VOLUME REDUCTION BY HYPERFILTRATION

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ABSTRACT

Ongoing testing being conducted at TVA's Sequoyah Nuclear Plant on the role that hyperfiltration (HF) can play in processing radioactive liquid streams is reviewed. Preconcentration of condensate demineralizer regeneration waste solutions by HF proved that acceptable volume reduction factors, rejection rates, and membrane life could be obtained while processing actual nuclear plant waste streams. Status of testing on floor and tritiated drain wastes, as well as the use of HF in decontaminating contaminated oil, is discussed.

BACKGROUND AND HISTORICAL OVERVIEW

In 1980, Commonwealth Edison Company, at its Zion Nuclear Plant, operated an ultrafiltration/reverse osmosis (UF/RO) test apparatus to verify the concept of boric acid reclamation by membrane technology as a volume reduction technique. Testing at Zion on its auxiliary building floor drains and tritiated drains verified that the concept of producing a reasonably contaminant-free, boron-rich, permeate stream could be achieved. Data on this testing was presented at the "Waste Management 81" ANS topical meeting.

Two areas of concern remained after the Zion testing. One was the degree of pretreatment needed and the second was that a dynamically formed HF membrane had not been fully evaluated. Dynamically formed HF membranes were to be evaluated because of their tolerance for suspended material and wider temperature and pH ranges than conventional cellulose acetate membranes. The only HF membrane available for the study was a membrane with a ceramic tube support. No acceptable membrane could be formed on the ceramic tubes, and several of the tubes broke during the attempted membrane formation.

A search for a durable HF membrane culminated in the selection of a sintered metal HF membrane unit produced by CARRE, Inc., of Seneca, South Carolina. Tennessee Valley Authority (TVA) Energy Demonstrations and Technology Division funded the procurement and testing of a pilot plant to verify HF's ability to reduce the volume of waste to be handled by other process equipment at TVA's nuclear plants.

EQUIPMENT DESCRIPTION

Figure 1 shows a schematic diagram of the TVA membrane test system as it was set up to run condensate demineralizer regeneration waste. Fluid entering the pumping system passed through the 40 mesh strainer. When in the recycle mode of operation, concentrate and permeate were both directed back to the recycle tank via flexible hoses not shown on the figure. When in the single pass mode, both the concentrate and permeate were discharged.

Three modules were used for the initial phase of this testing. Each had 13 square feet of membrane area. One module had 1/2-inch internal diameter porous stainless steel tubes and the other two modules had 5/8-inch internal diameter tubes. Zirconium oxide poly acrylic acid (ZOPA) membranes were deposited on the internal diameter of the tubes in each module. Design operating pressure was 1,000 psi. Later in the test program, a smaller module (labeled N-12) with 0.655 square foot of membrane area was added to the system.

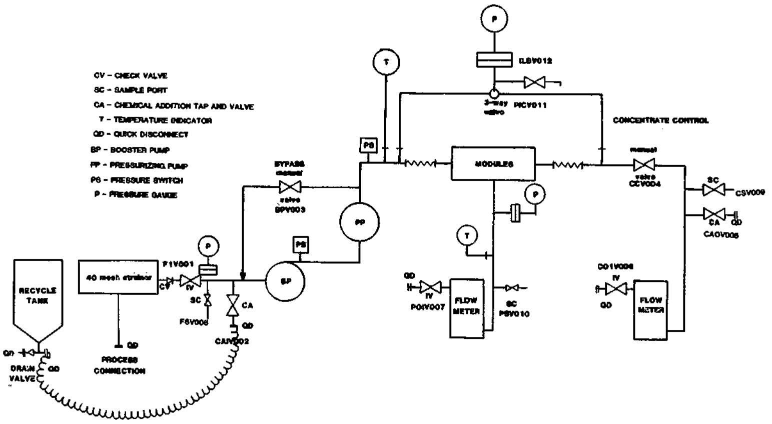

Fig. 1. TVA Membrane Test System.

