Testing of a Benchscale Reverse Osmosis/Coupled Transport System for Treating Contaminated Groundwater

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INTRODUCTION

The Reverse Osmosis/Coupled Transport process is a innovative means of removing radionuclides from contaminated groundwater at the Hanford Site. Specifically, groundwater in the 200 West Area of the Hanford Site has been contaminated with uranium, technetium, and nitrate. Investigations are proceeding to determine the most cost effective method to remove these contaminants. The process described in this paper combines three different membrane technologies (reverse osmosis [RO], coupled transport [CT], and nanofiltration [NF]) to purify the groundwater while extracting and concentrating uranium, technetium, and nitrate into separate solutions. This separation allows for the future use of the radionuclides, if needed, and reduces the amount of waste that will need to be disposed of. This process has the potential to concentrate the contaminants into solutions with volumes in a ratio of 1/10,000 of the feed volume. This compares to traditional volume reductions of 10 to 100 for ion exchange and stand-alone reverse osmosis. The successful demonstration of this technology could result in significant savings in the overall cost of decontaminating the groundwater.

Details of the CT processes for uranium, technetium, and nitrate were published by Chiarizia, et al[1]. Descriptions of the principles of RO and NF processes have been published in many technical journals and texts and will not be reviewed in this paper.

A 0.26-L/minute capacity field test unit was fabricated by Bend Research Incorporated (BRI) of Bend, Oregon. Bench-scale testing of the three membrane processes was conducted to provide an indication of what data to expect from the field test unit prior to field testing . A schematic diagram of the field test unit is given in Figure 1. The RO system concentrates the contaminants for feed to the CT system and provides clean water for discharge. The CT membranes remove the uranium, technetium, and some nitrate and concentrate these contaminants into solutions for disposal. The system is designed to recycle the effluent from the CT system to the RO feed to increase the efficiency of the CT membranes. Operating in this manner would lead to continual increase in the concentration of the total dissolved solids in the RO feed, eventually fouling of the RO membranes. The CT effluent is fed to the NF system to prevent the buildup of total dissolved solids. In the NF system, the calcium, magnesium, silica, and other naturally occurring ions are not easily rejected. The permeate stream containing these compounds is then returned to the clean water stream and released. The larger ions (i.e., uranium and technetium) are rejected at the NF membrane and are recycled to the RO feed tank were they are again sent to the CT system for removal.

Three bench-scale membranes systems (RO, CT, and NF) were used to simulate the field-scale system in a batch mode.

DESCRIPTION OF TEST

Seventy-two liters of contaminated groundwater from monitoring well (299-W19-24) were used as feed for the bench-scale testing. Twenty-four batches of 3 L each were concentrated using the RO system. After the RO step was completed, the resulting retentate was used as feed for the CT system. The water from the CT system was finally fed through the NF system. Process flow diagrams for these units are supplied in Figures 2 through 4.

Test Method and Test Equipment
Following the processing sequence in the field-test unit, the RO unit was tested first, followed by the CT and NF units.

Reverse Osmosis. The process flow diagram for the RO unit is shown in Figure 2. The unit used was a Millipore reverse osmosis bench-scale (PROLAB[1]) system, and the RO membrane module used was a thin film composite (TFC), brackish water membrane (module type Nanamax[2] 95) also procured from Millipore.

Groundwater (the feed for the RO unit) was treated with 95 wt% nitric acid (HNO_3) to lower the pH to 3 ± 0.5. The RO feed tank was filled with 3,000 mL of the feed and the throttle valve was fully opened. The permeate and retentate streams were recycled to the RO feed tank. The RO feed pump was started and the motor speed was increased using the control dial. The throttle valve was slowly closed to increase the feed pressure (14 to 25 Kg/cm^2). The unit was allowed to run for 3 minutes to establish steady state. The permeate was then allowed to drain into a graduated cylinder, and 2,500 mL of the RO permeate was extracted, while 500 mL of retentate was drained. The entire process was repeated until approximately 12 L of retentate had been collected.

To establish ion rejection and concentration factors for the RO unit, samples were drawn from the acid treated groundwater batches and the 2,500 mL permeate streams.

Coupled Transport. The RO retentate was used as feed for the CT unit which was designed and fabricated by Westinghouse Hanford Company. The process flow diagram for the CT unit is given in Figure 3. Two hollow fiber CT membrane modules, manufactured by BRI, were incorporated in the CT system.

Before the testing began, the CT membrane modules were loaded with ion exchange (IEX) agents. The IEX agent for the uranium extraction process (Module 1) was 0.1 $\underline{M}$ bis-(2,4,4-trimethyl pentyl) phosphinic acid in dodecane. The IEX agent for the technetium extraction process (Module 2) was 0.2 $\underline{M}$ triaurylamine (TLA) in dodecane. Using Tygon[3] tubing, the IEX agent feed tank was directly connected to the feed inlet of the module and the feed outlet was plugged. The strip inlet was closed and a vacuum pump was attached to the strip outlet. The vacuum pump was turned on and the IEX was allowed to flow through the module. This process was halted when the strip inlet was opened and some IEX drained out. The inlets and outlets of the modules were closed and the modules were allowed to remain idle for 8 h, after which the CT feed tank was filled with water and the modules were "gravity rinsed" until only water flowed from the feed side.

