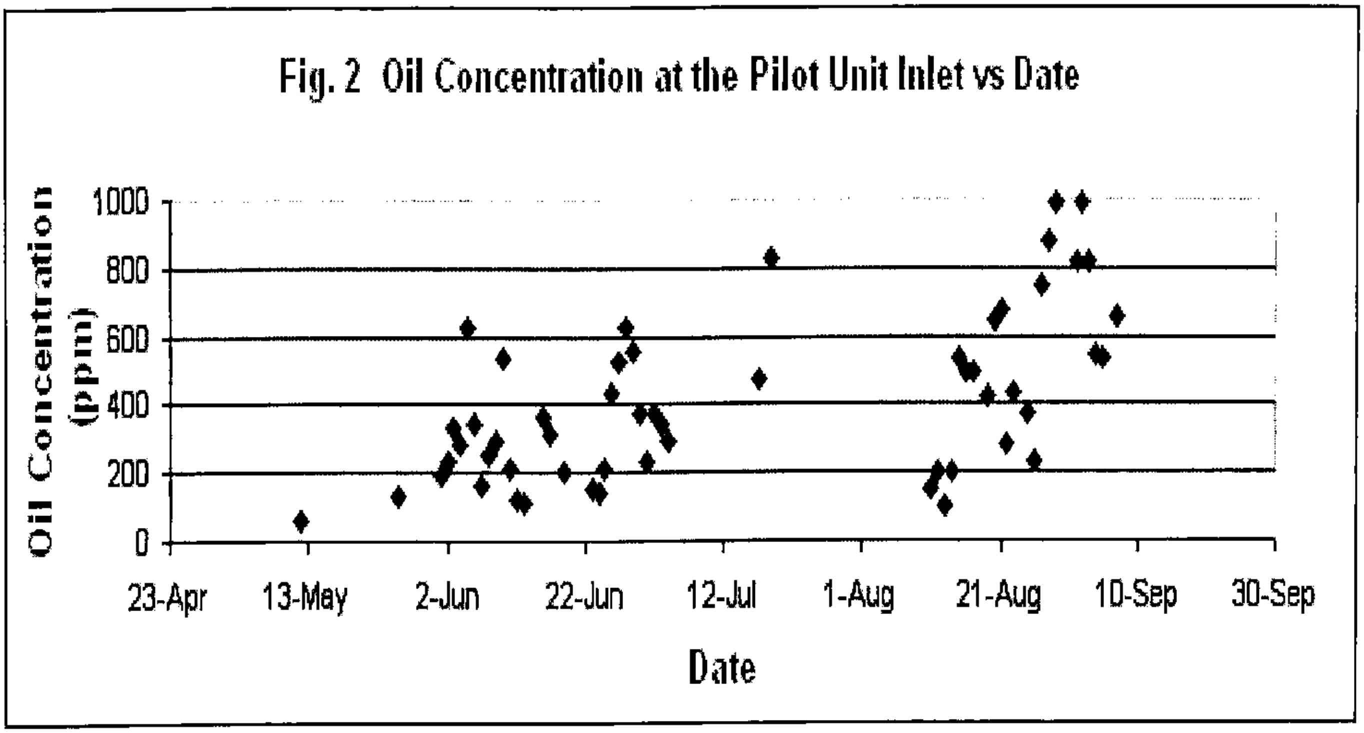


Fig. 2 Oil Concentration at the Pilot Unit Inlet vs Date
Oil Concentration (ppm)
1000
800
600
400
200
0
23-Apr
13-May
2-Jun
22-Jun
12-Jul
1-Aug
21-Aug
10-Sep
30-Sep
Date

