

FULL-SCALE TESTING OF TVA'S HYPERFILTRATION SYSTEM ON SIMULATED RADIOACTIVE WASTES

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ABSTRACT

The use of hyperfiltration (HF) in a nuclear application was the purpose of pilot tests conducted at Tennessee Valley Authority's (TVA) Sequoyah Nuclear Power Plant (SQN) in 1982. Using the pilot tests as the basis for full-scale operation, 90 gal/min HF systems have been designed and fabricated for TVA's Watts Bar Nuclear Power Plant (WBN) and SQN. The systems will be achieving the dual objectives of preconcentration of the radwaste evaporator feed stream and processing of the fluid stream to meet the discharge criteria of 10CFR20 after taking credit for the minimum cooling tower blowdown dilution flow. Floor drain wastes, tritiated drain waste and condensate demineralizer regeneration wastes can all be preconcentrated to a reduced volume as little as 5% of the initial waste feed stream. The decreased volume to be processed for solidification significantly increases the capacity of the radwaste disposal system while reducing the load, maintenance and operating costs associated with the evaporator. (1).

Prior to delivery to TVA, one of the HF systems was required to be fully shop assembled, functionally operated and performance tested. The testing included meeting defined HF module and system performance criteria for rejection of gross beta/gamma activity, total suspended solids (TSS), total dissolved solids (TDS), and boron. The performance test utilized nonradioactive streams formulated to simulate the drain wastes and condensate demineralizer regeneration wastes.

In addition to successfully achieving the expected performance, significant processing and operating data as well as operational experience were gained. The HF system is now at TVA awaiting installation.

HISTORICAL PERSPECTIVE

Preoperational testing of the SQN Nuclear Steam Supply System (NSSS) liquid radwaste system 7.5 to 15 gal/min auxiliary waste and 2 gal/min waste evaporators uncovered serious functional deficiencies. Neither evaporator was able to produce acceptable quality distillate when operated at greater than 60 to 70% of their design feed flow rates. In addition, the rated design capacity for the evaporators was inadequate to process the large volumes of liquid waste generated at SQN, which averaged as much as 25.8 gal/min over a month. As a result of these deficiencies, TVA installed portable demineralizers to process liquid wastes and began an evaluation of alternative liquid processing systems for permanent installation.

Initial results of prototype testing (2,3) of hyperfiltration membranes at SQN showed favorable results, which were incorporated into a

cost-benefit study (4) of alternative processing technologies. The process incorporating HF with polishing demineralizers for the permeate stream and evaporation of the concentrate stream via an existing crystallizer was found to have the lowest capital and operating costs.

Based on the recommendation of the cost-benefit study and the results of the prototype testing at SQN, TVA decided to remove the old evaporators and retrofit an HF system into SQN and WBN. Additional benefits expected from the HF system are:

- 1) recovery of boric acid for reuse or discharge,
- 2) increased radwaste resin life by a factor of 5 to 10 with significant reduction in resin buried volumes,
- 3) increased operating life of the crystallizer by concentrating radwaste feeds by as much as a factor of 20.

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A full-scale system test on simulated wastes was required by TVA to verify system design - requirements and vendor-guaranteed data prior to delivery to TVA. The additional cost for the full-scale testing was justified for the following reasons:

- 1) Testing would provide verification of prototype test results obtained at SQN on which the full-scale system was based.
- 2) Testing would minimize installation and preoperational test problems and delays by assembling the system components and verifying system operational parameters prior to shipment of equipment.
- 3) Full-scale testing would provide the opportunity to obtain operational data for system operation beyond design basis requirements, verify mathematical models, and develop useful correlations for system performance on simulated wastes.

Hyperfiltration Technical Description

Hyperfiltration represents state-of-the-art separation technology using a dual-layer zirconium (IV) oxide-polyacrylic acid (ZOPA) membrane dynamically applied to a stainless steel porous support. The shell of HF modules are constructed from capped and flanged stainless steel pipe while inside is a serpentine porous tube made from sintered 316 stainless steel powder (Fig. 1). Waste feed is pumped up to 1250 psig through the interior of the 5/8" I.D. tubes. The pressure forces the clean water (solvent) to diffuse through the ZOPA membrane and the porous support to the low pressure shell side where it is collected. This is the "permeate". The stream solids (solutes) are retained by the membrane and concentrated in the high pressure tubing as the clean water permeates through the membrane. This stream is termed the "concentrate." The HF modules are connected in a series - parallel configuration dependent on systems flow rate and recovery requirements. An array of modules in parallel is termed a "stage," and a series of stages forms a system. The flow throughout the system is designed to remain highly

turbulent in order to reduce the tendency of suspended solids in the tubing to settle (5) and tendency of dissolved solids to accumulate at the membrane surface.

The performance and efficiency of an HF system are characterized by its "rejection" capabilities and its "recovery" rate. Rejection is the measure of the system's ability to concentrate the feed constituents in the concentrate stream. System rejection is the difference between the feed and permeate concentrations, divided by the feed concentration. HF membranes give essentially 100% rejection of all suspended solids, but they do not reject 100% of all solute molecules. Recovery refers to the relative amount of clean water recovered from the feed and is defined as the permeate flow rate divided by the feed flow rate. The volume reduction factor varies directly with the recovery rate. The design of an HF system is based upon a membrane material selected for the rejection of the species of interest at specific ranges of recovery. The TVA HF system is designed for rejection of radioactive species at 95% recovery. A more detailed discussion of the hyperfilter module construction, the system design, and its application at TVA can be found in (1).

DEVELOPMENT OF SYSTEM TEST PLAN

Test Objectives

The major objective of the system test was to verify the performance criteria for floor drain and regeneration wastes as listed in Table I. Performance criteria verification was a significant objective in light of the following:

- 1) The system design was scaled up from prototype test results.
- 2) The system was the first full-scale application of HF technology for a nuclear power plant.
- 3) The performance criteria had formed the basis for a cost benefit evaluation of HF technology that recommended installation at SQN and WBN.