During testing, the CT feed tank was filled with 10 L of RO retentate. Module 1 and Module 2 strip tanks were filled with 4 L of 0.1 $\underline{M}$ hydroxyethyl-1, 1-diphosphonic acid (HEDPA) in water and 0.1 $\underline{M}$ sodium hydroxide in water, respectively. The tank drain valves were opened and the feed pumps were turned on. Module feed pressures were monitored and pump speeds were changed so that the feed pressures were equal and a 0.7-Kg/cm^2 pressure differential through the membrane was maintained. The strip pumps were started and the flowrates adjusted so that the inlet pressures to the two-strip side of the two modules were equal and there was a pressure drop of 0.7 Kg/cm^2 psig across each module. The time that the feed pumps were started was designated as t=0 s.

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[1]PROLAB is a registered trademark of Millipore Corporation.

[2]Nanamax is a registered trademark of Aqua Air Inc.

[3]Tygon is a registered trademark of the Norton Corporation.

Samples were drawn from the feed tank at 1-minute intervals for 5 minutes, 5-minute intervals for 25 minutes, 10-minute intervals for 30 minutes, and finally 1 hour later when the entire process was terminated. Samples of the strip solutions also were taken after the process was halted. Flowrates through the feed and two strip pipelines were determined by timing the collection of 100 mL of fluid.

Nanofiltration. The treated water from CT unit was used as feed for the NF unit. The process flow diagram for the NF unit is shown in Figure 4. The NF unit (Model TTM-20) was manufactured by Aqua Air Environmental (AAE) Incorporated.

The NF feed tank was filled with 1,500 mL of the CT processed water. A feed sample was taken. The feed pump was started and the unit was allowed to recycle for 5 minutes. The throttle valve was then slowly closed to increase the feed pressure (4.9 to 5.6 Kg/cm^2). The permeate stream was drained until 750 mL was extracted. The time for this process was noted and a sample of the collected NF permeate was drawn. This process was then repeated with 1,000 mL feed and 700 mL extraction, and 1,000 mL feed and 900 mL extraction.

TEST RESULTS

The following is a summary of the results of each of the three units (RO, CT, and NF).

Reverse Osmosis

Two sets of samples were drawn during the RO unit operation. The volume feed extraction of these sets were 81.3% and 83.3%, respectively. The concentration of the feed groundwater apparently varied drastically between the two runs (i.e., 1,929.7 versus 4,124 μg/L for uranium, and 0.8 versus 1.39 μg/L for technetium). This was probably caused by improper draining of the RO lines, and fresh feed mixing with the concentrated residue from the previous batch. The permeate flowrate for the two runs were 4.12 mL/s and 3.83 mL/s, respectively. The discrepancy in these results can best be explained by experimental error and was not a result of the RO unit's declining performance. Equations used for the RO calculations are as follows:

$$\% \text{ Rejection} = \frac{\text{(Feed Conc. * Feed Volume - Permeate Conc. * Permeate Volume)}}{\text{Feed Conc. * Feed Volume}} *100\% \qquad (1)$$

$$\text{Conc. Factor} = \frac{\text{(Feed Conc. * Feed Volume - Permeate Conc. * Permeate Volume)}}{\text{(Feed Volume - Permeate Volume) * (Feed Conc.)}} \qquad (2)$$

$$\% \text{ Volume Reduction} = \frac{\text{Permeate Volume}}{\text{Feed Volume}} * 100\% \qquad (3)$$

$$\text{Permeate Flowrate} = \frac{\text{Volume of Extracted Flowrate}}{\text{Elapsed Time}} \qquad (4)$$

The results from the RO unit are summarized in Table 1. A " > " symbol indicates that the analytical results for the feed or permeate streams were below detection limits, therefore, the percent rejection and concentration factor are above those given. Calcium, magnesium, and strontium, all of which are alkali earth metals with di-valent charges, had rejection rates higher than

99% and concentration factors well above 5. Sodium and potassium, which are alkali metals with monovalent charges, had rejection rates between 40% and 80% and concentration factors between 2.4 and 4.3. This suggests that the RO membrane has superior performance for multivalent ions versus monovalent ions.

This is consistent with the performance of technetium, which is present in aqueous solutions, as the pertechnetate anion having a -1 valence. The rejection rates of 75.6% and 84.4% were much lower than the anticipated 99% rejection. A high rejection rate for technetium was anticipated because of the size of the pertechnetate anion (TcO_4^-). This result suggests that the membrane module used in the RO system did not favor the rejection of technetium. The chemistry of technetium may be such that a different membrane is needed to optimize the rejection of technetium. The uranium ion rejections and concentration factors for both runs were 99% and 5.3, respectively. This is expected as the molecular size, charge density, and ionic charge were very high. The concentrations of barium, boron, copper, iron, and vanadium were not detectable in the permeate stream, therefore, the RO process performed satisfactorily for these ions. Sulfur had a high rejection, above 99.7% and concentration factors above 5.4. The RO process also performed well for silicon with a rejection above 97.1% and a concentration factor of 5.2. Zinc had a surprisingly low rejection of 83.4 % in the first test, and a rejection of 97.2% during the second test. This apparent discrepancy probably was the result of analytical error and at this time it is not known which is the correct value.

The expected rejection rate was 99% for all ions and a concentration factor of 10. The maximum concentration factor that was achieved was 5.96 for the uranium ion in the second test. A higher concentration factor could have been achieved by extracting a higher volume of feed through the permeate. However, because of equipment considerations to avoid cavitating the pump or destroying equipment with a high inlet pressure, this was not practical. The rejection rates lower than the predicted 99% can best be attributed to the chemistry of the respective ions (especially for technetium).

