THE USE OF ULTRA-FILTRATION AND REVERSE OSMOSIS TO REMOVE HYDROCARBONS AND HEAVY METALS FROM OILFIELD PRODUCED WATER

The Produced Water Seminar
January 2001
Houston, TX

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ABSRACT

A produced water treatment system consisting of ultra-filtration and reverse osmosis membranes in series was pilot tested on Unocal Thailand's Floating Storage Operation, the FSO-Erawan, in the Gulf of Thailand. The UF membrane was treated to render it hydrophilic and resistant to fouling by dispersed hydrocarbons. The membranes successfully removed hydrocarbons, mercury, and arsenic from the produced water. The presence of soluble hydrocarbons limited the overall performance of the membranes, however, and incoming arsenic was sufficiently high that even with 95% rejection, the product water did not meet Unocal Thailand's self-imposed water quality standards. The test campaign established criteria for the design of a full scale water treatment system for this facility and demonstrated the feasibility of using this technology for cleaning problematic oilfield produced waters.

INTRODUCTION

Unocal Thailand's daily production exceeds 1 BSCF of gas, 40,000 barrels of condensate and approximately 75,000 barrels of water. Condensate with 0.1 to 0.5% BS&W is pumped from five processing platforms to a floating storage facility before transport via shuttle tankers. Water arriving on the storage tanker is contaminated with hydrocarbons, mercury and arsenic. Water on the ship must be cleaned to Unocal Thailand's strict, self-imposed discharge specifications before overboard disposal is permitted. Alternatively, the contaminated water can be transported to a nearby platform for disposal by injection into a depleted gas well. For overboard disposal, Unocal Thailand requires that produced water contain less than 40 PPM of oil (measured as Total Petroleum Hydrocarbons, TPH, by IR), less than 10 PPB of Mercury, and less than 250 PPB of Arsenic.

To determine the feasibility of cleaning the ship-retained produced water, Unocal Thailand conducted pilot scale testing of a combined ultra-filtration (UF) and Reverse Osmosis (RO) membrane system. The ultra-filtration membrane from Osmonics-Desal was pre-treated to render it hydrophilic. As a result, the UF membrane resists fouling by dispersed hydrocarbons in the water being filtered.

PROCESS DESCRIPTION

Produced water along with contaminant solids settle to the bottom of the ship's tanks. Tank levels are varied to permit gravity drainage of the water and fluidized solids into one of two smaller tanks that are dedicated to waste holding service. Water along with settled solids from the waste tanks was used as feed to the membrane pilot plant.

A process flow diagram for the membrane pilot plant is shown in Figure 1. A photograph of the pilot skid mounted on the FSO is shown in Figure 2. Contaminated water was pumped to the 1000-liter process feed tank through a 1" FloChamp desanding hydrocyclone. The purpose of the hydrocyclone was to remove as many of the particulate solids as possible and to pre-coalesce condensate in the water going to the feed tank. To maximize hydrocyclone efficiency, about 5% of the feed was continuously bled off from the bottom of the hydrocyclone. The feed pressure to the hydrocyclone varied between about 20 and 40 PSIG. Despite the relatively low pressure drop, the hydrocyclone effectively rejected solids and coalesced condensate droplets in the feed water. In order to prevent the build up of a condensate layer in the feed tank, a continuous skimming was maintained.

From the process feed tank, water was pumped through a 50-micron bag filter and then through two spiral wound UF cartridges in series. Each cartridge had 150 ft^2 of surface area. UF filter permeate went to the RO feed tank while concentrate (non-permeated feed water) was recycled either to the inlet of the UF membrane or returned to the process feed tank. It was observed that as the condensate became more concentrated in the recycle water, there was a tendency for the liquid hydrocarbons to coalesce and separate out in the process feed tank.

Flow to the UF membrane was varied from about 6 to 15 GPM. 11 to 15% of the UF feed was recovered in the RO feed tank as permeate.

Because the RO feed tank was open to the atmosphere, it was necessary to inject small amounts of citric acid into this water to prevent iron hydroxide precipitation. Water from the RO feed tank was pumped through a single spiral wound RO membrane. RO permeate was either discharged overboard or returned to the ship's tanks while RO concentrate (non-permeated water) was recycled back to the RO feed tank.

Feed water chemistry is summarized in Table 1. Note the relatively high iron content and the high alkalinity of the feed water, making scale mineral precipitation a significant risk for this water. The concentration of solids and condensate in the water entering the process feed tank varied significantly. Suspended solids varied from 175 to over 10,000 mg/liter ahead of the desanding hydrocyclone. The particle size distribution for the solids is shown in Figure 3. XRD analysis indicated that the bulk of the solids were precipitated carbonate minerals. Condensate in the water entering the process feed tank varied from circa 0.1 to 100%. Most of the condensate was removed as feed tank skimming, however, so the actual UF membrane feed water typically contained only 100 to 900 mg/liter of condensate.

The UF membranes used for the pilot test program were polyacrylonitrile that had been specially treated by Osmonics-Desal to be rendered hydrophilic. The UF membrane pore size is 0.01 microns. Two types of materials were tested for the RO. The first set of RO membranes was polyamide and the second set was Cellulose Acetate. Both membranes have a pore size rating of 0.0005 microns.