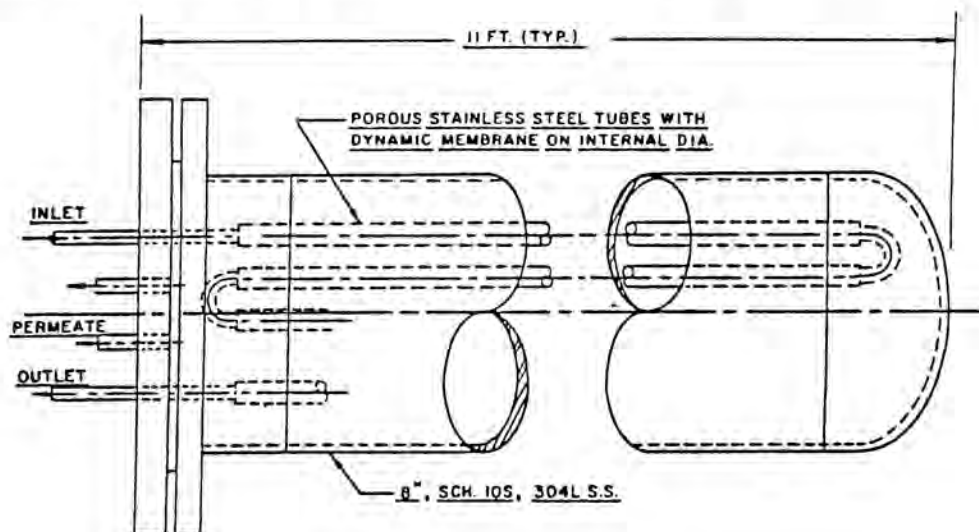


Fig. 1. Typical Recovery System Module

- 4) The system performance criteria were a contractual requirement.

Secondary objectives of the full-scale performance test were:

- 1) to obtain data for system operation beyond design basis performance requirements,
- 2) to minimize installation delays and pre-operational test problems by assembling the system and verifying system operation prior to shipment,
- 3) to investigate boron system rejection as a function of pH, and
- 4) to provide data to verify mathematical models and develop correlations between permeate quality, feed concentration, recovery and rejection for use during plant operation.

To conduct the system test in the most efficient manner, a detailed test plan was prepared. Development of the test plan and the associated methodology is described below.

TABLE I
Performance Test Criteria

Waste Type and Specie	Module ^a (%)	System (%)	
		Recovery 65%	Recovery 95%
1. Floor Drain Waste			
Total Suspended solids (TSS) ^b	99 ^c	99	99
Gross beta/gamma activity ^b	88	80	70
Boron ^d	70	90	90
2. Regeneration Wastes			
TSS ^b	99 ^c	99	99
Gross beta/gamma activity ^b	80	75	50
Total dissolved solids (TDS) ^b	80	75	50

- a) First stage performance.
- b) Rejection.
- c) All rejections and reclamations are expressed as percentage.
- d) Reclamation.

Acceptance Criteria

The performance test criteria for each waste stream listed in Table I are given for a single module and for the system. The module rejection and reclamation percentage for TSS, TDS, boron, and gross activity are based on TVA's prototype test results obtained at SQN. Rejection and reclamation percentages for a single module differ from those

specified for the system because of the relationship between feed concentration, recovery, and rejection. As system recovery increases, the system rejection decreases. Therefore, the system composite permeate quality declines. System rejections and reclamation for the two waste streams at 65% and 95% recoveries were calculated using the following two equations:

$$\frac{\bar{C}_p}{C_f} = \frac{1 - (1 - R)^{1 - \gamma_m}}{R} \quad \text{and} \quad (1)$$

$$1 - \frac{\bar{C}_p}{C_f} = \gamma_s \quad (2)$$

where:

\bar{C}_p = Average composite permeate concentration

C_f = feed concentration

R = system recovery = (permeate rate/feed rate) * 100

γ_m = module rejection

γ_s = system rejection

By assuming that γ_m in Equation 1 is constant, for every module in the system, an estimate of the resulting system rejection can be obtained. System reclamation is calculated via the first equation and corresponds to the ratio \bar{C}_p/C_f .

The 99% rejection of TSS required for both a module and the system is based on SQN prototype test results and operating history of HF systems outside the nuclear industry. The HF system can be thought of as a tight filter medium with a very small pore size. The 99% rejection for TSS will provide the capability to meet the 30 ppm discharge criteria under the maximum design basis TSS concentration of 750 ppm.

The HF performance criteria for boron are expressed as percent reclamation or passage. Boron reclamation is dependent upon pH, which determines the degree of boric acid ionization: the higher the ratio of ionized species to molecular species for boric acid, the lower the reclamation. At a pH of around 6.5, boric acid molecules pass through the HF membranes and can be either recovered for reuse or discharged to the environment. At pH values of 9.0 to 9.5, boric acid can be directed to the concentrate stream for solidification.

Waste Streams

The hyperfilter will be operated on three different waste streams when it is installed in the power plant (WBN or SQN). The first two are floor drain wastes with the primary difference being the amount of tritium present. A profile of the drain wastes is given in Table II. For the purpose of simulation of the drain wastes in the system test, the tritiated and nontritiated floor drain wastes were considered identical.

TABLE II
Liquid Drain Radwaste Feed

Constituent	Approximate Normal Values
Conductivity	150 μ mhos/cm
Boron	500 ppm
Chloride	1.0 pm
Fluoride	0.5 ppm
Silica	1.0 ppm
pH	4 - 9
Total Suspended Solids	50 ppm
PO ₄	2 ppm
Na	10 ppm
Li	2 ppm
Oil and Grease	5 ppm
Gross Beta/Gamma Activity (52 isotopes)	10 ⁻² μ Ci/mL
Temperature	80°F

The third stream is the condensate polishing demineralizer regenerant which, in the event of a steam generator tube leak will be radioactive. Each plant is equipped with a mixed bed demineralizer system which will deionize the full process flow of condensate and injected steam generator blowdown during such an event. The average character of the regenerant stream from the condensate polishing system is given in Table III. As shown in Table III, the primary constituents are sodium and sulfate, which result from the use of caustic and sulfuric acid as the regenerants for the mixed bed condensate polishing demineralizers.