MEMBRANE OPERATION ON CONDENSATE DEMINERALIZER REGENERATION WASTE

During initial startup operation, the membrane test unit was run during first shift only. The test procedure called for operation in a single pass mode when fresh waste was available and in a recycle mode from the test unit recycle tank when waste was not available.

Important points that we learned from the test which should be stressed were the ease of operation of the unit and the actual adverse environment in which the unit operated. At one point, as much as 10-percent resin was fed into the unit. The presence of resin in the feed has caused minor problems with the operation of the hyperfiltration unit. These problems were associated with tripping of the feed pump because of low suction pressure and the breakdown of the resin beads because of recycle operation. Once during the testing, fresh feed was run bypassing the 40 mesh strainer. Resin beads subsequently recirculated in the test unit during recycle operation and were broken down by the action of the pumps in combination with operating temperatures up to 50°C (near the upper temperature limit for the beads). A crud buildup on the sight glasses and tank indicated that the resin was decomposing and plating out on the surfaces of the unit. This may have been the cause of the modification of the membrane.

System operating conditions were recorded at 60-minute intervals including permeate and concentrate flow rates, module inlet and outlet pressures, feed and permeate temperatures, feed and permeate pH, concentrate and feed conductivities. Calculated quantities including percent system recovery, percent membrane conductivity rejection, membrane flux (gal/ft^2/day, GFD), and membrane permeability (GFD/psi) were included on the data sheet with the time and comments as required.

Following the initial operation on waste and a period of membrane evaluation and washing, the test unit was run on waste on a 24-hours-per-day basis with a new membrane test section (N-12) installed downstream of the previously existing membrane modules.

A short period of membrane evaluation and washing concluded testing on condensate demineralizer regeneration waste fluid. Membrane test to single pass operation on radioactive waste fluids. Samples of feed, concentrate, and permeate from the radioactive waste testing were sent to the Sequoyah Nuclear Station Laboratory for analysis of pH, conductivity, total suspended solids, total dissolved solids, sodium, chloride, and activity.

MEMBRANE PERFORMANCE

Membrane performance data is shown in Fig. 2 and the range of feed parameters is shown in Table I. The data covers a period of nearly 1,000 hours of operation, 3 weeks of first-shift operation on waste, a week of membrane evaluation and washing, and a final 4 weeks of continuous operation on waste with a short period of washing and membrane evaluation at the end of the eighth week. The figure includes conductivity rejection and membrane permeability normalized to 35°C for operation on demineralizer regeneration fluid.

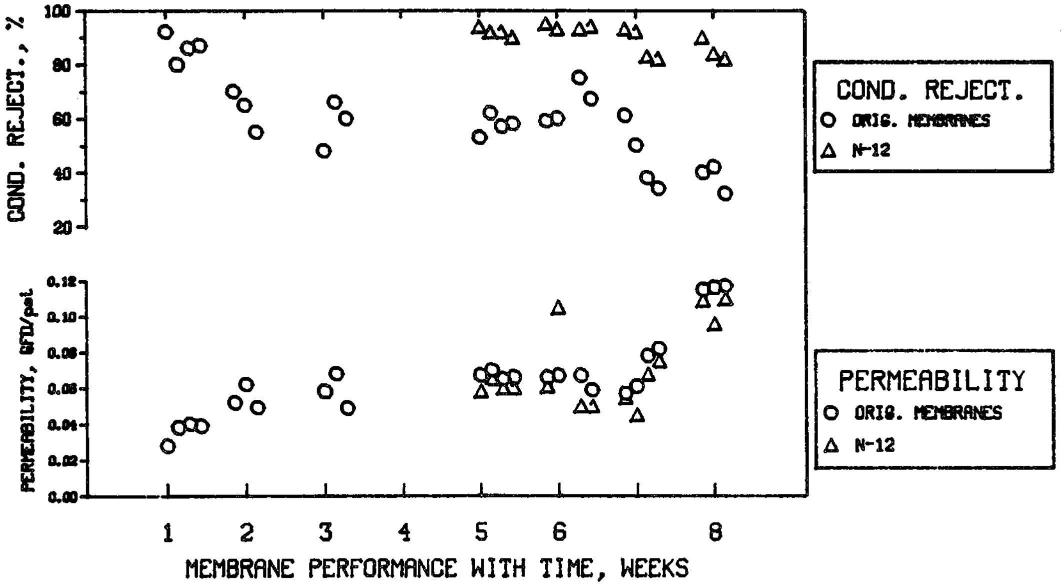

Fig. 2. Membrane Performance on Condensate Demineralizer Regeneration Waste Solutions.