RESULTS & DISCUSSION

Figure 4 visually illustrates the quality of water being fed to and recovered from the membrane treatment pilot plant. Much of the black color in the feed water is from suspended solids that were removed by the desanding hydrocyclone ahead of the process feed tank. The UF permeate typically retained a very light haze while the RO permeate was crystal clear. The samples shown in Figure 4 were analyzed with the following results:

	TPH	**Mercury**	**Arsenic**
Pilot Plant Feed	530 PPM	6,017 PPB	22,020 PPB
UF Permeate	174	5	4,540
RO Permeate	34	1	1,450

The successful removal of mercury and arsenic at this point in the test (42 hrs of run time on the membrane) suggests that both the UF and RO membranes are mechanically intact. Later in the test program this was not the case as RO permeate tube collapse and possible mechanical failure of UF membrane adhesive bonds was observed. However, given the mechanical integrity of the membranes at this point, the high permeation rate through the UF membrane for hydrocarbons, in contrast with the visual clarity of the sample and the lack of sheen on the sample's surface, suggests that the concentration of dissolved hydrocarbons in the process water is quite high. High levels of BTEX hydrocarbons in the produced water would not be surprising since the Thai condensate is relatively rich in aromatics.

Tables 2 – 4 summarize additional data on the performance of the pilot plant membranes during the course of the test program.

Hydrocarbon Reduction:

Hydrocarbon removal efficiency by the UF membrane is somewhat difficult to interpret. Under some run conditions, e.g., relative clean membranes, low ΔP across the UF membrane, and/or low percent of recycle water, TPH removal by the UF membrane ranged from 86 to 98%. At other times, the measured removal efficiency was far lower.

Several considerations suggest that the high concentration of hydrocarbons passing through the UF membrane are dissolved rather than dispersed. First, the UF permeate was visually clear. Second, the Unocal Thailand condensate is reasonably aromatic in nature with a substantial BTEX content. Third, the water arriving on the FSO is known to be contaminated with water-soluble corrosion inhibitors and water treatment polymer. Also, water treatment experience in nearby platforms has demonstrated that high levels of dispersed condensate in the produced water are associated with high levels of residual mercury. As will be discussed below, the concentration of mercury in the permeate water was very low, quite independent of the residual hydrocarbon levels. Finally, attempts to measure the TPH of the UF permeate using UV-fluorescence was not successful. Typical UV-fluorescence signals were 10 – 100 X the expected values based upon IR analysis of the same produced water sample. This suggests the presence of excess aromatics in the produced water compared to the aromatics content of the bulk condensate.

It should be noted that when a high fraction of recycle water is being fed to the membranes, the timing of sampling could be critical as most of the dissolved hydrocarbons would permeate the membrane early in the day's run, leaving fewer dissolved hydrocarbons to be detected in later samples.

Hydrocarbon removal by the tandem UF-RO membrane system was excellent, generally exceeding 95%. The RO membranes showed no evidence of fouling from exposure to hydrocarbon liquid, further suggesting that dissolved rather than dispersed hydrocarbons were passing through the UF membrane.

Mercury Reduction

Overall, the removal of mercury from the feed water was highly efficient, exceeding 99%. This result is consistent with water treatment tests that were conducted in 1996 (see OTC Paper 8712, May 1998) wherein it was determined that mercury present in the Gulf of Thailand produced water was elemental and tended to be present in particulate form. Both colloidal mercury droplets and mercury chemisorbed onto carbonate solids were found on the test filters. The data showed that mercury could be removed from the produced water by filtration at less than 1.2 microns.

Operational experience in the Gulf of Thailand on the Funan, Satun, and Platong platforms confirmed that efficient removal of hydrocarbons from the produced water was associated with high levels of mercury removal. Generally speaking, when the produced water TPH meets the Unocal Thailand self-imposed discharge limit of 40 PPM, the mercury levels fall below the self-imposed discharge limit of 10 PPB. However, at higher TPH levels, e.g., >100 PPM, the mercury in the produced water tends to exceed 10 PPB.

Arsenic Reduction

Arsenic is present in the condensate as As^{+3} that is extracted into the water phase. The equilibrium between arsenic in the condensate and in the water appears to be pH dependent. In the water, the thermodynamically favored form for arsenic is arsenite, AsO_3^{-3}. The equilibrium between As^{+3} and Arsenite is also pH dependent. Two reasons can be proffered for the unexpected success of the UF membrane in rejection of arsenic. First, some arsenic probably remains associated with the condensate and may thus be rejected when the UF membrane separates dispersed hydrocarbons.

Alternatively, the formation of Ferric Arsenite solid ($FeAsO_3$) may be responsible for limiting the passage of arsenic through the UF membrane. It is interesting to note that data in Table 4 show the ability of the UF membrane to reject arsenic was lowest early in the testing of UF membrane Set #1, when it would have had the fewest solids deposited within the canister. The use of the 1" hydrocyclone and the cartridge filters during the testing of UF membrane Set #2 limited the deposition of iron-based solids in the membrane canister and the ability of the UF membrane to reject arsenic was found to be correspondingly lower.

Until mechanical problems with the RO membranes were encountered late in the pilot plant campaign (collapsed inner collection tube), arsenic rejection by the UF and RO membranes in series average a respectable 92%. Unfortunately, the arsenic in the produced water feed to the pilot plant was sufficiently high that the discharge specification of <250 PPB could not be met by this system.

Operations

The major problems encountered during the course of the pilot test campaign were related to solids and to the accidental introduction of high concentrations (up to 100%) of condensate to the UF membrane. Figure 3 shows the particle size for solids in the FSO water. These solids were determined by XRD to be mainly precipitated carbonate minerals. Figure 5 shows how the normalized permeation rate varied over time for the UF membranes. Despite regular attempts to clean the membrane, it became progressively fouled by the very fine solids over time.

After about 140 hours on-line, the UF membranes were removed for inspection by Osmonics-Desal and a new set of membranes installed. The disassembly and inspection confirmed the presence of substantial solids that blocked over 50% of the membrane surface from the cross-flow of produced water. To control solids, a 2" desanding hydrocyclone was installed on the inlet to the process feed tank. This was then replaced with a 1" FloChamp desanding hydrocyclone with an improved ability to capture solids in the 5 to 10 micron particle size range.