Coupled Transport

The CT unit served to extract uranium, technetium, and nitrate from the concentrated groundwater provided by the RO unit. Uranium and technetium concentrations as a function of time in the CT process are provided in Table 2. A graphical representation of the data is given in Figures 5 and 6. Standard deviations, average data, and a curve fit are displayed on the graphs. As is apparent in both figures, the data varied drastically for the first 5 minutes after process initiation. This is attributed to the unit reaching steady state. For this reason, a curve was fit to the data above t=330 s. Also, the overall flux was calculated between t=330 s and t=7,230 s (process termination). The overall flux was defined as:

$$\text{Overall Flux} = \frac{[\text{Conc. at } (t = 330) - \text{Conc. at } (t = 7,230)] * 10 \text{ L}}{(7,230 \text{ s} - 330 \text{ s}) * 10 \text{ ft}^2} \tag{5}$$

For the uranium extraction, the overall flux was determined to be 1.33 micrograms per second per square foot ($\mu g/(s*ft^2)$) and for the technetium extraction, 8.64E-5 $\mu g/(s*ft^2)$. The uranium extraction followed a very smooth trend. The concentration of uranium in HEDPA (uranium strip solution) was 1,062 $\mu g/L$ while the sodium hydroxide (technetium strip solution) registered 0 $\mu g/L$ as expected. Performing a mass balance (Eq. 6), 91,850 μg of uranium should have been stripped away. However, only 4,248 μg of uranium was present in the strip solution. The missing uranium

was most likely still in the organic portion of the membrane (in transit from the feed to the strip solution).

Mass Balance: [Initial Feed Conc. (t=330 s) - Final Feed Conc. (t=7,230 s)] * Feed Volume.   (6)

The data does indicate that the CT module for uranium worked well as more than 90,000 μg of uranium was extracted from an initial 112,000 μg. The CT unit did not perform as well for the technetium; the low flux being an indication. Figure 6 shows how slowly the technetium was extracted. Deviations from the smooth trend that was fitted by a curve can be attributed to analytical error. The concentration of technetium was 0.18 μg/L in the uranium strip solution and 0.93 μg/L in the technetium strip solution. The presence of technetium in the uranium strip suggests that the fiber pores might not have been properly saturated with the uranium IEX. A mass balance indicates that 6.1 μg of technetium should have been stripped away. The uranium strip had 0.72 μg and the technetium strip had 3.72 μg. The balance of the technetium (1.66 μg) could have been embedded in the fiber pores.

Overall, the CT unit performed well for the uranium extraction. The weak technetium extraction needs to be investigated further.

Nanofiltration
The results for the NF unit are given in Table 3. The percent rejection was calculated using an equation of the same form as Eq. 1. The volume reduction (Eq. 3) is listed in parentheses in the table header. Data from each volume reduction (50%, 70%, and 90%) allows the performance of the NF unit to be evaluated at different feed concentrations. The NF unit was expected to reject the larger radionuclides and allow smaller ions to pass through. The permeate flowrate was 0.23 mL/s for the 50% permeate extraction, 0.21 mL/s for the 70% permeate extraction, and 0.21 mL/s for the 90% permeate extraction.

The NF unit performed exceptionally well for uranium in all three volume extractions. The 100% rejection, although expected, indicates a high performance rating for the NF process. The surprising result, as in the RO and CT processes, was in the technetium rejection. Sixty-nine percent of the technetium was rejected in the 50% permeate extraction, 41% in the 70% extraction, and only 24% in the 90% extraction. These low rejections are consistent with the technetium ion performance in the RO. The ions (calcium, copper, zinc, and iron) having a negative percent rejection must be ignored because of the obvious analytical error of either the feed or permeate sample. The concentrations of boron and vanadium also may be ignored as they could not be analytically detected.

The data clearly show a correlation between percent volume extraction and percent rejection. With each 20% volume reduction, there seemed to be a correlating 20 $\pm$ 10% decrease in ion rejection. For example, barium exhibited a 21% rejection decrease between the 50 and 70% permeate extraction, and a 26% rejection decrease between the 70 and 90% permeate extraction. There was a definite decrease in percent rejections for every increase in percent volume extractions. This indicates the sensitivity of the NF process to concentration of the contaminants in the feed.

Overall, it is evident from the generated data that a 90% permeate extraction scenario would optimize the NF unit allowing the maximum amount of noncontaminant ions to pass through the membrane. However, as mentioned above, the low technetium rejection suggest a lower extraction may be best.

CONCLUSIONS

This experiment demonstrated the effectiveness of the RO/CT process. The RO, CT, and NF units performed as theorized for all ions except for technetium. This suggests that design modifications in the pilot plant may be necessary. The following is the list of recommendations that may improve the experimental results for technetium.

- Replace the current RO/NF membrane with one more apt to reject technetium. This can be coordinated with the membrane manufacturer.

- Conduct further research on other IEX agents that may complex better with the technetium ion.

- Increase the strip solution flowrates in the CT unit.

REFERENCES

1. R. Chiarizia, E. P. Horwitz, P. G. Rickert, and K. M. Hodgson, "Application of Supported Liquid Membranes for Removal of Uranium From Groundwater," Sep. Sci. and Tech., 25, 13-15 (1990).