The first 2 weeks of operation show a general trend of rejection decline accompanied by a permeability increase over 36 hours of operation on waste. Initial rejection for all species was nearly 90 percent but quickly dropped to 80 percent, and eventually declined to below 60 percent. Following a period of operation on demineralized water, the rejection of most species improved to nearly 70 percent. Rejection of suspended solids should be nearly 100 percent; however, the accuracy of suspended solids rejection calculations is poor because the feed concentration is very near the limits of detection and the permeate concentration is probably far below the detection limit. The lower limit of detection was reported as the suspended solids concentration in permeate and was used to calculate rejections.

Table I

Condensate Demineralizer Regeneration Waste Ranges

Parameters	Low	High
Conductivity	7,700 micro-ohms	23,800 micro-ohms
pH	5.7	8.5
Total Suspended Solids	18.6 ppm	10% of feed volume
Total Dissolved Solids	4,118 ppm	10,143 ppm
Sodium	2,600 ppm	23,800 ppm

The membrane permeabilities, while operating on sodium nitrate solution for 2 days, varied between 0.04 and 0.06 GFD/psi while rejections of conductivity ran consistently near 60 percent. Washing with an anionic detergent resulted in permeability greater than 0.08 GFD/psi and rejection below 40 percent on sodium nitrate solution. It appeared that these detergents removed the resin plateout, but also affected the membrane. The detergent used normally should not have affected the membrane. Apparently, the membrane was modified by the plateout of the resin or the waste stream and thus was affected by the cleaning.

A test section was installed to tun on waste in an attempt to repeat the previous membrane experience. The initial salt point data on membrane test section N-12 was 0.039 GFD/psi and 94 percent rejection. The initial performance characteristics on waste were 0.041 GFD/psi and 96 percent conductivity rejection.

Membrane operation on waste continued for 145 hours with nearly constant membrane rejection and permeability characteristics. Rejections for module N-12 were above 90 percent. Rejections for the previously existing membranes ranged between 60 and 70 percent. Membrane permeability for N-12 and the existing modules started at 0.065 GFD/psi and declined to 0.048 GFD/psi.

A new waste batch was introduced to the recovery system and a notable change in membrane rejections and permeabilities occurred (possibly another resin-induced effect). On the new waste membrane, rejections for module N-12 dropped from 90 percent to 80 percent, and for the existing modules rejections dropped from approximately 60 percent to 30 percent. Membrane permeability increased from 0.05 GFD/psi to 0.06 GFD/psi for N-12 and from 0.05 GFD/psi to 0.08 GFD/psi for the other modules. Most of the rejection data appears erratic compared to previous data, but conductivity rejections remained under previous levels. Membrane permeability was above 0.11 GFD/psi for both N-12 and the existing modules.

Following an anionic detergent wash, rejections for N-12 and the individual modules ranged between 10 and 30 percent and permeabilities ranged between 0.12 and 0.19 GFD/psi on the nitrate solution. At this time, module N-12 was stored onsite for further testing and the three original modules were returned to CARRE, Inc., for membrane reformations.

Test Section N-12 was returned to service where it was run on contaminated floor drain waste and then tritiated drain waste the following day. The tests consisted of running the system in a single pass model until steady conditions existed prior to obtaining samples for analysis. Analysis results and species rejections are shown in Table II for N-12 operation on floor drain and tritiated drain wastes. Solute and solid concentrations and activity in the floor drain waste fluid were low and analysis results were inconsistent. High concentrations and activity in the tritiated drain waste fluid resulted in more accurate analysis results, and thus rejection percentages listed are more accurate than for those listed in the floor drain section of Table II. The actual average rejection rate should be higher since the activity rejection rates were generated near the end of the membrane life.