Cartridge guard filters were later installed on the inlet to the UF filters. However, few solids deposited on the cartridges. With better solids control, the second set of UF membranes retained a higher and relatively constant permeation rate until they were fouled by the introduction of 100% condensate. Based upon Figure 5 data, the design for a full scale treatment system for this produced water system would be based upon a normalized permeation rate of 15 $\pm$ 5 GPM/(ft^2-day).

Figures 6 – 7 illustrate how the pressure drop across the second set of UF canisters and through the UF membrane varied with run time. Data in Figure 7 illustrate the impact of the 1' desanding hydrocyclone on the system's performance. The steep pressure drop immediately following the installation of the FloChamp resulted from a detergent flushing of the membrane. However, contrary to earlier experience, no pressure increase was observed subsequent to the washing.

Normalized permeation rates (gallons of permeate per ft^2 of membrane surface per day) are shown in Figure 8 for both of the RO membranes used in the test program. Note the loss of permeation that occurred early in the life of each membrane. This loss was most likely due either to swelling resulting from exposure to dissolved aromatics, or to membrane compression at the relatively high pressures being employed in the test campaign. In this system, the cellulose acetate membrane's relative permeability exceeded that of the polyamide membrane. However, selectivity and rate of arsenic rejection was better for polyamide.

Based upon Figure 8 data, the design for a full scale treatment system for this produced water system would be based upon an RO membrane normalized permeation rate of 8 ± 3 GPM/(ft^2-day).

SUMMARY AND CONCLUSIONS

The pilot test of a tandem UF and RO membrane system for cleaning highly contaminated produced water successfully demonstrated the capability of the subject technology. Controlling the solids content of feed to the membrane was the most important parameter for maintaining system performance. The UF membrane was resistant to fouling by dispersed hydrocarbons and successfully protected the RO membrane from exposure to liquid organics.

The presence of substantial levels of dissolved organic compounds limited the ability of the membranes to meet the Unocal Thailand discharge TPH standard of < 40 PPM. Under some running conditions, the UF membrane rejected in excess of 90% of the hydrocarbons in the process feed water. The tandem membranes together typically rejected 95% to 99% of the hydrocarbons in the feed water.

Mercury removal from produced water exceeded 99%. This result is in line with expectations since earlier work demonstrated that the mercury was either colloidal in nature or associated with dispersed hydrocarbons and solids.

Arsenic rejection was unexpectedly high across the UF membrane, exceeding 80% at times. Possibly the arsenic rejection resulted from the precipitation of ferric arsenite on iron-based solids trapped in the spiral wound UF membrane. Together, the RO and UF membranes generally rejected over 95% of the arsenic in the process feed water. However, residual arsenic levels in the product water still exceeded Unocal Thailand's self-imposed discharge standard of 250 PPB.

Table 1. The composition of feed water to the FSO Membrane Pilot Plant is summarized

Calcium	85	mg/liter
Magnesium	60	
Sodium	2400	
Iron	37	
Chloride	1690	mg/liter
Sulfate	21	
Bicarbonate	3900	
Total Alkalinity as $CaCO_3$	3200	
Arsenic	15 – 28	mg/liter
Mercury	0.4 – 9.2	
Total Suspended Solids	175 – 10,000	

Table 2. Hydrocarbon removal data are summarized for the FSO Membrane Water Treatment Pilot Plant

	Membrane Run Time (Hours)	Hydrocarbons in Feed (PPM)	TPH of UF Permeate (PPM)	TPH Reduction (%)	TPH of RO Permeate (PPM)	Total TPH Reduction (%)
Membrane Set #1	4	122	17	86	4	97
	23	361	7	98	3	99
	32	910	240	74	10	99
	42	530	174	67	34	94
	52	420	256	39	40	90
	62	328	130	60	10	97
	75	176	70	60	6	97
	89	102	81	20	10	90
	99	312	115	63	58	81
	122	1895	27	99	2	>99
	128	2240	22	99	–	–
Membrane Set #2	5	975	18	98	7	99
	24	486	387	20	35	93
	37	614	435	29	19	97
	42	449	395	12	10	98
	54	492	376	30	32	94
	67	444	38	91	22	95
	72	314	34	89	15	95
	131	228	102	55	21	91
	165	500	370	26	40	92

Table 3. Mercury removal data are summarized for the FSO Membrane Water Treatment Pilot Plant

	Membrane Run Time (Hours)	Mercury in Feed (PPB)	Hg in UF Permeate (PPB)	Hg Reduction (%)	Hg in RO Permeate (PPB)
Membrane Set #1	4	588	0.7	99.9	0.3
	23	7139	4	99.9	0.2
	32	9170	2	>99.9	0.3
	42	6017	5	99.9	0.9
	52	6943	2	>99.9	0.6
	62	3144	3	99.9	0.6
	75	539	2	99.6	0.4
	89	1700	5	99.7	4.2
	99	1763	3	99.8	2.1
	122	988	0.6	99.9	0.5
	128	--	—	—	--
Membrane Set #2	5	261	1.3	99.5	0.5
	10	—	--	—	—
	37	105	0.9	99.1	0.2
	42	—	—	—	--
	54	—	—	—	--
	67	44	1.9	95.7	0.2
	72	49	2.9	94.1	0.5
	131	433	—	--	0.6
	148	67	0.9	98.7	0.6

Table 4. Arsenic removal data are summarized for the FSO Membrane Water Treatment Pilot Plant

	Membrane Run Time (Hours)	Arsenic in Feed (PPB)	As in UF Permeate (PPB)	UF As Reduction (%)	As in RO Permeate (PPB)	Total As Reduction (%)
Membrane Set #1	4	13120	12670	3	1856	86
	23	17980	7260	60	807	95
	32	22640	14600	36	1616	93
	42	22020	4540	79	1448	93
	52	28700	4060	86	1058	96
	62	16920	3320	80	1768	90
	75	13800	4080	70	876	94
	89	8220	635	92	142	98
	99	11180	1695	85	602	95
	122	6590	1145	83	684	90
	128	–	–	–	–	–
Membrane Set #2	5	28680	11670	59	1476	95
	10	21060	10290	51	2544	88
	37	14790	10080	32	1193	92
	42	–	–	–	–	–
	54	–	–	–	–	–
	67	19760	19720	1	2296	88
	72	18540	15910	<1	2004	89
	131	12980	6950	47	–	–
	148	16480	14670	11	8920	46