TABLE III
Regeneration Waste Water Characteristics

Constituent	Value
pH	6.0 - 8.5
Conductivity	15,000 μ mhos/cm
SO ₄	6,000 ppm
Cl ⁻	100 ppm
Na ⁺	3,000 ppm
TDS	10,000 ppm
TSS	400 ppm
Fe	50 ppm
Mg	15 ppm
Ca	25 ppm
Silica	10 ppm
Temperature	80-90°F
Gross Beta/Gamma Activity (48 isotopes)	5x10 ⁻¹ μ Ci/mL

Chemical Formulation of Simulants

Formulation of test solutions containing the gross constituents such as those listed in Tables

II and III posed no particular problems. To simulate the radioisotopes in solution, however, was a much more difficult task. Since the test was to be performed in a shop in which radioactive tracers could not be used, cold analogs of the radioactive species had to be implemented. In the actual waste solutions, the radioisotopes are present at extremely low concentrations. For example, cesium in the floor drain waste is present at a concentration level of approximately 1 x 10⁻⁵ mg/L. To utilize cold analogs for the various species present in the water, the concentration must be maintained above the analytical detection limit and below the solubility limit of possible precipitates. Again, considering cesium, the detection limit using atomic absorption is approximately 0.1 mg/L or about 10,000 times higher than the expected isotope concentration in the actual waste. There are no particular solubility problems associated with cesium; however, solubility is a problem with many of the other species such as barium, cobalt, chromium, iron, and manganese. These elements have fairly low solubilities in either the hydroxide or sulfate forms.

Another factor that had to be accounted for in simulating the waste streams was the ion exchange capacity of the polymer that forms the HF membrane. The polymer had significant cation exchange capacity and therefore could reduce the aqueous concentration of species of interest to below detection limit during the system test. This potential problem was addressed by performing a test at the CARRE, Inc. facility in Seneca, S.C. In this test, solutions containing nonradioactive heavy metals (Ba, Co, Fe, Mn, Sr, and Cs) and iodide were processed through a single hyperfilter module which is identical to one of the modules in the TVA system. The results from this test indicate that the hyperfilter strongly absorbs cobalt, manganese, and iron. Cesium, potassium, sodium, and iodide are not sorbed by the membrane. Barium and strontium appear to be absorbed at an intermediate level. Calcium appears to have been desorbed from the membrane in exchange for some of the more tightly bound metals. For the species that were sorbed, it appears that the residual amount in the aqueous phase after contact with the membrane is proportional to the amount initially added.

The ultimate simulants used during the systems test were a compromise between chemical solubilities, sorption behavior, analytical detection limits and required methods, and chemical availability. The elements that are potentially present in the power plant wastewater streams as radioisotopes are summarized by chemical group in Table IV. As noted in the table, there is a wide range of constituents present, ranging from group 1a to 7a, as well as lanthanides and actinides. The cold analogs chosen to represent the range of elements potentially present in the feed are cesium, barium, strontium, manganese, iron, cobalt, and iodine. Prior to conducting the systems test, a fairly high level of confidence was placed in the ability to successfully use all of these elements for the purpose of simulating the radioactive species. A discussion of which analogs worked and which did not and why is provided in a later section of this paper.

It was decided to operate the HF system test using three different simulant solutions. The first formulation, summarized in Table V, was a

TABLE IV
Elements Present in Floor Drains and Condensate
Demineralizer Regenerant Solutions

Element	Chemical Group	Chemical Behavior	Utilized in System Test
Rb ⁺	1a	Very soluble; fair membrane rejection; low affinity for ion exchange media.	
Cs ⁺	1a		X
Ba ²⁺	2a	Adequate solubility; good membrane rejection; measurable affinity for ion exchange media.	X
Sr ²⁺	2a		X
La ³⁺	3b	Very low solubility; good membrane rejection; strong affinity for ion exchange media.	
γ ³⁺	3b		
Zr ⁴⁺	4b		
Nb ⁵⁺	5b		
Mo ³⁺	6b		
Mn ²⁺	7b		X
Tc ⁷⁺	7b		
Fe ²⁺	8 ₁	Borderline solubility; good membrane rejection; strong affinity for ion exchange media.	X
Ru ³⁺	8 ₁		
Co ²⁺	8 ₂		X
Rh ³⁺	8 ₂		
Te ⁴⁺	6a	Very soluble; high atomic weight, therefore may have good membrane rejection; low affinity for ion exchange media.	
Br ⁻	7a		
I ⁻	7a		X
Ce	Lanthanide		
Pr	Lanthanide		
Np	Actinide		

mixture of metal salts in demineralized water and was termed "trace metals solution." The trace metal solution was tested to maximize the probability that data for each of the metals would be available for calculation of system performance. An analytical technique was not available within the project budget constraints that could ensure determination of all of the trace metals at the mg/L concentration range in the presence of large concentrations of salt, such as sodium sulfate or boric acid. The metal concentrations for the trace metals solution were measured by inductively coupled argon plasma spectroscopy (ICP). The samples were preconcentrated by a factor of 10 to increase the detection limit of the method; with this preconcentration, the analysis technique is labeled 10XICP.