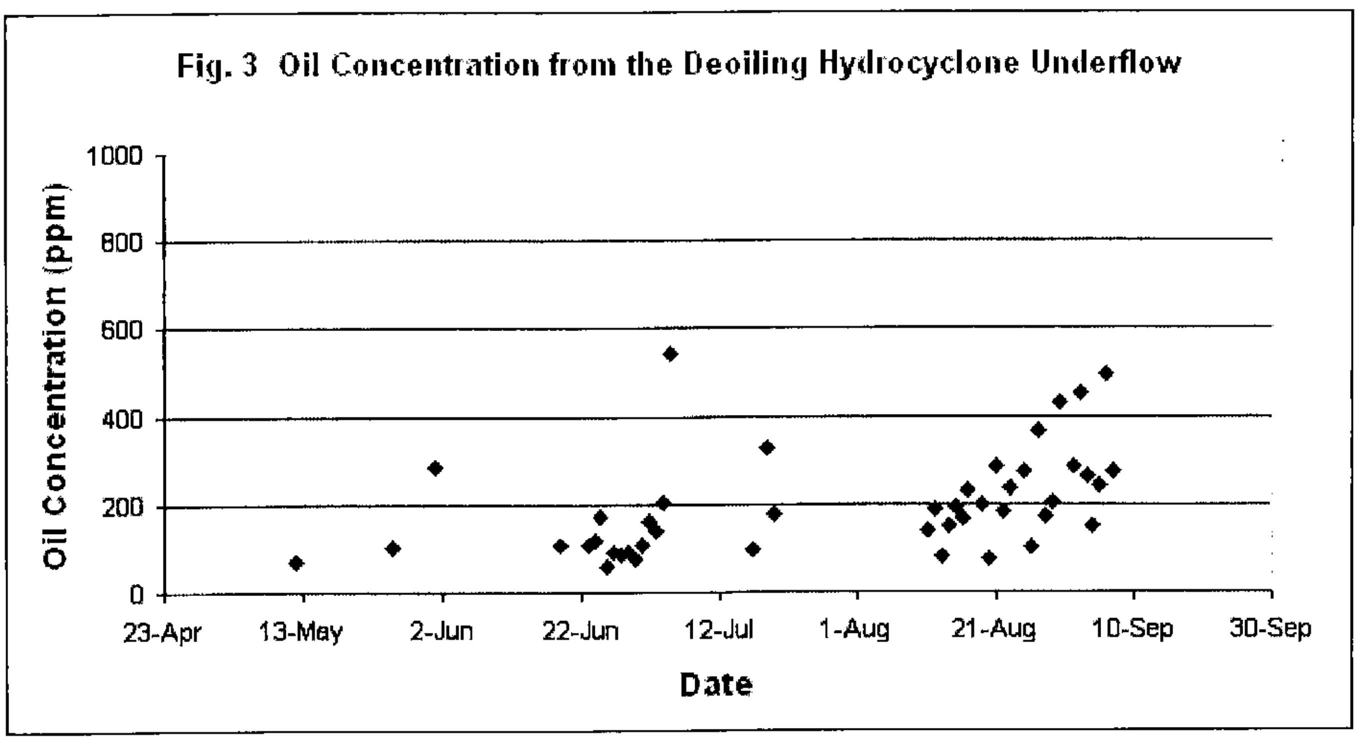


Fig. 3 Oil Concentration from the Deoiling Hydrocyclone Underflow
Oil Concentration (ppm)
1000
800
600
400
200
0
23-Apr
13-May
2-Jun
22-Jun
12-Jul
1-Aug
21-Aug
10-Sep
30-Sep
Date