Table II

N-12 Performance on Floor and Tritiated Drain Waste

		FLOOR DRAIN WASTE				TRITIATED DRAIN WASTE			
		FEED	CONCEN.	PERMEATE	% REJECT	FEED	CONCEN.	PERMEATE	% REJECT
Conductivity	(umho/cm)	85	88	21	75	99	100	29	70
TSS	(ppm)	12	13.2	0.1	97	8	8	0.4	95
Boron	(ppm)	65	67	61.3	5	343	346	289	16
ACTIVITY									
Na-24	(mci/ml)	ND	2.5E-06	ND		9.0E-06	9.0E-6	3.2E-06	65
Mn-54	(mci/ml)	ND	6.9E-07	ND		1.8E-05	1.6E-05	4.1E-07	98
Co-58	(mci/ml)	ND	2.8E-06	ND		1.5E-04	1.5E-04	8.1E-06	95
Co-60	(mci/ml)	ND	1.6E-06	ND		3.1E-05	3.4E-05	2.2E-06	93
I-131	(mci/ml)	ND	9.0E-07	2.2E-07		1.7E-04	1.8E-04	2.1E-05	88
I-133	(mci/ml)	ND	8.3E-07	2.9E-07		1.3E-05	1.5E-05	1.9E-06	85
Cs-134	(mci/ml)	ND	ND	ND		4.1E-05	4.2E-05	8.1E-06	80
Cs-137	(mci/ml)	6.5E-07	9.3E-07	ND	>99.9	9.8E-05	1.0E-04	1.8E-05	81

ND = Below lower limit of detectability.

SUMMARY OF CONDENSATE DEMINERALIZER REGENERATION WASTE PROCESSING

In all, the unit performed better operationally than other membranes tested at other nuclear plants even though rejection rates were not as high. The dependability and ease of operation of the unit, in our opinion, outweigh the reduced rejection for this application.

Membrane life met our minimal acceptable goals (greater than 12 months of normal expected processing), but fell slightly short of our expectations (greater than 24 months of normal expected processing). Two possible reasons for the shortened membrane life have been speculated. One possible reason was the resin problem discussed above and a second is the method of membrane formation. Discussions with CARRE indicate that the ZOPA membrane performance may be improved by altering the formation procedure. Also a new neutral membrane being developed by CARRE may exhibit improved characteristics. Additional testing is planned to evaluate the altered ZOPA membrane formation and new neutral membrane on condensate demineralizer regeneration waste solutions.

Initial testing of the HF pilot unit was successfully completed on processing condensate demineralizer regeneration waste solutions. This will reduce the volume of waste to be sent to the condensate demineralizer waste evaporator, thus allowing its remaining processing capacity to be available to process condensate demineralizer regeneration waste solutions from two reactor units when the demineralizers are used in conjunction with full-flow processing philosophy during primary-to-secondary leakage. The goals of this segment of testing were to demonstrate that the unit could produce a dischargeable quality permeate stream, withstand the regeneration solutions, and give an adequate throughput before membrane reformation was necessary. These goals were achieved.

MEMBRANE OPERATION ON FLOOR AND TRITIATED DRAIN WASTE

Initial testing to verify the reduced pretreatment required for processing auxiliary building floor and tritiated drains by HF was conducted and reviewed in relationship to the previous testing completed by Commonwealth Edison. The testing goals are (1) operation of the unit over a wide feed temperature, (2) operation without the need of pH adjustment, (3) operation with minimal operator attendance, and (4) production of dischargeable quality permeat or a permeate enriched in boron which can be recycled to the chemical and volume control system with minimal additional polishing.

Figure 3 shows the boron rejection curves for several different membrane types. It also shows that the CARRE, Inc., HF membrane compares favorably with other membranes for boron rejection.

Figure 4 is a photograph of the test unit as set up to process floor and tritiated drain waste. Figure 5 shows the data available after approximately 450 hours of operation. The figure includes conductivity rejection and membrane permeability normalized to 35°C. Table III shows activity rejection obtained after about 450 hours of operation. Testing will be conducted on the new neutral membranes and compared to the current membrane. This comparison will be reported at a later date.