The floor drain waste simulant is outlined in Table VI. As noted in Table VI, the primary constituent is boric acid, with lesser quantities of lithium and phosphate also present. Iodide, a major contributor to the radioactivity of the waste solutions, was also added to provide data on iodide rejection. It was purposely left out of the trace metals solution to prevent possible analytical interferences, since the concentration necessary for the chosen analytical technique was much higher than any of the trace metal constituents. The behavior of boron through the HF system is of great interest, since the material can ostensibly be directed to either the permeate or concentrate stream by control of the pH fed to the system. The chemicals listed in Table VI were added to the existing trace metals

TABLE V
Trace Metals Solution Formulation

Metal Salt	Metal Ion Concentration (mg/L) ^a
BaCl ₂ · 2H ₂ O	2.0
Co(NO ₃) ₂ · 6H ₂ O	2.0
FeCl ₂ · 4H ₂ O	2.0
MnCl ₂ · 4H ₂ O	2.0
SrCl ₂ · 6H ₂ O	2.0
CsNO ₃	3.0

^a Basis: 1500 gal. demineralized water

solution, thus providing for the potential measurement of further trace metals rejection data in the presence of boric acid and the other salts added in this step. Assays for the trace metals and boron were conducted via ICP and iodide was measured by ion chromatography.

The final solution prepared for the HF system test was the solution to simulate the condensate demineralizer regeneration stream. The chemicals utilized in this step are listed in Table VII; as noted, the primary ingredient is sodium sulfate. The trace metals listed in Table V are also added; again, this was done to provide the potential for measurement of further metals rejection data in the presence of high salt concentrations. As a final addition to the chemicals listed in Table VII, a dissolved specie in the form of a water soluble dye was added to the system feed tank. The dye, a high molecular weight dye, that is commonly used by the hyperfilter manufacturer to test membrane integrity, was used in this instance to simulate the presence of suspended solids, since it would be very difficult to actually introduce suspended solids to the test unit. As with the other solutions, metal concentrations were measured by ICP. Dissolved solids (primarily sodium sulfate) were assayed via the standard TDS technique^a, while dye concentration was determined spectrophotometrically.

Test Methodology

The overall system test logic, consisting of nine basic steps, is schematically represented in Fig. 2. To start the test sequence, the test solutions were prepared in the system feed tank. The unit was then started and correct operating conditions established; the unit was then allowed to operate for an extended period to equilibrate the system prior to sampling and data collection. A simple tanks-in-series dynamic model of the system

^a Standard Methods for the Examination of Water and Wastewater, 16th ed., American Public Health Association, Washington, D.C. 1985

TABLE VI
Simulation of Floor Drain Waste

Reagent Used	Ion Concentration (mg/L) ^a
H ₃ BO ₃	1000 (B)
KH ₂ PO ₄	15 (PO ₄)
LiOH - H ₂ O	5 (Li)
KI	150 (I)

^a Basis: Reagents to be added to the 1500 gal of trace metals solution as described in Table V.

was written and implemented using the IBM Continuous Systems Modeling Program (CSMPTM) available on the ORNL PDP-10 computer system. This model indicated that hydraulic equilibration should take between 35 to 90 min, dependent on system throughput. Following equilibration, operating data, including flow rates, pressures, temperature, pH and recovery were logged, all of which were available from the operator's console. Aqueous samples were then collected for later analysis by the Analytical Chemistry Division at ORNL. Samples were always taken of the system feed, concentrate, and composite permeate and of the first-stage concentrate and permeate. In addition, samples were collected at intermediate stages to assist in later detailed analysis of system performance. Following sampling, the flow verification procedure was performed.

TABLE VII
Demineralizer Regenerant Solution Simulation

Reagent	Concentration (mg/L) ^a Target
Na ₂ SO ₄	6000 (salt)
Blue Water Soluble Dye ^b	150 (dye)
Trace Metals	See Table V

^a Basis: 1500 gal of demineralized water.

^b Sirius Supra Grey CGLL167 (Mobay Chemical Corp., Rock Hill, S.C.) added prior to the last test step to simulate suspended solids.

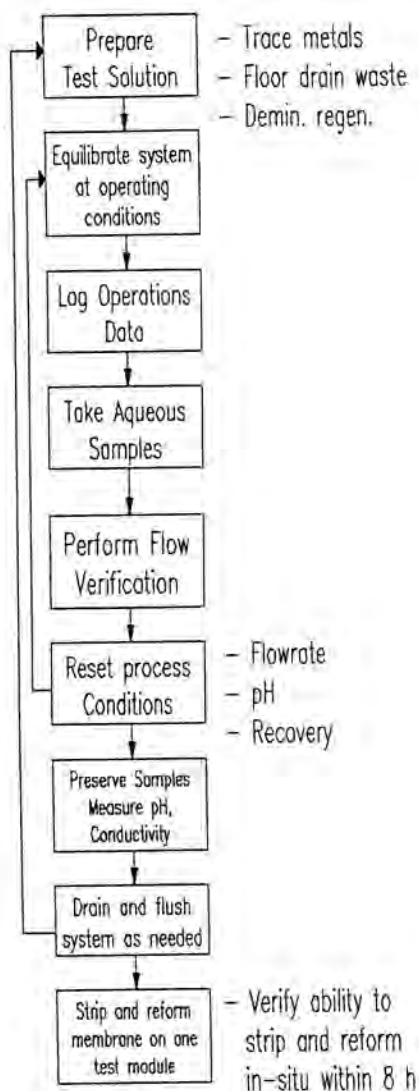


Fig. 2. Hyperfiltration System Test Logic

Flow verification was required to measure permeate flow rates from each module to close the flow balance around each stage and to allow later calculation of module permeabilities (gal/ft² - d - psi of permeate) and to measure the variance in permeability that corresponds to the manufacturing technique and hydraulic design of the system. Since interstage flowmeters were not built into the system, the flow verification was performed by manually diverting the permeate from each module to the sampling station where it was collected for a fixed time interval in a graduated cylinder or other suitable container. The data thus collected allowed calculation of the permeate rate from each module and thus from each stage. These data then allowed stage recoveries, and hence the permeabilities, to be calculated. Determining the permeability also requires knowledge of the average pressure in each tube, which was calculated based

upon the system inlet and outlet pressures and a simple hydraulic model of the system.