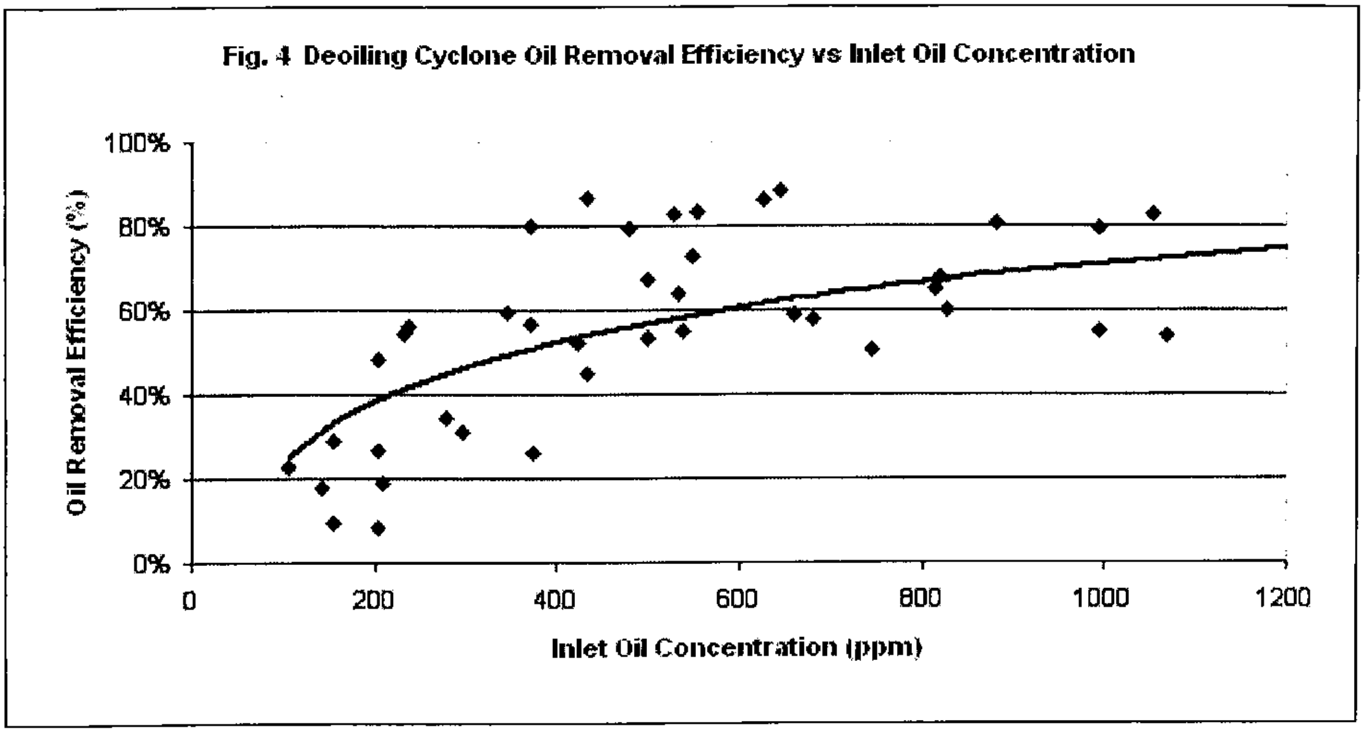


Fig. 4 Deoiling Cyclone Oil Removal Efficiency vs Inlet Oil Concentration
100%
80%
60%
40%
20%
0%
Oil Removal Efficiency (%)
0
200
400
600
800
1000
1200
Inlet Oil Concentration (ppm)