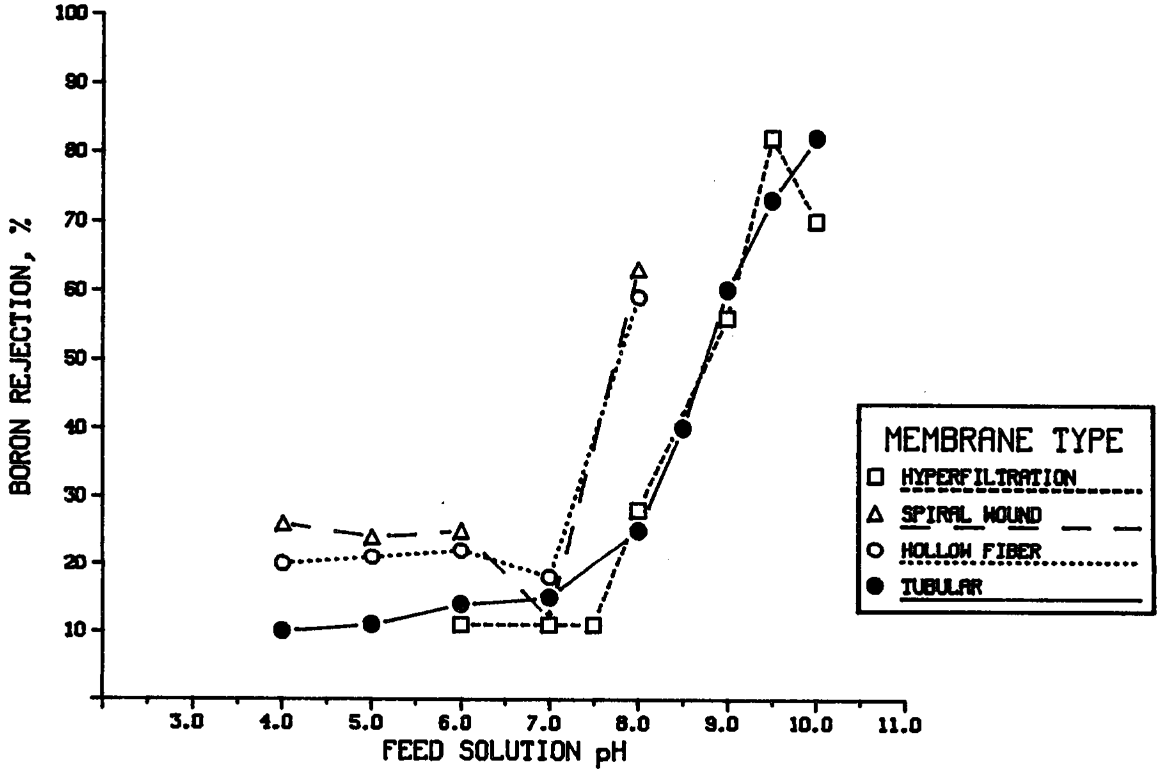

Fig. 3. Boron Rejection with Change in pH.