After flow verification, system operating conditions, including flow rate, recovery, and pH, were reset. Implied in the flow rate and recovery settings are module restagings required to allow system operation at the given conditions.

Once the samples for a given test solution were collected, they were analyzed on-site for pH and conductivity and then preserved per Standard Methods and sent to ORNL for detailed analysis. After testing with one solution was completed, the next solution was formulated and testing restarted.

The final test step was demonstration of the stripping and reforming of one hyperfilter module. This procedure was performed to verify that a membrane could be stripped and reformed in the field within an 8 hour time period and that a membrane with a quality commensurate to that obtained in the factory could be obtained.

A summary of actual test conditions is provided in Table VIII. As shown, testing proceeded from trace metals in demineralized water to floor drain waste to regeneration solution, and finally the stripping and reforming test was performed. During the testing period, approximately 125 samples were collected for analysis at ORNL. However, since each sample resulted in several analytical results, there were many more actual data points recorded than there were samples.

SHOP TESTING

Before the WBN system was shipped to the plant, it was assembled in a fabrication shop for the system test. Prior to testing, the instrumentation was calibrated and equipment subsystems were performance verified in accordance with TVA approved written procedures. The process flow diagram for the complete TVA waste evaporator preconcentration system is schematically portrayed in Fig. 3. For the system test, a temporary tank served as the feed source to which the concentrate and the permeate streams were recycled. With the exception of the demineralizers, which were not included in the test, the remaining equipment, instrumentation, and controls were installed and interconnected as they will be in the WBN plant. As the waste simulants were recirculating through the HF system, samples were taken at points selected to provide intermediate and overall rejection of the various waste constituents.

When processing the trace metals solution and the drain wastes at 95% recovery, the 17 double-housing modules are staged in a 6-4-3-2-1-1 configuration. When sampling was performed, samples of the feed, permeate, and concentrate were taken on one module from stages 1, 4, and 6 and a sample of the composite system permeate was also taken. The sample locations were chosen to provide sufficient information to predict the system rejection for the various waste constituents at different operating recoveries. The system was operated near a second recovery of 65% in order to provide operating data to verify theoretical predictions.

Condensate demineralizer regeneration waste simulant was tested in a manner similar to that for the drain waste. When processing regeneration

TABLE VIII

Hyperfiltration System Test
Operating Conditions

Test Step ^a	Test Solution	Feed Flow rate (gal/min)	System Recovery (%)	Feed pH	Comments
2	Trace Metals Solution	30	95	7.2	Obtain trace metal rejection data at two pH values.
		30	67	7.1	
3	Floor Drain	30	95	6.7	Obtain trace metal and TDS rejection at high and low recovery.
		30	70	6.8	
		30	67	7.8	Measure boron rejection at high and low recovery and at intermediate and high pH.
		30	97	7.6	
		30	95	9.1	
4	Demineralizer	85	95	7.0	Test regenerant solution at high and low recovery.
		84	71	6.8	
		78	95	7.1	Measure dye rejection and TSS analog.
5	In-situ Membrane Reformation Solution	Varied	N/A	Varied	Chemically strip and remotely reform one HF module membrane.

^a Step number is keyed to written system procedure prepared for TVA by ATI.

waste, the system is capable of operating at a 90 gal/min feed rate with 95% recovery. When operating on regeneration waste, the modules are staged in a 9-5-2-1 configuration for 95% recovery and in a 9-5 configuration for 65% recovery. These stagings yield a more uniform velocity profile through the tubing of the modules in the system. Velocity is an important parameter in system design because it affects the rate of membrane fouling as well as dissolved solids rejection. The optimum velocity in HF systems is 5 to 10 ft/sec.

In addition to verifying the staging configurations, this test addressed the mechanism by which the rejection of the radionuclides is affected by the high concentration of sodium sulfate in the stream. In the pilot testing performed at SQN, the radionuclide rejections across one module remained high in the presence of comparable levels of sodium sulfate. However, since the system, at 95% recovery, concentrates the sodium sulfate to levels at least 8 times the feed concentration, this high concentration of sodium sulfate may affect the rejection of the radionuclides.

RESULTS OF THE SYSTEM TEST

Flow Verification

The method of flow verification, initially considered crude and prone to error, was exceedingly accurate. The permeate from each module was individually diverted and collected to determine the module permeate flow rate.

Flows from each of the 17 modules were totaled and compared with the instrument reading for the system permeate flow rate. Of the ten different system configurations and test steps, the permeate percentage variance error is less than 5% in six instances and greater than 10% in only one.

Derived from the flow rate verification data are module, stage, and multiple-stage or progressive system data that can be extracted and interpolated. Combined with the system pressures (feed, permeate, and concentrate) and calculated pressure losses, a simple hydraulic model of the system can show the module permeabilities and fluxes, module and stage