Figure 1. PFD for FSO Membrane Water Treatment Pilot Plant
Figure 2. Photo of FSO Membrane Water Treatment Pilot Skid
Figure 3. Particle Size Analysis of Solids from FSO Water
Figure 4. Photo of Membrane Pilot Plant Feed and Product Water
Figure 5. Normalized Permeation Rate for UF Membrane vs. Time
Figure 6. Pressure Drop Across UF Membrane Canisters vs. Time
Figure 7. Pressure Drop Through UF Membrane vs. Time
Figure 8. Normalized Permeation Rate for RO Membrane vs. Time

Figure 1. PFD for FSO Membrane Water Treatment Pilot Plant

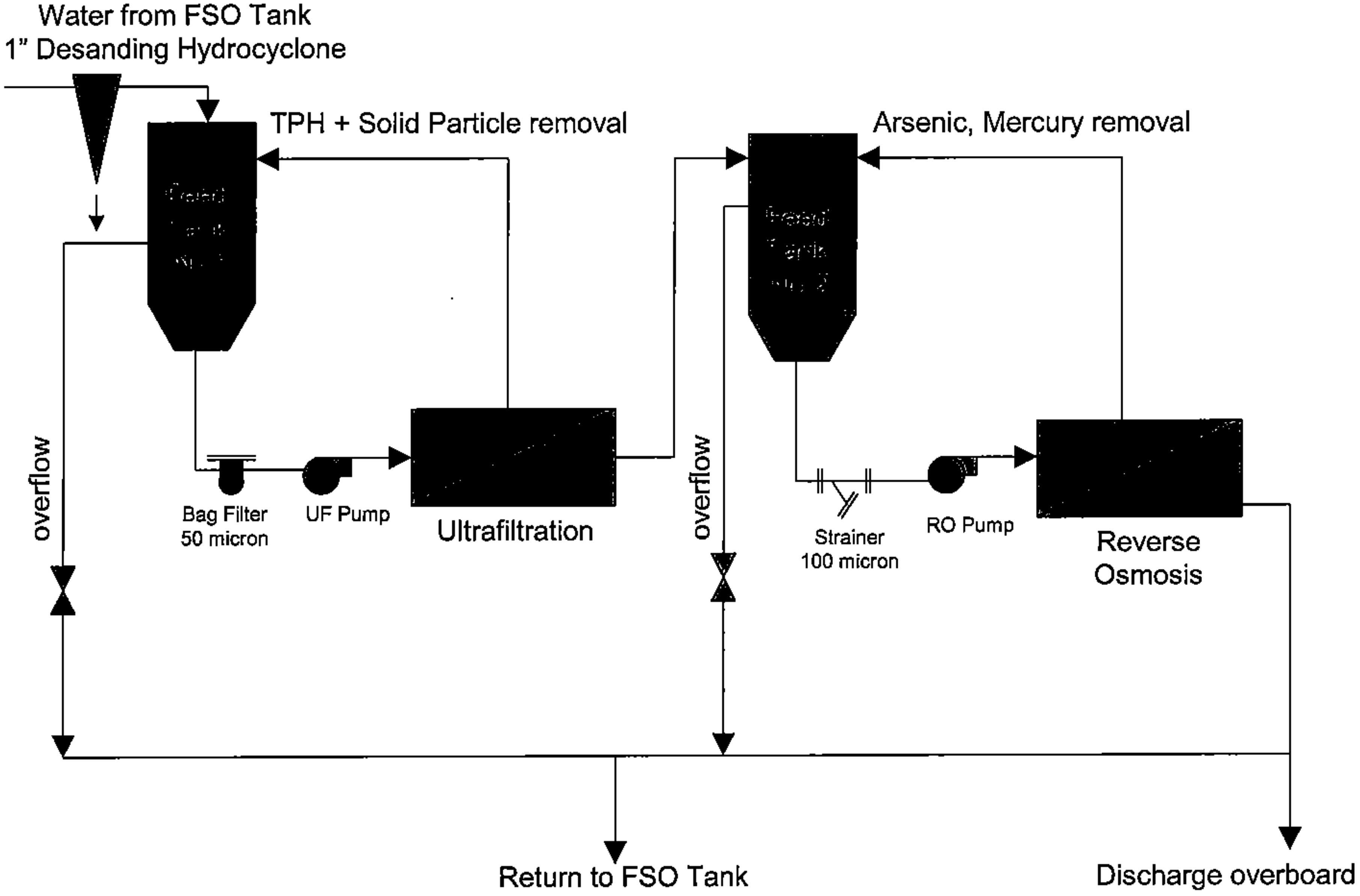

Figure 2. FSO Membrane Water Treatment Pilot Skid

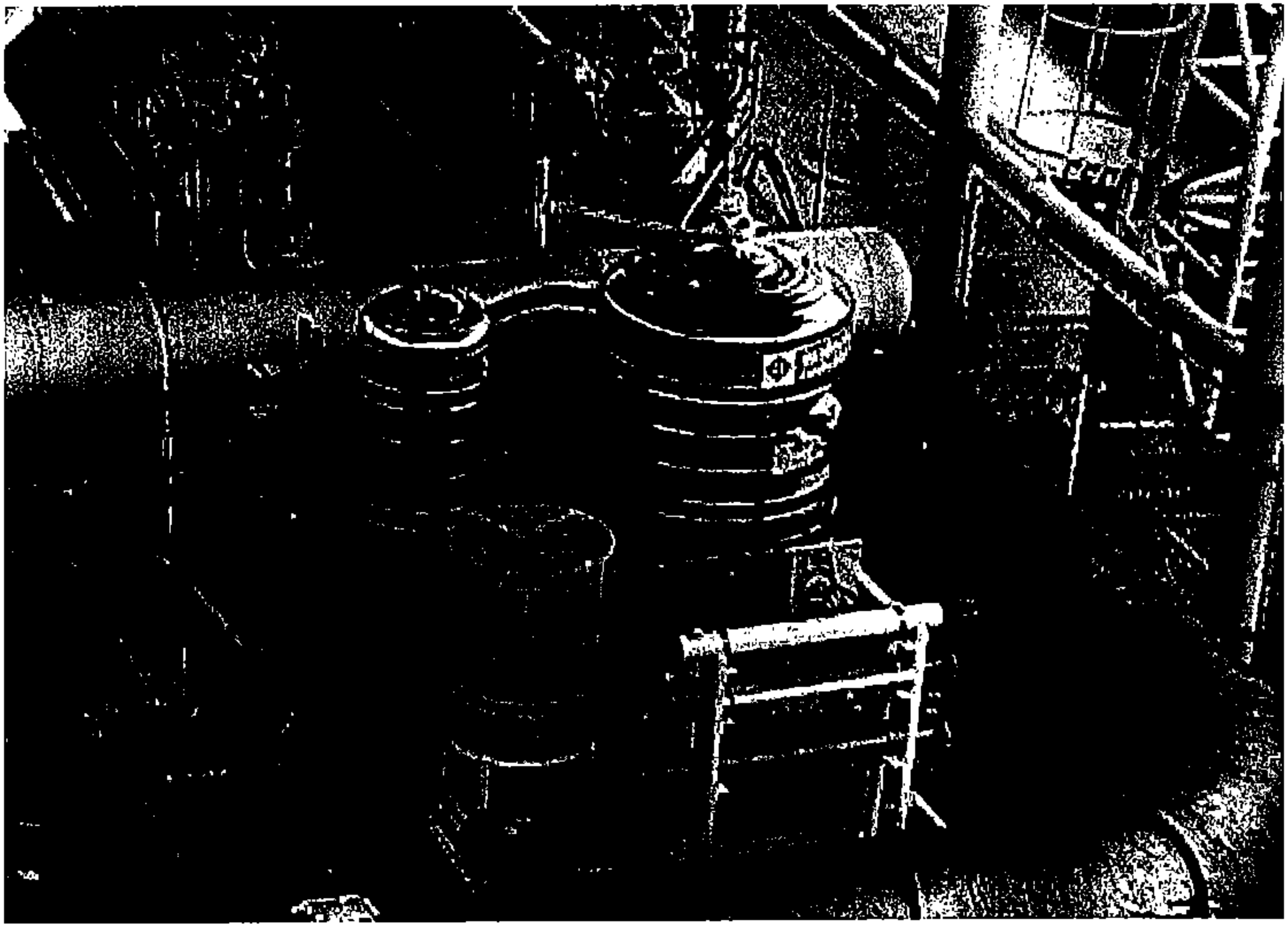