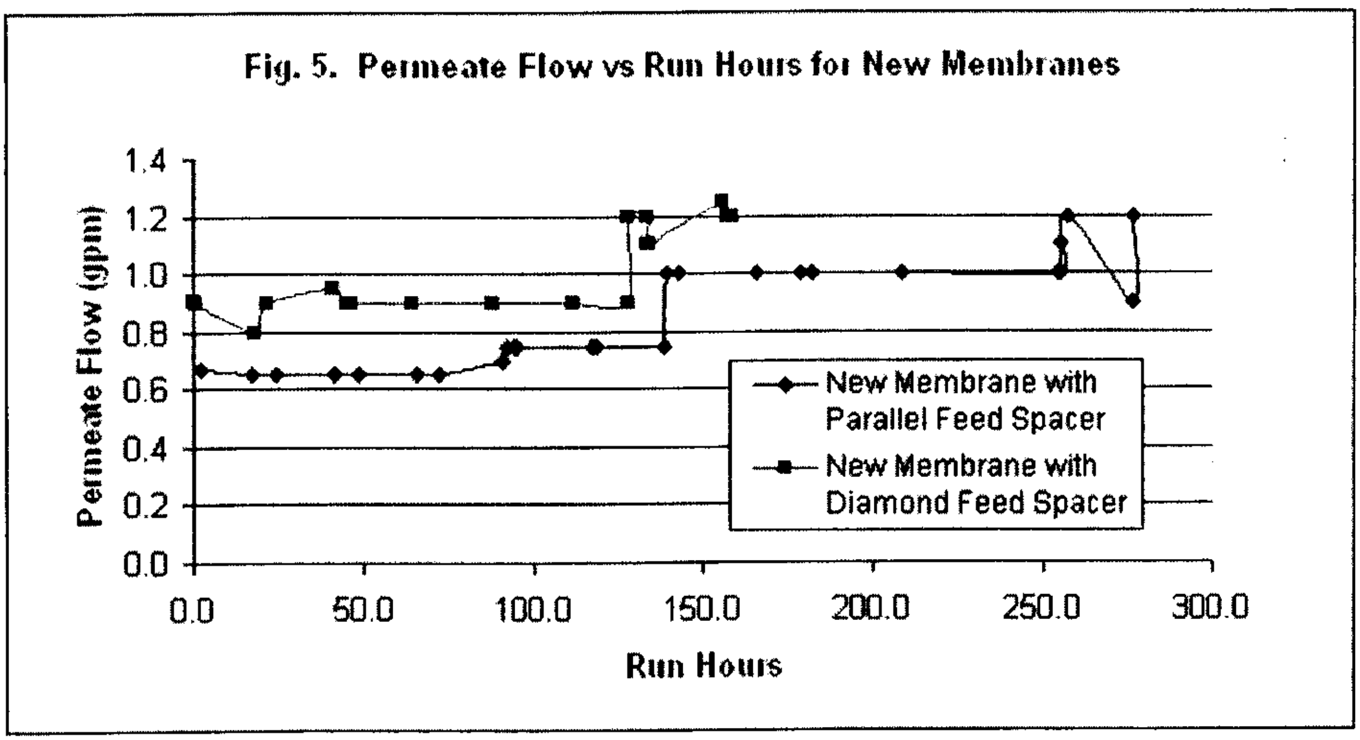


Fig. 5. Permeate Flow vs Run Hours for New Membranes
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Permeate Flow (gpm)
0.0
50.0
100.0
150.0
200.0
250.0
300.0
Run Hours
New Membrane with Parallel Feed Spacer
New Membrane with Diamond Feed Spacer