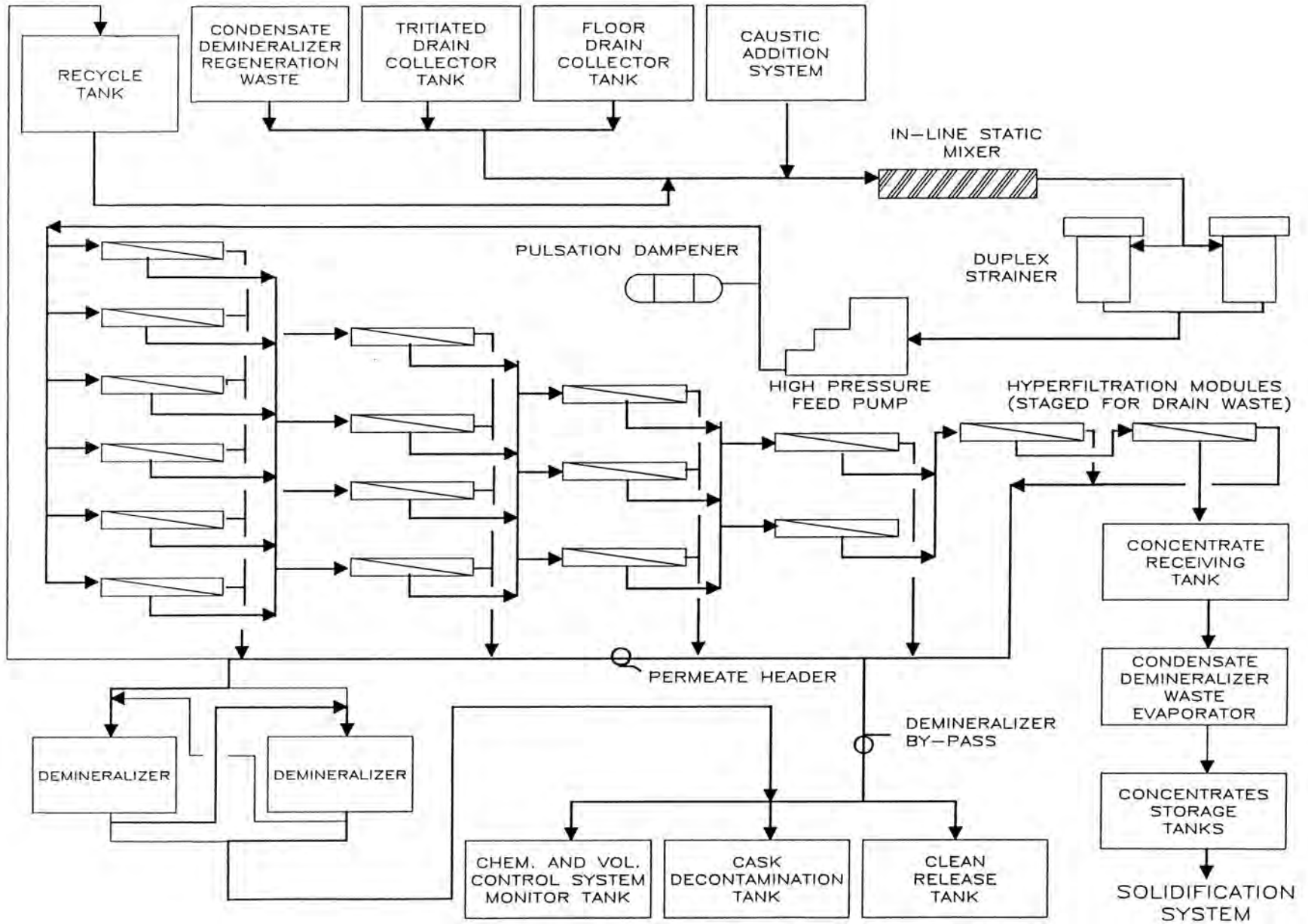


Fig. 3. Hyperfiltration Process Flow Diagram

recoveries, and the intermediate system recoveries. The benefit of this component and subsystem knowledge is the future verification of quantitative models for systems with alternate staging and recoveries. For instance, although in the first test step the system recovery is 95% with a six stage, 6-4-3-2-1-1 configuration, the data and sample analysis provide information on equivalent systems at 63% recovery (two stage, 6-4 configuration) 79% recovery (three stage, 6-4-3 configuration); plus three more recovery/stage arrangements.

Sample Analysis

The analyses of 128 samples were conducted by the Analytical Chemistry Division at ORNL in accordance with its quality assurance (QA) program. Associated Technologies, Inc., then compiled the raw data by test step and by a weighting factor for each waste type.

Using the computer spreadsheet Lotus 123, average membrane rejections were calculated using three different techniques as well as a composite system rejection. If the mass balance closes, the three equations provide the same answer. Mass balances were also checked by calculating a feed concentration from the permeate and concentrate sample concentrations. The mass balance error percentage was then defined as the calculated value minus the actual sample value divided by the actual sample value. The use of the three rejection calculations with the mass balance error percentage made identification of inconsistencies in the sample analysis obvious.

Lab results for the trace metals solution provided 7 data points for each of the 30 samples. All of the data appeared reliable with reasonable mass balances except for the iron data. Isolated cases indicated that the iron rejection was acceptable, but the overall data lacked consistency, particularly in the permeate concentrations. It is hypothesized that analytical constraints were encountered and that iron solubility was exceeded.

Analyses of the samples taken during the drain waste test had mixed results in analyzing for the trace metals in the solution. The high concentration of the boric acid apparently swamped and invalidated the ICP method. A pretreatment separation technique to isolate the trace metals was developed and may be useful for similar analyses in the future. Of the remaining data, reasonable accuracy was obtained for boron, iodine, TDS and conductivity. One half of the permeate concentrations of the phosphates and virtually all of the lithium concentrations were below the limits detectable by the ICP method employed.

Initial submittals of regeneration waste samples for ICP analysis were limited to those necessary for determination of the vendor-guaranteed data. This limitation was the result of problems in analyzing for the analog metals combined with the desire for efficient usage of available funds. The ICP process utilizes a light signal generated in an argon plasma to differentiate between the metals. In solutions with large concentrations of sodium relative to the other metals, the scattered sodium light swamps out the other much lesser signals from the trace

metals. This phenomenon is similar to the problems encountered with the high boron concentration in the drain waste solution. Results of the lab analyses were sufficient to evaluate the performance versus the criteria using only the feed and permeate concentrations. Concentrations of lithium, barium, and the permeate of the iron were below the limits of detection for the ICP process used. The remainder of the data appeared reasonable and consistent.

Analysis of the samples resulting from the in-situ membrane stripping and reformation were performed by CARRE, Inc. After the new membrane was applied, the conductivity (i.e., sodium nitrate) of the samples and the appropriate flow rates were used to verify reformation. Later absorbance analysis at a wavelength of 610 nm measured the rejection of the same blue, water soluble dye as identified in Table VII.