Figure 3. Particle Size Analysis of Solids From FSO Water, 18Jul99

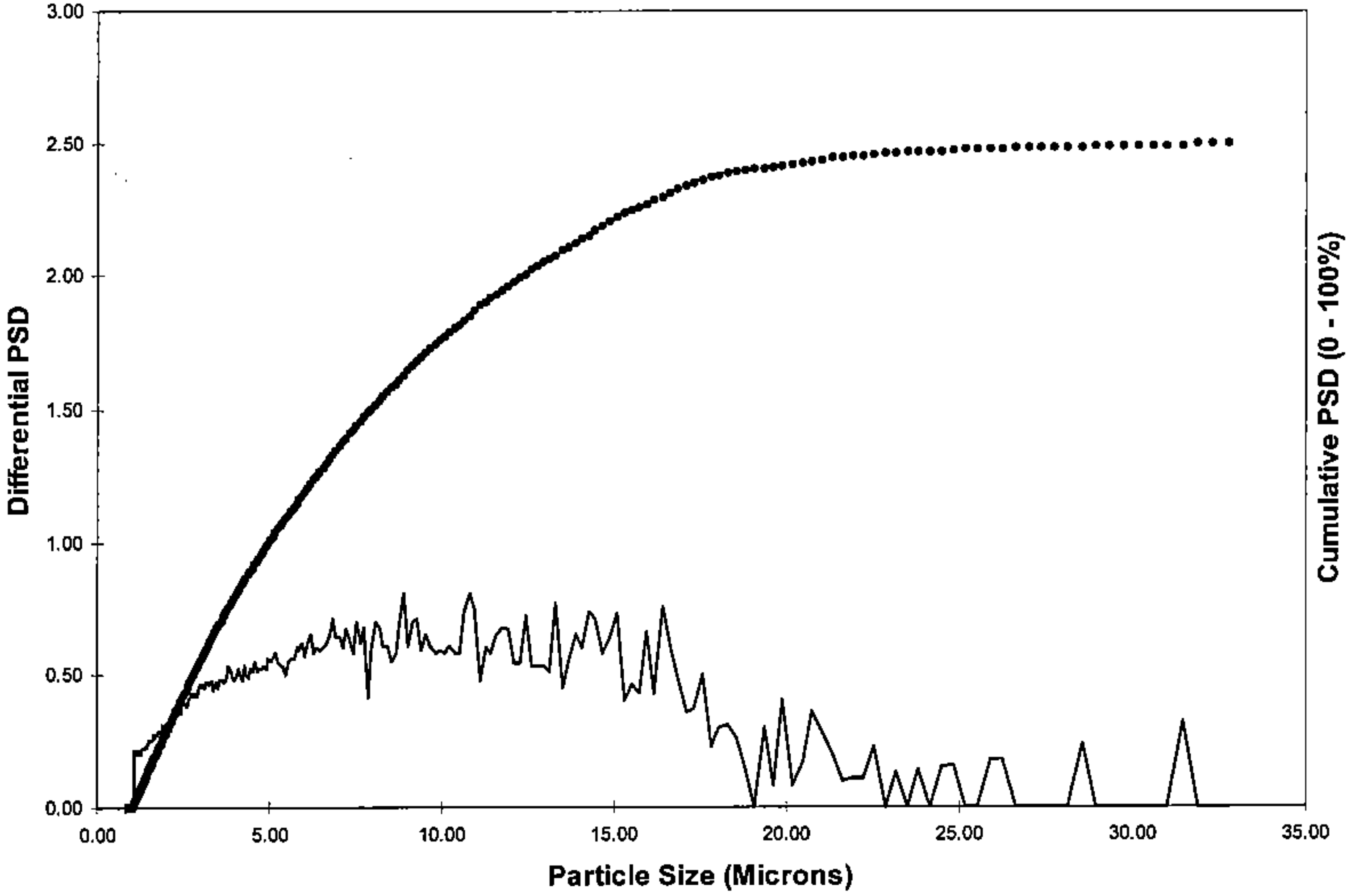

Figure 4. FSO Membrane Pilot Plant Feed and Product (UF & RO Permeate) Water Samples

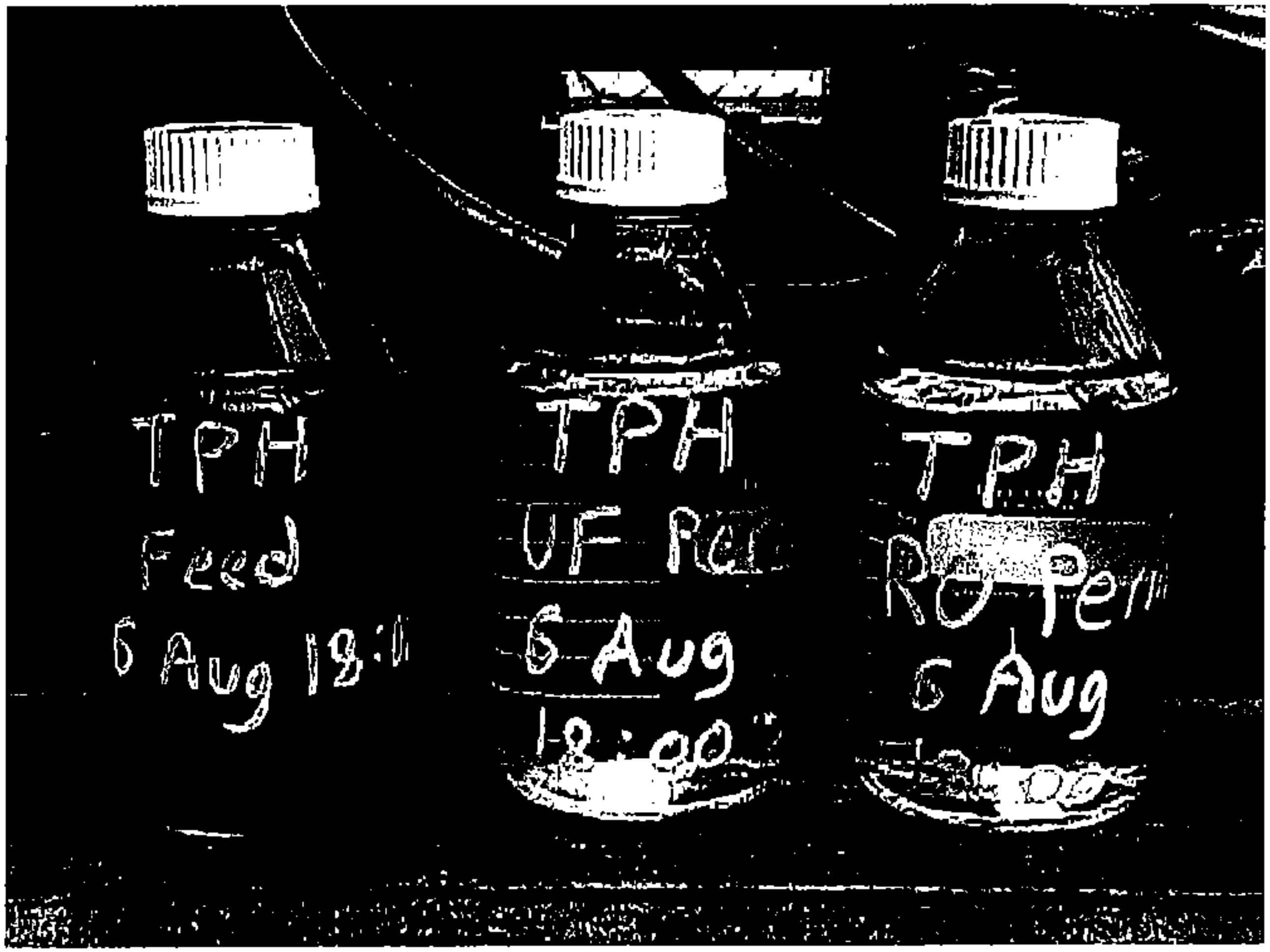

Figure 5. Normalized Permeation Rate vs Time for Ultra-Filtration Membrane
(Trend Line is 10 pt. Moving Average)