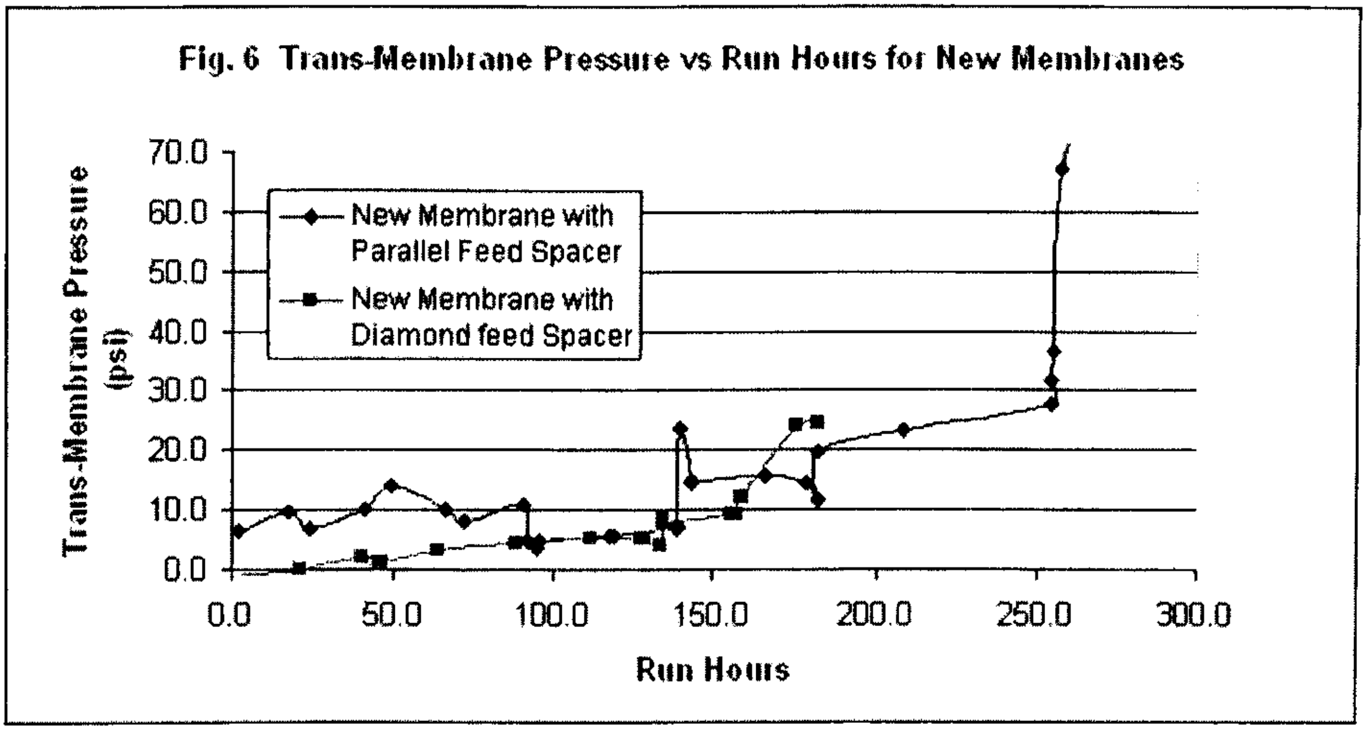


Fig. 6 Trans-Membrane Pressure vs Run Hours for New Membranes
Trans-Membrane Pressure (psi)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
New Membrane with Parallel Feed Spacer
New Membrane with Diamond feed Spacer
0.0
50.0
100.0
150.0
200.0
250.0
300.0
Run Hours

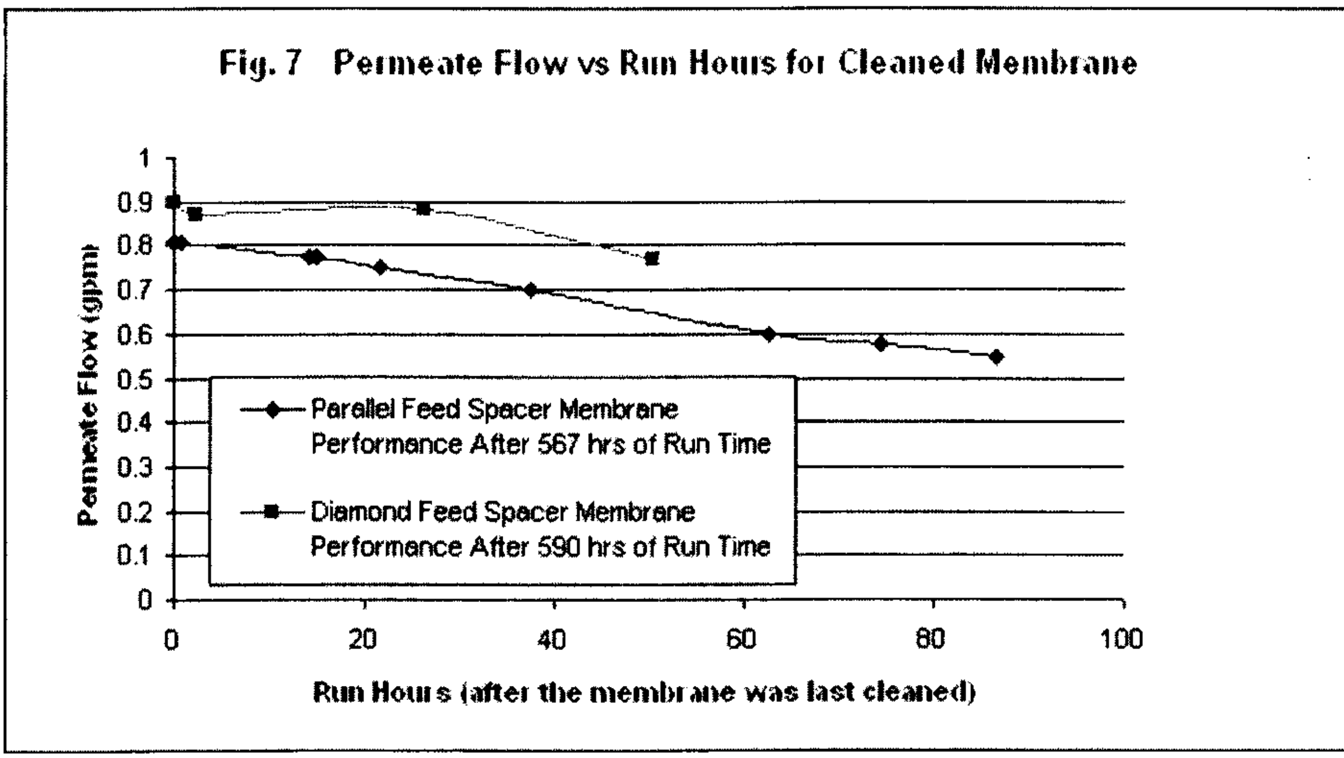


Fig. 7 Permeate Flow vs Run Hours for Cleaned Membrane
Permeate Flow (gpm)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Parallel Feed Spacer Membrane Performance After 567 hrs of Run Time
Diamond Feed Spacer Membrane Performance After 590 hrs of Run Time
0
20
40
60
80
100
Run Hours (after the membrane was last cleaned)