**Table 1. Ion rejection and concentration factor in
the Reverse Osmosis unit (Two runs)**

Compound	% Rejection (1)	Concentration Factor (1)	% Rejection (2)	Concentration Factor (2)
Uranium-238	99.4	5.3	99.3	6.0
Technetium-99	75.6	4.1	84.4	5.1
Barium (>)	73.9	4.0	86.1	5.2
Boron (>)	18.7	1.0	86.1	5.2
Calcium	99.4	5.3	99.1	5.9
Copper (>)	69.9	3.7	86.1	5.2
Iron (>)	80.7	4.3	86.1	5.2
Magnesium	99.4	5.3	99.3	6.0
Potassium	63.8	3.4	40.5	2.4
Silicon	97.2	5.2	97.1	5.8
Sodium	79.9	4.3	70.7	4.2
Strontium (>)	99.3	5.3	99.1	5.9
Vanadium (>)	18.7	1.0	86.1	5.2
Sulfur (>)	99.8	5.3	99.7	6.0
Zinc	83.6	4.5	97.2	5.8

Table 2. **Technetium and uranium concentrations as a function of time during the Coupled Transport process.**

Time (s)	μg Tc99/L	μg U238/L
90	4.26	9,410
150	4.18	9,896
210	4.24	11,200
270	4.23	9,456
330	4.26	11,300
630	4.17	9,899
930	3.98	9,124
1230	3.90	7,677
1530	3.85	8,000
1830	3.77	7,177
2430	3.70	6,092
3030	3.65	5,354
3630	3.73	4,928
7230	3.65	2,115
HEDPA (t=7230 s)	0.18	1,062
NaOH (t=7230 s)	0.93	0

HEDPA = hydroxyethyl-1, 1-diphosphonic acid.

Table 3. Percent ion rejection with various permeate extractions for
the Nanofiltration process.

Compound	Rejection (50%)	% Rejection (70%)	% Rejection (90%)
Uranium-238	100.0	100.0	100.0
Technetium-99	68.96	40.96	24.09
Barium	57.94	36.80	10.84
Boron (>)	50.00	30.00	10.00
Calcium	-4.84	-85.66	-158.06
Copper	-1906.94	-775.00	-1600.00
Iron	7.72	-60.51	-104.36
Magnesium	68.00	45.47	18.20
Potassium	64.96	21.99	13.70
Silicon	63.70	29.52	12.47
Sodium	62.39	23.30	9.22
Strontium	65.77	40.00	14.50
Vanadium (>)	50.00	30.00	10.00
Sulfur	73.16	50.42	24.89
Zinc	-108.40	-31.76	100.0
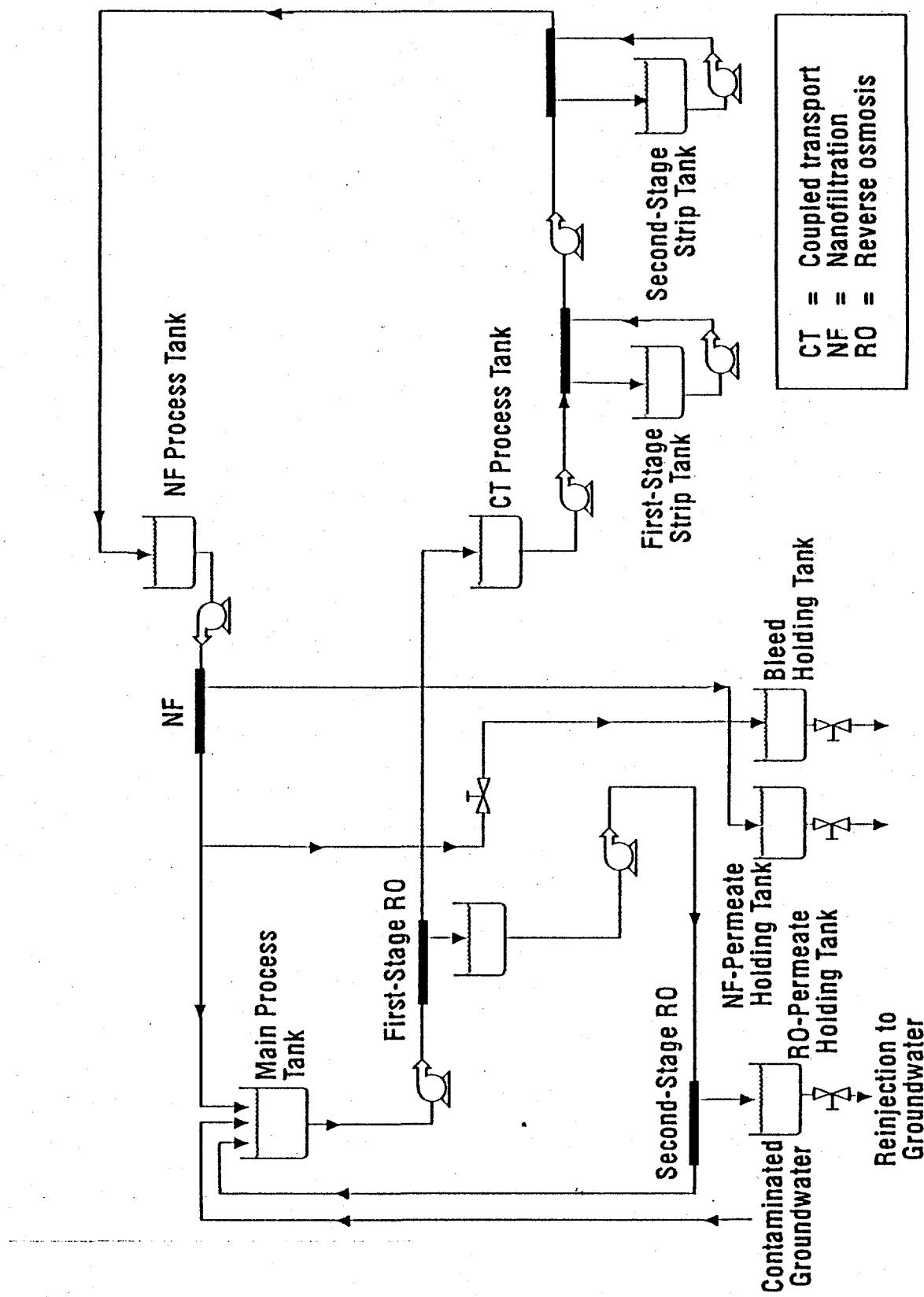
Figure 1. Reverse osmosis/coupled transport schematic.