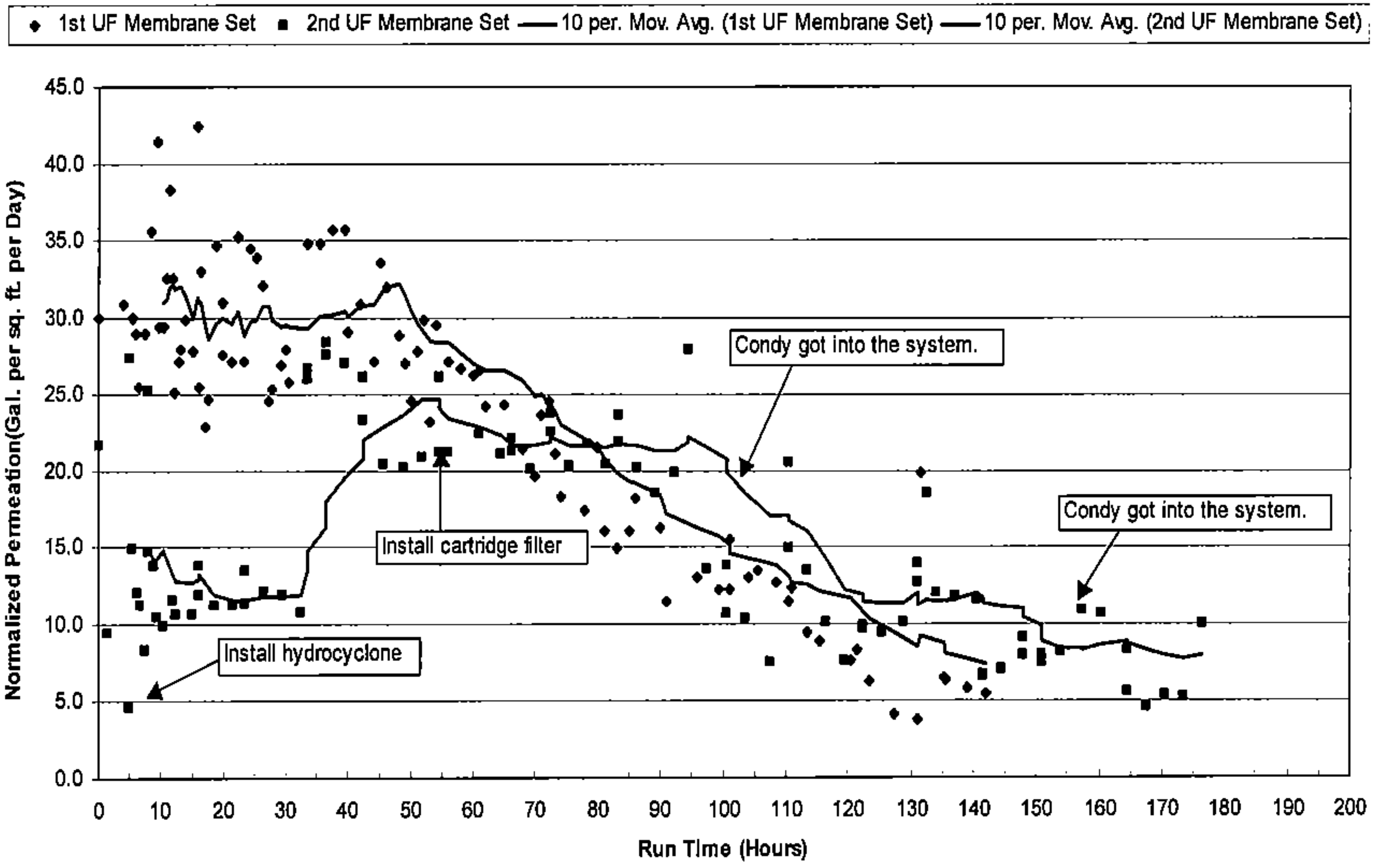

Figure 6. Pressure Drop Across UF Membrane Cannisters vs time (2nd Set)