EVALUATION OF RESULTS VERSUS PERFORMANCE CRITERIA

The release for shipment of the HF system was contingent upon successfully meeting the performance criteria of Table I. Using Eq. (2) for overall rejection, it can be seen in Table IX that the system's performance was predicted with reasonable accuracy.

During drain waste simulant testing, suspended solids rejection was not modeled; therefore, no achieved TSS rejection is given in Table IX.

For achieved gross activity rejections of the drain waste, two values are given. The first value is a weighted average rejection of the individual radioisotope-model rejections, weighted according to the isotope's abundance in the plant's actual floor drain waste. The second value is a weighted average based on the concentrations in the plant's tritiated drain waste. The system met the predicted rejections for a single module and for 65% system recovery; however, the rejections for 95% recovery fell below the expected 70%. This is likely due to the fact that, since the membrane is a charged membrane, rejection is dependent upon the ionic strength of the waste. In the test, the radionuclide models were added in concentrations 100 to 1,000,000 times the actual waste concentrations in order to remain above the limits of the detection; therefore, the ionic strength of the simulant was much higher than that expected in the plant's waste. At high recoveries, the system produces a concentrate stream of high ionic strength, reducing the overall rejection that the system can achieve. It is expected that when the system processes the more dilute plant waste, the rejection at 95% recovery will meet the projected 70%.

The boron data listed in Table IX are percent reclamation values. They are presented as reclamation rather than recovery due to boron's affinity for passage through the membrane. This phenomenon allows the boron in the plant's waste to be recovered by recycling the permeate stream, which is reduced in radionuclides and other dissolved solids, to the boron recovery system.

During the test, the pH of the waste was increased in steps from 6.7 to 9.4 to determine the effect of pH on the system rejection of boron. The HF membrane, having a negative fixed charge at a pH greater than 4 (7) uses an ion exclusion mechanism

to influence the system rejection of ionically charged molecules. In the case of a weak electrolyte solute, such as boric acid, where the dissociation equilibrium is highly pH dependent, it was predicted that the system rejection of the weak electrolyte can be controlled by controlling feed stream pH.

TABLE IX

Comparison of Rejections Achieved in System Test with Predicted Rejections

Waste Type and Specie	Module (%)	System (%)	
		Recovery 65%	Recovery 95%
1. Drain Waste			
TSS - Predicted	99 ^a	99 ^a	99 ^a
Activity - Predicted	88	80	70
Achieved	89,89 ^b	81,79	65,61
Boron - Predicted	70 ^c	90	90
Achieved	90,49 ^d	90,49	94,71
2. Regeneration Waste			
TSS - Predicted	99	99	99
Activity	98	^a	99
Activity - Predicted	88	75	50
Achieved	89	81	68
TDS - Predicted	80	75	50
Achieved	82	74 ^e	50

^a Not tested.

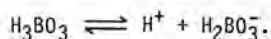
^b First rejection listed uses weighting factors determined by the floor drain waste analysis; second rejection listed uses tritiated drain waste weighting factors.

^c Boron values listed are "Reclamation" values or passage through the membrane.

^d Boron reclamations listed are for feed pH 6.7 and 9.4, respectively.

^e The 74% rejection shown is adjusted to 65% recovery from the 71% rejection achieved at 70% recovery during the test.

In the pH range of 5 to 7, the boric acid side of the chemical equilibrium equation is dominant. As pH increases, the equilibrium shifts toward the dissociated, positively charged hydrogen ion and negatively charged borate molecule:



The ZOPA membrane has a lower rejection or, conversely, a higher reclamation or passage through the membrane of the boric acid molecular species

than it does for the borate ionic species. This phenomenon also occurs to some extent with uncharged reverse osmosis membranes. By controlling the feed solution pH, the relative concentration of boric acid/borate molecules is fixed by the equilibrium ratio. It is estimated that the ratio is 1:1 at a pH of 9. At a low pH, as the predominant boric acid molecules pass through membrane to the permeate stream, the equilibrium ratio drives the borates in the feed stream to reassociate into the boric acid compound. The reassociated boric acid itself then passes through the membrane thereby driving more borate to reassociate. The cycle continues, thereby giving a high boron reclamation value for the system.

At a higher pH, dissociated molecules dominate the equilibrium ratio; thus, they are at a much higher concentration in the feed. The charged borate ionic species are rejected by the negatively charged ZOPA membrane. The boric acid molecules still pass through the membrane, but because of the equilibrium ratio, they are at a much lower concentration; therefore, in absolute numbers, less boron passes through.

The initial pilot tests performed in 1982 at SQN indicated that control of the feed pH could generate a boron-enriched permeate (3). This theory was tested in the shop and showed that the behavior of the boron during the system test was as predicted. The test for samples at pH 6.7, 8.0, and 9.4, at both high and low recoveries, verified that boron can be directed to either the permeate stream or the concentrate stream. An empirical model for boron passage is presented by Spencer (8).

The results also show that the composite system boron reclamation is more susceptible to concentration dependencies at higher recoveries when at a higher pH. This is evident by the steeper slope of the boron reclamation curves at the higher pH levels (Fig. 4).

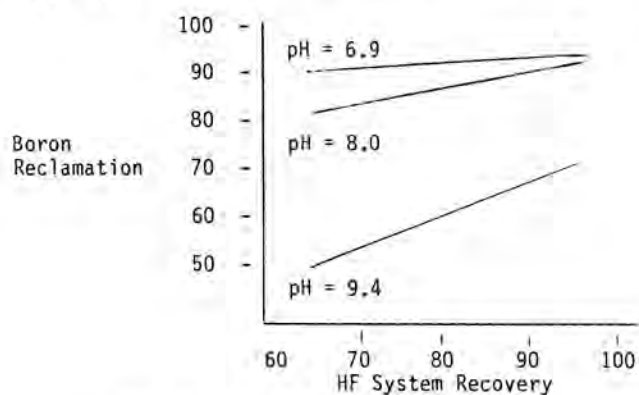


Fig. 4. Boron Reclamation varies with pH and Recovery

The achieved boron reclamation exceeded the predicted reclamation for all three categories at the feed pH of 6.7, as shown in Table IX. The second number shown illustrates the impact of pH adjustment as it is for a pH of 9.4.