Permeate

Retentate

Module

PI-2

PI-1

TV-1

P-1

TK-1

BV-1

LEGEND

TK = Tank
TV = Throttle Valve
BVD = Ball Valve
P = Pump
PI = Pressure Indicator (gage)
Module = Reverse Osmosis membrane
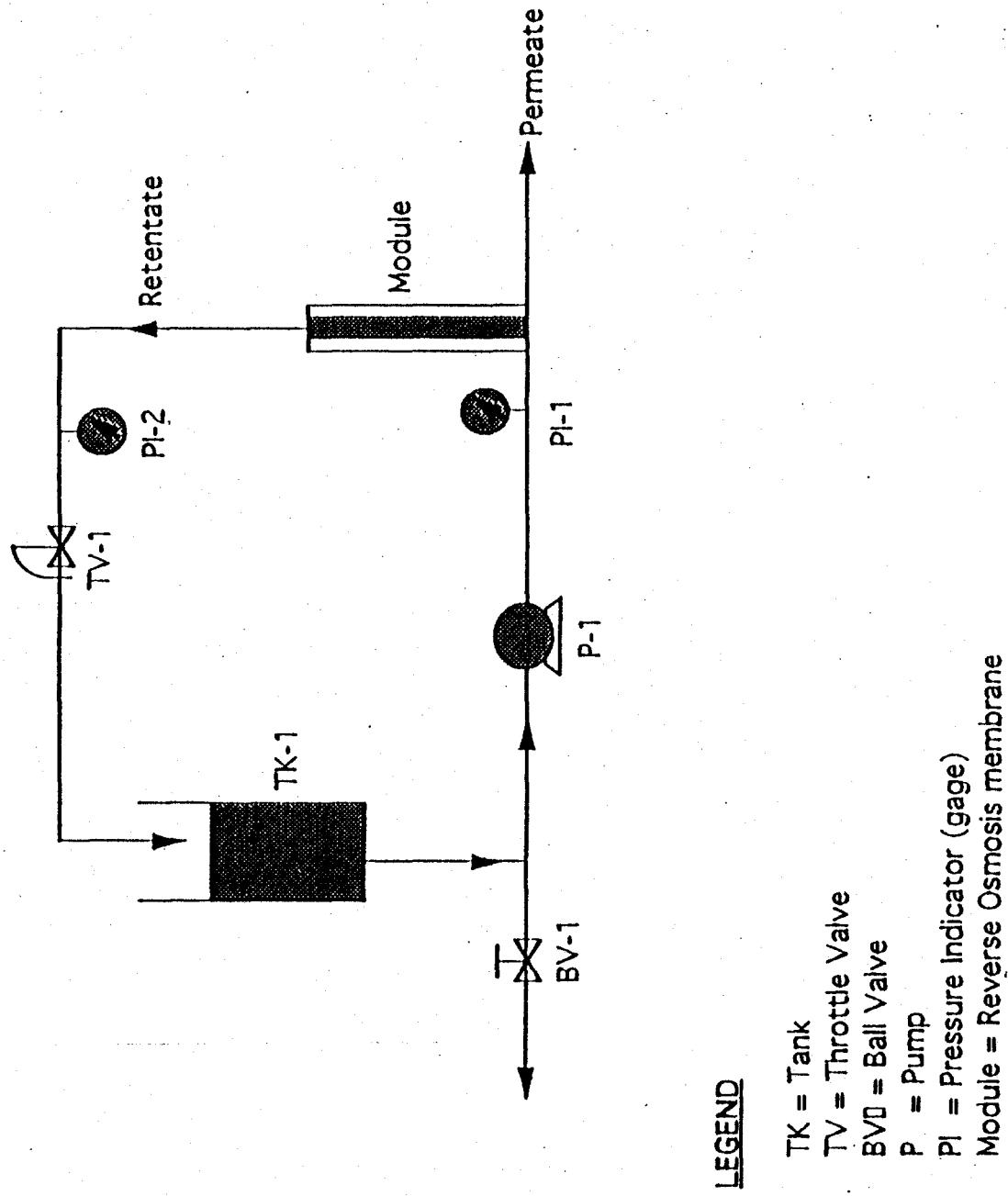
Figure 2. Reverse osmosis benchscale schematic.