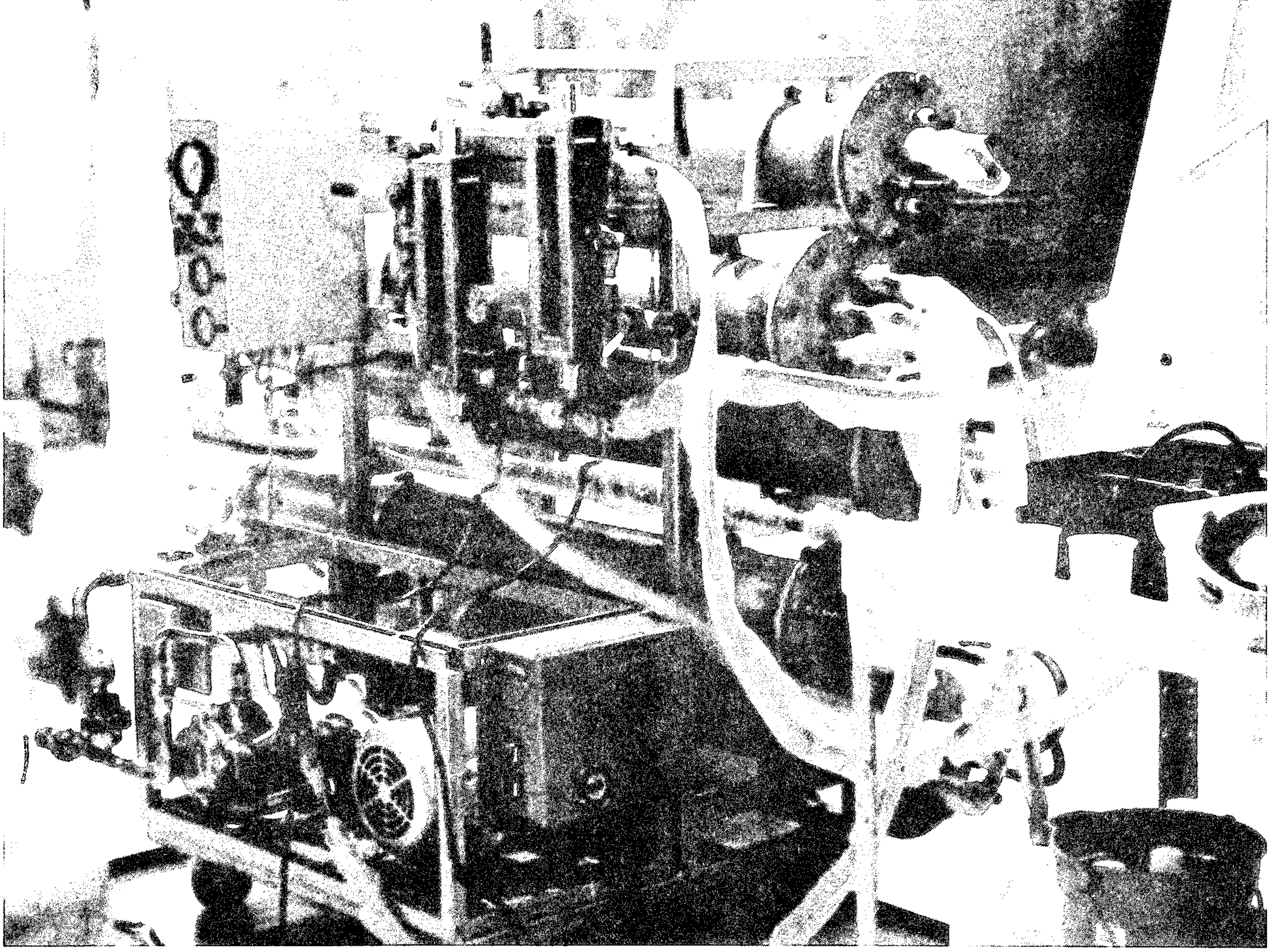

Fig. 4. Test Unit.