For the regeneration waste simulant, TSS rejection was modeled by the addition of a water soluble,

high molecular weight dye. The dye, its molecular size being an order of magnitude smaller than most suspended solids, was used in place of suspended material due to the ease of flushing it from the system. Three data points were taken to measure dye rejection. Across module 6 and module 15, the rejections were 98.11% and 99.97%, respectively, while the system rejection measured 99.06%. Within the accuracy of the dye measurements, it is believed that all these are essentially the same number. It is expected that in plant operation, the system will achieve the predicted 99% TSS system rejection, since the rejection of the water soluble dye was at least 98%.

The regeneration waste gross activity rejections exceeded the predicted values in all three cases. The rejections presented are weighted averages based on the predicted concentrations that will be seen in the plant's regen waste. However, barium and iron rejections were omitted from the averages due to inconsistent analytical results, and iodine data were included from corresponding drain waste data due to the regen waste's high predicted concentrations of iodine. (No iodide was added in this simulant in order to reduce the number of analytical methods required.) The presence of high concentrations of sodium sulfate in the simulant seemed to have no effect on the rejection of the nuclide models; the rejections matched those seen in the trace metals test.

Sodium sulfate rejections in the test were evaluated by analyzing for TDS, since the simulant was largely a sodium sulfate solution. The TDS rejections were predicted accurately. A 70% recovery was achieved in testing rather than the 65% target rate. At 70%, TDS rejection was 71%, which, when extrapolated to 65% recovery, corresponds to a 74% rejection, nearly matching the 75% which was predicted.

The remote stripping and reformation of the HF membrane was achieved but took twenty minutes more than the eight hours predicted. Verification of the chemical stripping and removal of the membrane was accomplished through membrane permeability measurements. Feed and concentration conductivity measurements of the new membrane indicated an 87% sodium nitrate rejection and the rejection of the blue water soluble dye measured greater than 99.6%.

Evaluation of Specie Rejections

Analysis results of the individual specie rejections, performed by using the sort functions of the Lotus 123 program, are summarized and presented in Table X. The analysis did not involve rigorous mathematical or statistical methods but rather relied upon judgments as to the data validity. Data from samples with high mass balance error percentages or incomplete mass balances (except for cesium) were not used. Data showing a rejection greater than 100% and data that appeared to be abnormally high or low were deleted. The tabulated rejections shown are classified principally as the module rejections or average membrane rejections as calculated by the three equations referred to earlier. These equations neglect the effect of ionic strength on the rejections so the rejections calculated in this manner decrease as the ionic strength increases. This

effect contributes to the range of rejection results. However, these rejections provide meaningful comparisons of the rejections of the ionic species. With the exception of iron which appears to be anomalous, the rejections of the multi-charged cations are about 10% higher than the single charged cesium and iodide, which is consistent with previous performance of Zopa membranes.

The data obtained are considered to be representative of the results that were expected. The cesium data warrants further discussion due to the wide range of results and the number of data entries. A significantly higher number of entries were available for cesium, as atomic adsorption was used specifically for cesium detection at ORNL. The added number of data points did not provide a clearer picture of a definitive rejection for cesium.

The rejections were evenly distributed throughout the range with 15 rejection data points less than 75%, 20 points at the average rejection + 5%, and 16 points greater than 85%. Several of the cesium rejection numbers are not supported with mass balances as data from one of the three streams, which were needed to calculate the error percentage, were not available.

A more in-depth evaluation of the cesium rejections versus recovery, pH, or concentration may provide the insight to optimize the rejections in actual operations. Later reports are expected to provide more detailed analysis of all of the data generated including the cesium data.

TABLE X

Average Membrane Rejection
for Specific Radioisotopes

Specie	% Rejection			Data Points	Error ^a
	Low	High	Avg.		
Barium	82	97	89	16	7
Cesium	62	93	80	51	11 ^b
Cobalt	82	97	90	23	13
Iodine	75	92	81	21	25
Iron	72	90	82	9	21
Manganese	80	94	88	23	10
Strontium	85	96	91	19	15

^a Error percentage is the largest of the mass balance error percentages for the data points

^b Mass balances of all cesium data points were not performed due to missing data.

SUMMARY

The knowledge gained by performing the system test has provided TVA with the information necessary to determine its operating objectives based on the

type of waste being processed. If boron rejection is of primary importance, then the pH of the waste should be increased and the system operated in the range of 65% recovery. If volume reduction and boron reclamation are needed, and operating combination of no pH adjustment and 95% recovery is best. For a waste which is highly contaminated with radioactivity, the system can be operated at a lower recovery in order to ensure that the permeate will contain levels of radioactivity low enough to meet discharge limits. If the waste is less contaminated, operation at a higher recovery will still produce a dischargeable permeate while reducing the concentrate stream feeding the waste evaporator. Since the concentration of dissolved solids in the permeate stream increases with increasing recovery, the recovery at which the system is operated is vital in producing a permeate stream which can be discharged, thereby reducing the load on the waste evaporator. In plant operation, the recovery that provides the optimum combination of separation and volume reduction will be determined.

Installation of the hyperfiltration system at Watts Bar is scheduled for 1987. Since the system is totally skid-mounted, installation should proceed quickly, and startup of the system will follow shortly thereafter. The knowledge of the system performance, acquired through full-scale testing, should ensure that the transition from startup to normal operation will proceed more smoothly.

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