LEGEND

TK = Tank
SV = Sample Valve
DV = Drain Valve
PRV = Pressure Relief Valve
P = Pump
PI = Pressure Indicator (gage)
Module = Coupled Transport membrane
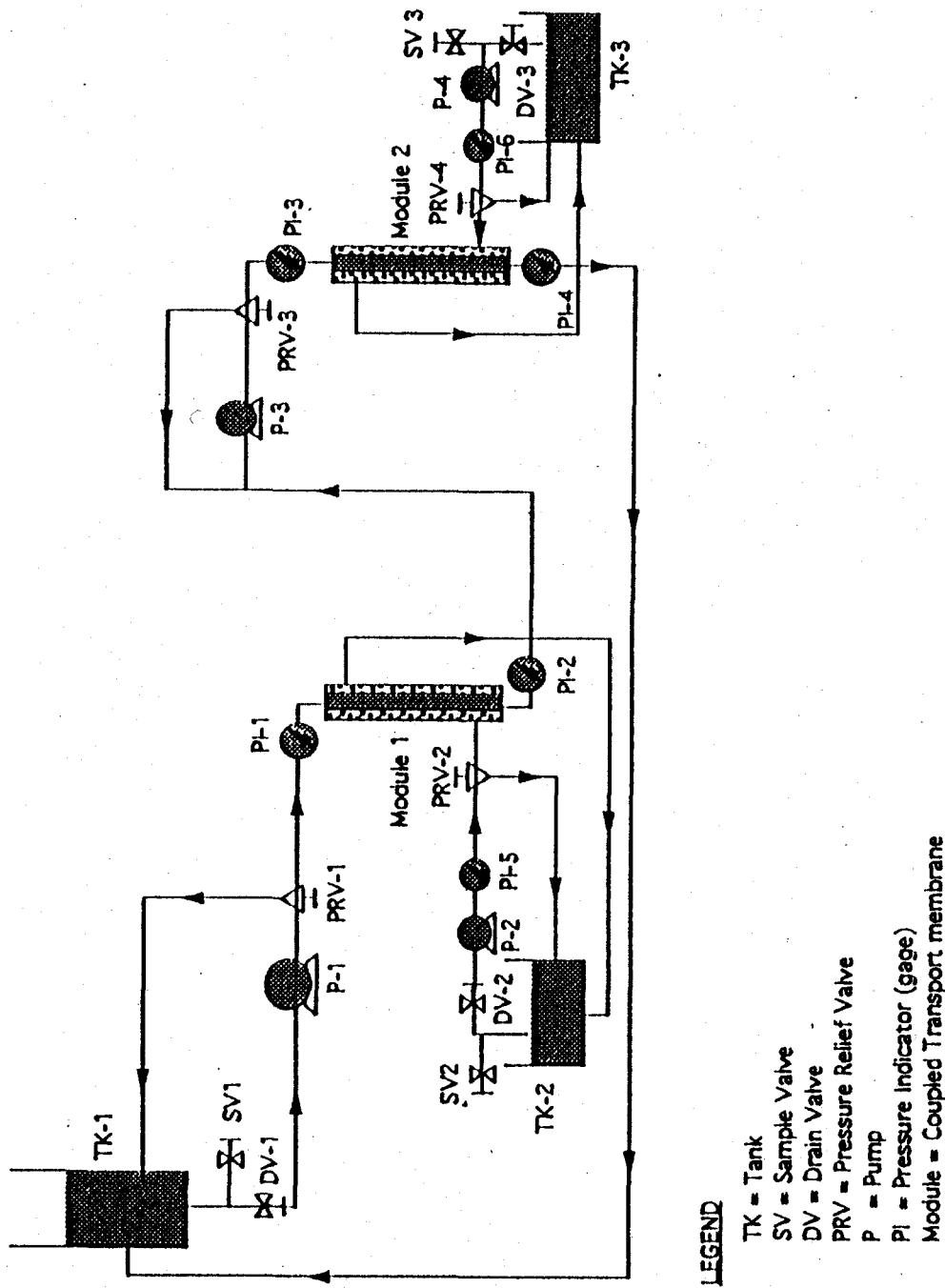
Figure 3. Coupled transport benchscale schematic.