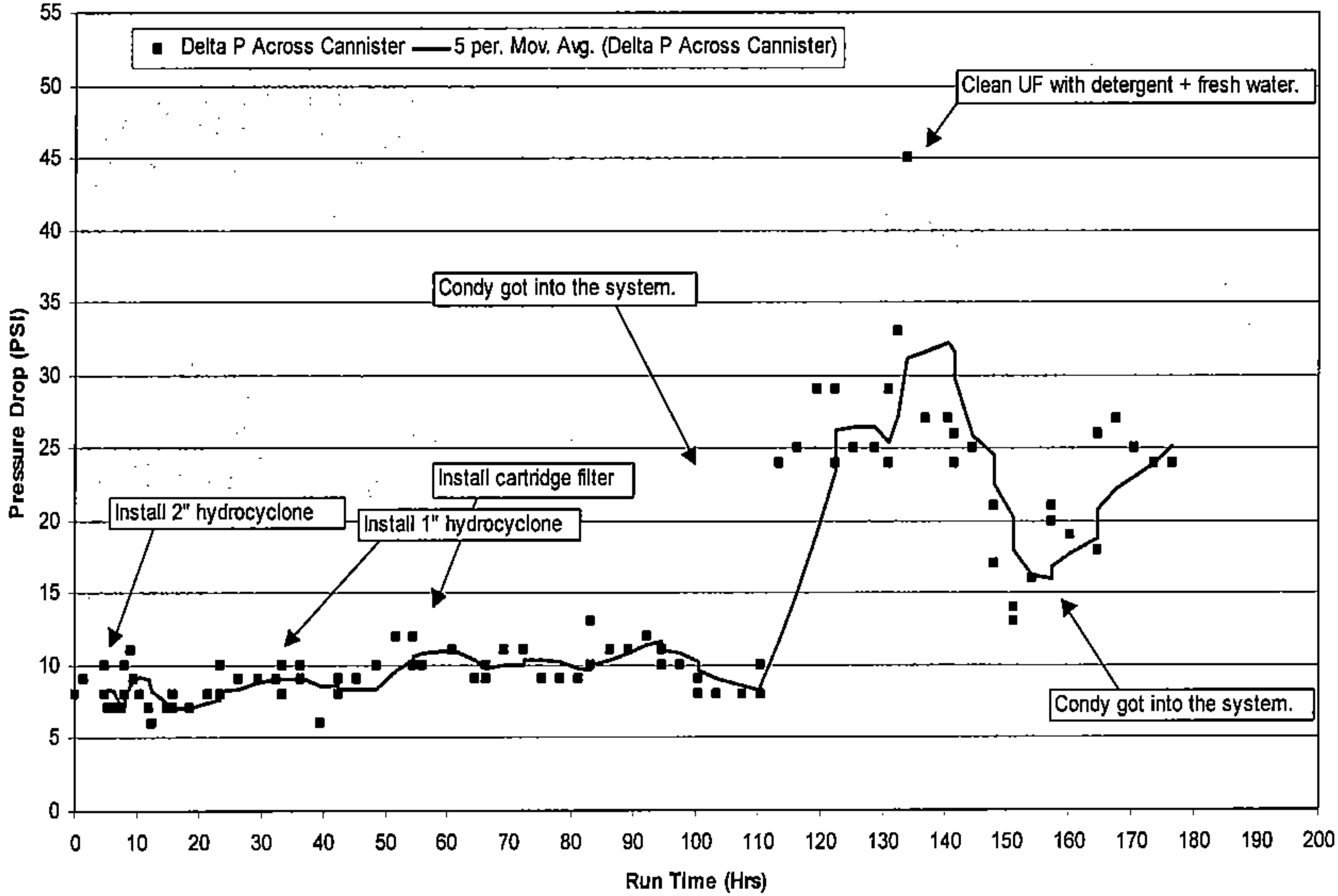

Figure 7. Pressure Drop Through UF Membrane vs Run Time (2nd Set)

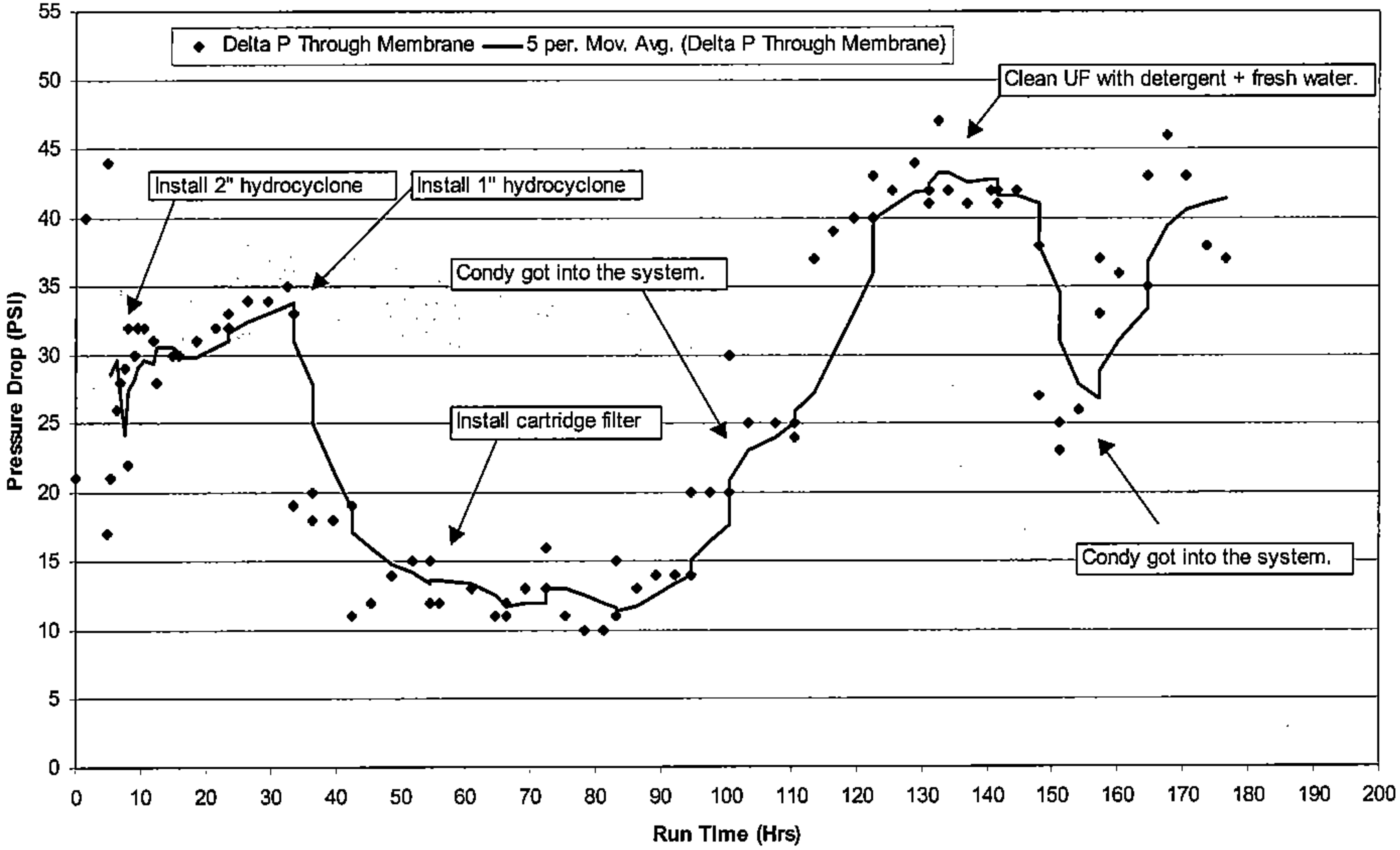

Figure 8. Normalized Permeation Rate for RO Membrane vs Time