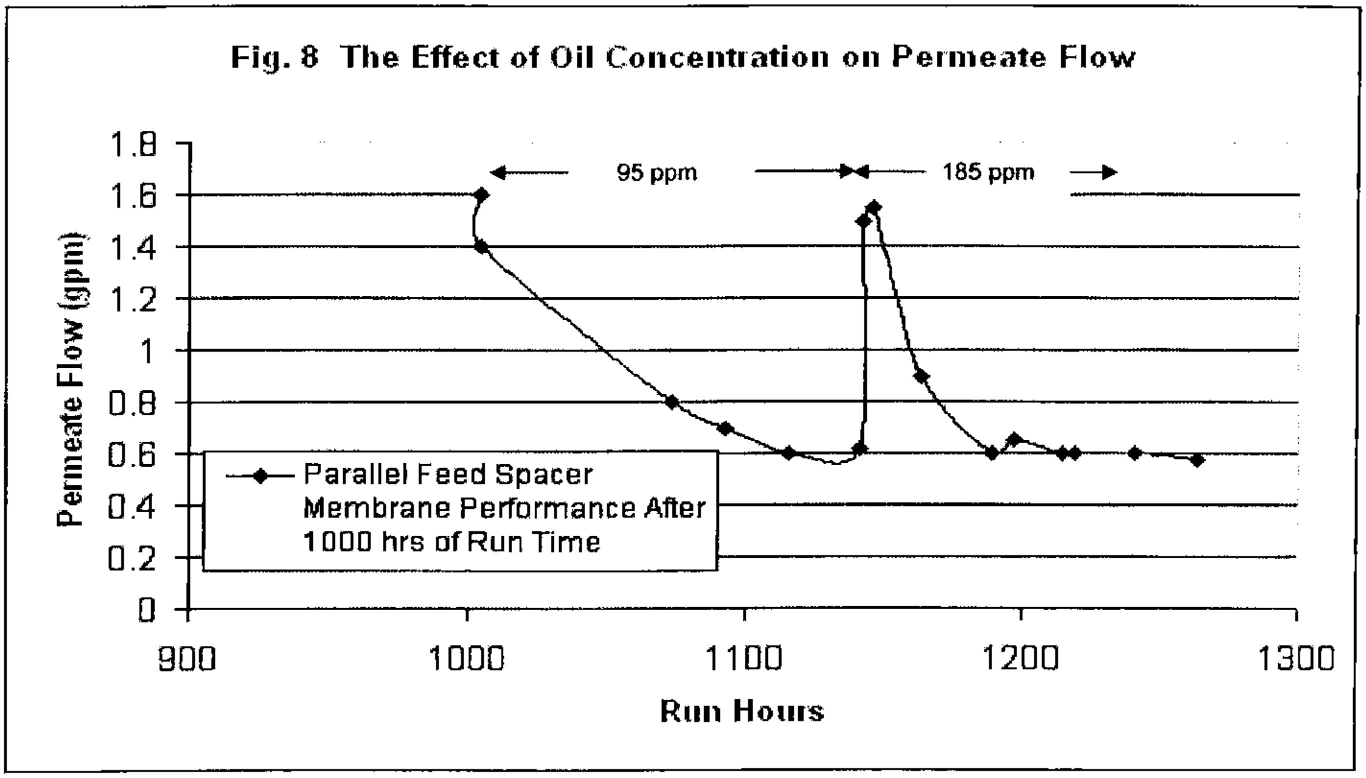


Fig. 8 The Effect of Oil Concentration on Permeate Flow
95 ppm
185 ppm
Permeate Flow (gpm)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
900
1000
1100
1200
1300
Run Hours
Parallel Feed Spacer Membrane Performance After 1000 hrs of Run Time

Fig. 9 UF System 4 Modules in Parallel