LEGEND

TK = Tank
P = Pump
PI = Pressure Indicator (gage)
V = Ball Valve
VB = Back Pressure Regulator
Module = Nano-Filtration membrane
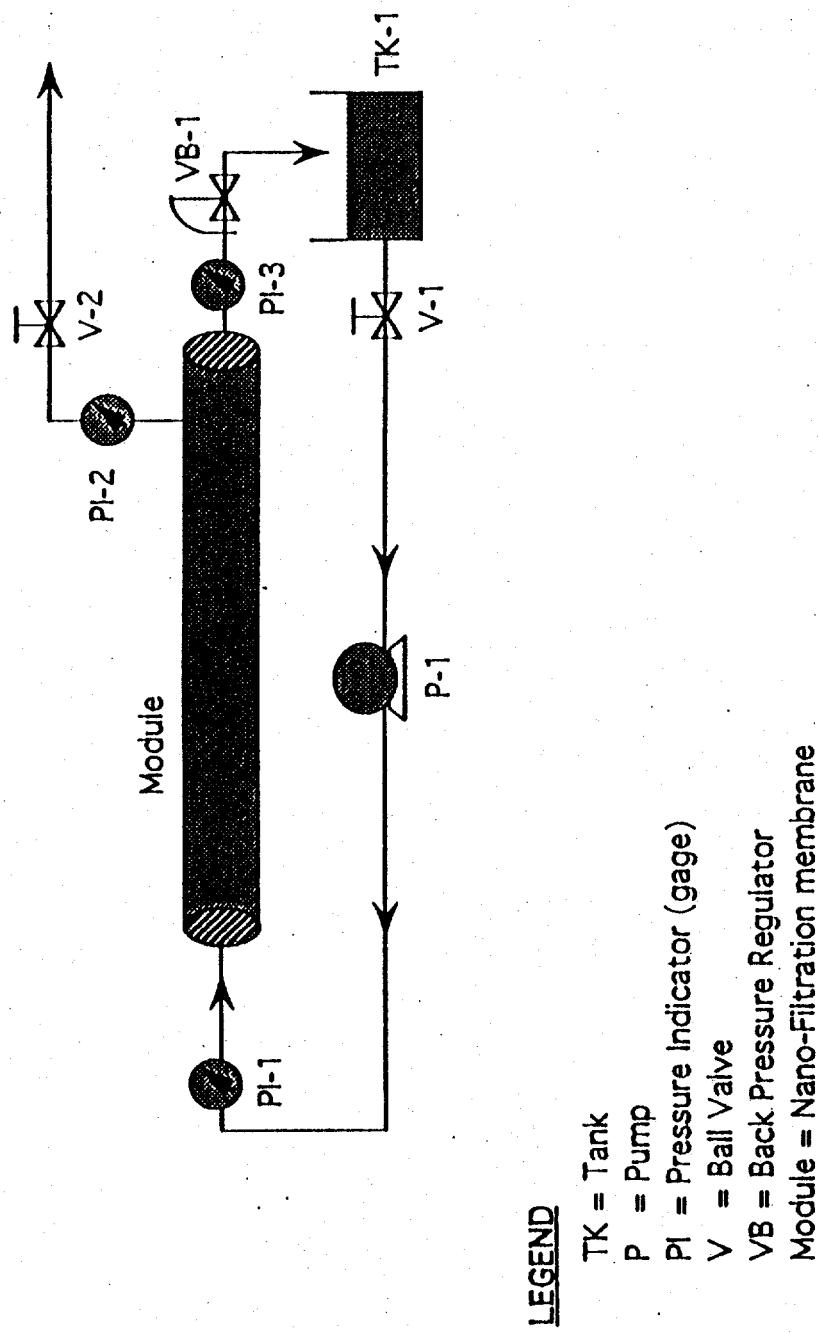
Figure 4.   Nanofiltration benchscale schematic.