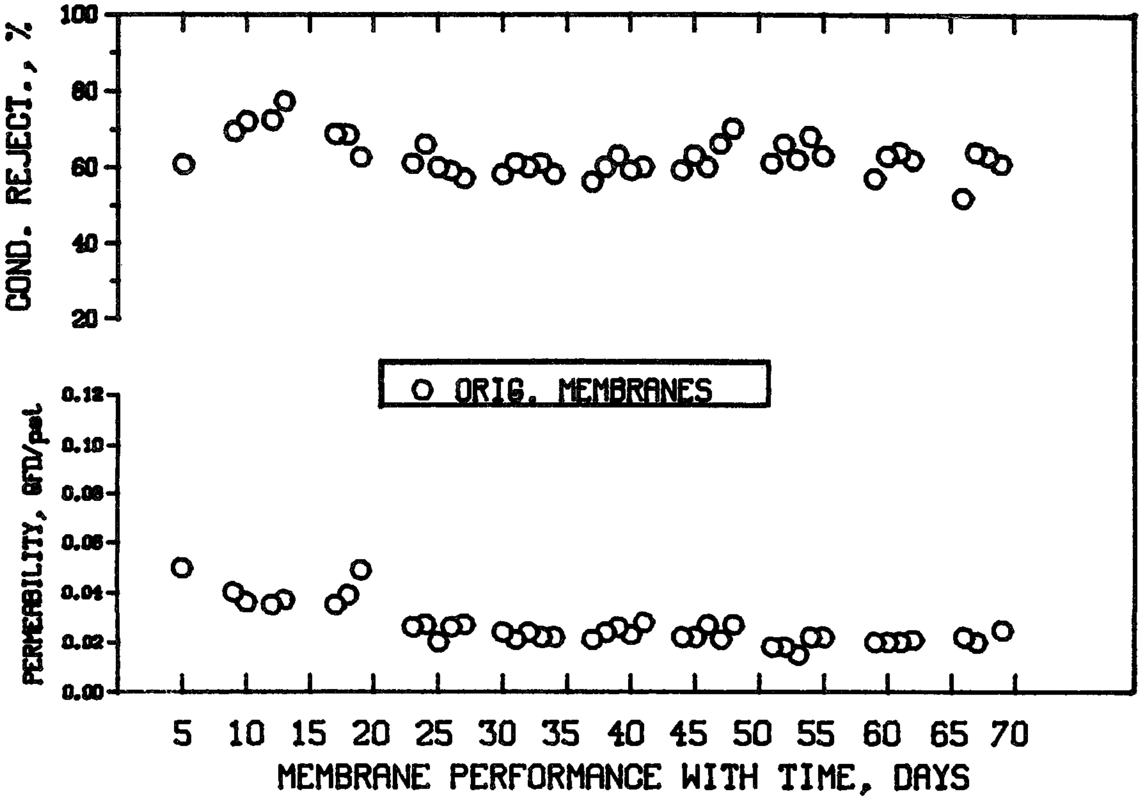

Fig. 5. Membrane Performance on Floor and Tritiated Drain Waste,

Table III

Activity and Rejection for Floor and Tritiated Drains

Nuclide	Feed	Permeate	Rejection
Mn-54	1.152E-04	4.256E-05	63
Co-57	1.466E-05	1.254E-06	91
Co-58	1.234E-02	5.216E-04	96
Co-60	6.048E-04	2.630E-05	96
Tc-99M	5.252E-05	2.429E-06	95
I-131	2.126E-04	6.184E-05	71
Cs-134	5.824E-05	3.420E-05	41
Cs-137	6.088E-05	4.411E-05	27
Total Activity =	1.35E-02 uCi/ml	7.35E-04 uCi/ml	94%

MEMBRANE OPERATION ON CONTAMINATED OILS

The test unit was set up with a CARRE, Inc., ultrafiltration membrane installed on its stainless steel support structure to determine if contaminated oils, mainly reactor coolant pump motor oil, could be decontaminated to releaseable limits. Testing was initiated in January of this year. Information to be determined from the testing is the amount of oil that can be recovered from each batch, the lowest level of contamination that the oil can be decontaminated to, and the optimum operational parameters, such as flow rate and feed pressure. This data will also be reported at a later date.

SUMMARY OF TESTING

The testing of hyperfiltration on condensate demineralizer regeneration waste solutions verified that the installation of such a unit could achieve the needed volume reduction of the feed input to TVA's existing condensate demineralizer waste evaporator thus allowing sufficient evaporator capacity to process two regenerations per day and still have enough extra capacity to be used to evaporate normal radwaste inflows. The installation of hyperfiltration equipment will eliminate the need to install additional evaporator capacity for both condensate solutions and radwaste processing. Additional testing will be conducted to evaluate new membranes which might further improve membrane life.

Testing on radwaste processing to determine the cost benefit of installation of hyperfiltration or reverse osmosis as pretreatment and volume reduction effect prior to existing radwaste evaporators will be conducted. The major benefit would be to determine if the radwaste inflow rate could be reduced to match the limited processing capacity of existing radwaste evaporators. The effect of processing (pretreating) radwaste by membrane technology prior to a demineralizer will also be evaluated as well as the economic benefit of boron recovery from radwaste.