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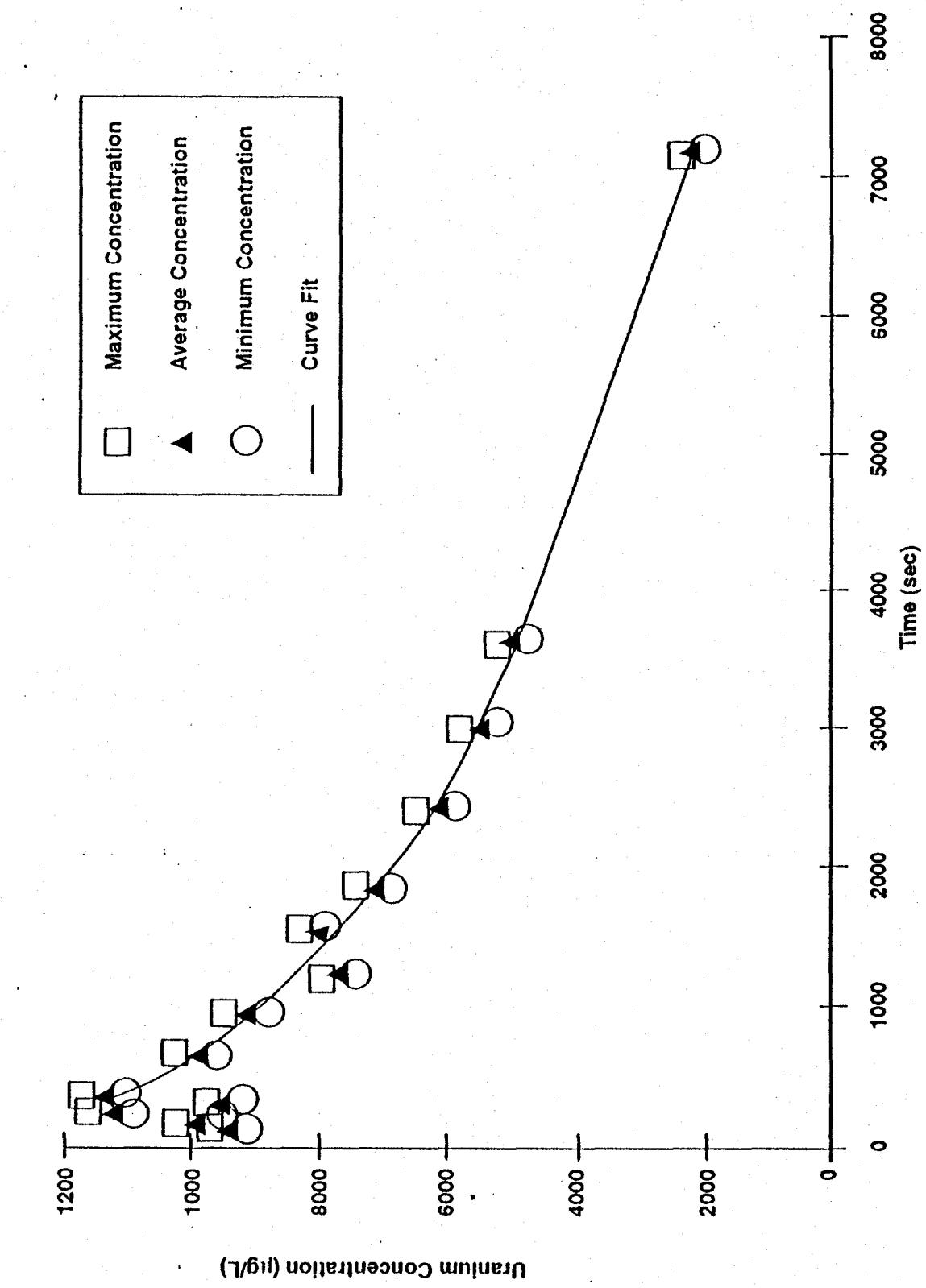
Figure 5. Uranium extraction by coupled transport.
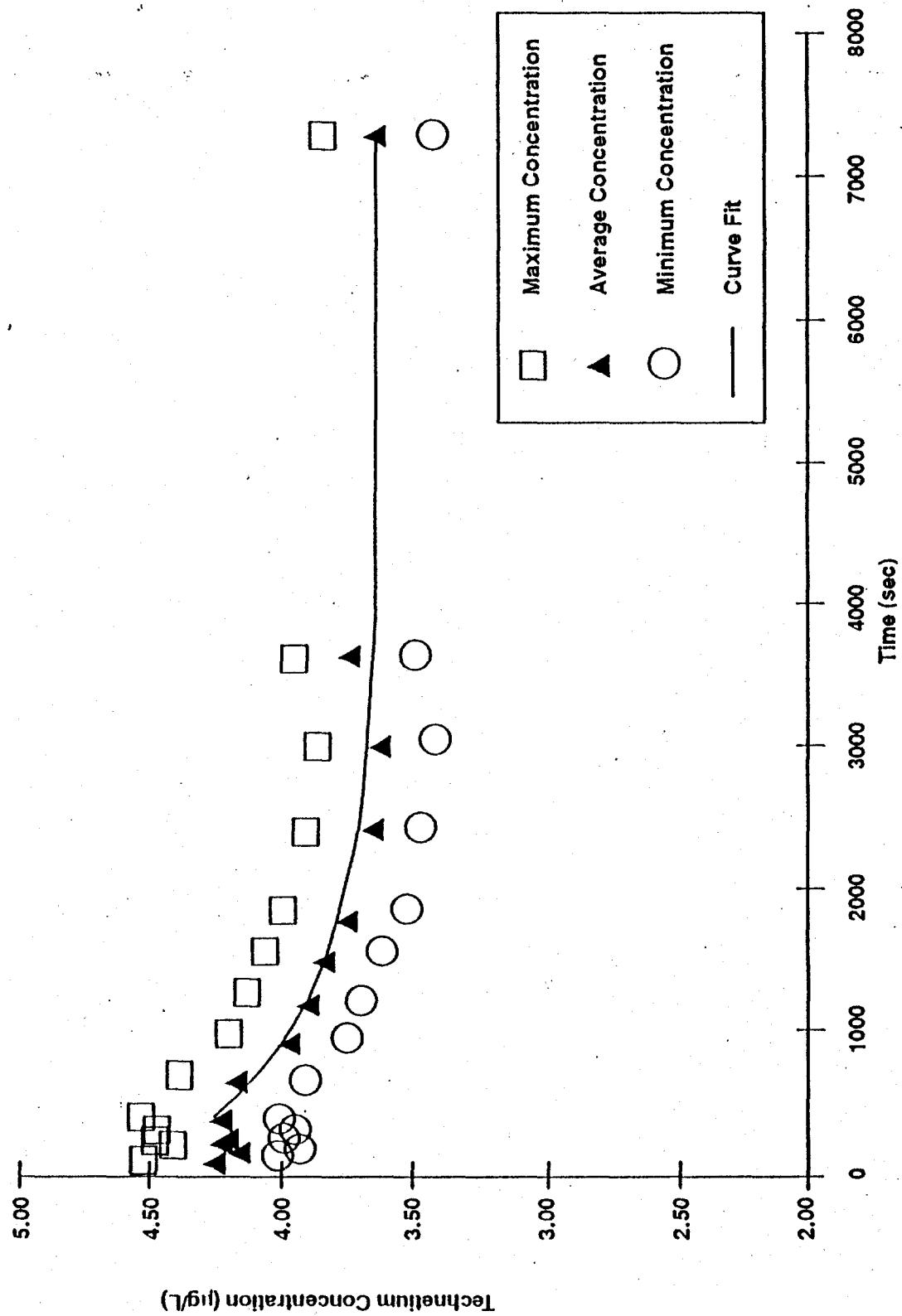
Figure 6.   Technetium extraction by coupled transport.