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Scouting Treatability Studies Performed in Support of the Nonradiological Wastewater Treatment Facility Feasibility Study

J. F. Walker
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Chemical Technology Division

SCOUTING TREATABILITY STUDIES PERFORMED IN SUPPORT OF THE NONRADIOLOGICAL WASTEWATER TREATMENT FACILITY FEASIBILITY STUDY

J. F. Walker
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CONTENTS

LIST OF FIGURES

LIST OF TABLES

SCOUTING TREATABILITY STUDIES PERFORMED IN SUPPORT OF THE NONRADIOLOGICAL WASTEWATER TREATMENT FACILITY FEASIBILITY STUDY

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ABSTRACT

A developmental program was undertaken to partially investigate the flowsheet being considered for the treatment of nonradiological wastewater produced by the Oak Ridge National Laboratory. The proposed flowsheet contains the following unit operations: equalization, carbon adsorption, ozonation, biodenitrification, biooxidation, filtration, reverse osmosis, and ion exchange. This report details an initial scouting program in which granular activated carbon (GAC) adsorption and reverse osmosis (RO) were operated on two of the waste streams that will be treated in the nonradiological waste treatment (NRWT) facility (190 pond influent and Building 3544 effluent).

The GAC system was operated on both the 190 pond influent and the 3544 effluent, using Filtrasorb-300 activated carbon. Mercury removal was measured to be greater than 94% at an inlet concentration of 0.02 to 0.04 mg/L of mercury. Total organic carbon (TOC) removal was 40 to 70%, with inlet values of 4.6 to 5.3 mg/L of TOC.

The removal of TDS, nitrate, sulfate, and mercury from the 3544 effluent was examined by RO with a cellulose acetate membrane (Osmonics) and a thin film composite membrane (FilmTec). The Osmonics membrane was operated in the feed recovery range of 64 to 95%. The corresponding rejection values were: 66 to 22.5% for nitrate, 74 to 45% for TDS, and 92 to 85% for sulfate. Mercury was not rejected at any recovery. The FilmTec membrane was operated at between 60 and 94% recovery. The corresponding rejection values were: 95.5 to 68.4% for nitrate, 95.4 to 84.5% for TDS, and 54.9 to 33% for mercury. Sulfate rejection was greater than 98.5% in all cases.

Both membranes rejected more mercury upon the addition of sulfide to the feed stream, probably due to the formation of colloidal mercury sulfide. Both membranes were found to concentrate radioactive species.

1. INTRODUCTION

As a result of the announcement by the Environmental Protection Agency (EPA) and the State of Tennessee of their intent to require permits on all process wastewater discharges from Oak Ridge National Laboratory (ORNL), steps are under way to establish discharge limits and to assure compliance with these limits.[1] These steps include a sampling program to characterize the various process waste streams as well as initiation of the engineering design effort of a facility to treat the nonradiological wastewater (NRW) streams. The feasibility study, performed by Martin Marietta Energy Systems, Inc., Engineering, has produced a treatment scheme that includes the following processes: equalization, carbon adsorption, ozonation, biodenitrification, biooxidation, filtration, reverse osmosis, and ion exchange.[1] In order to assist in this design effort, a developmental program is being initiated to evaluate these processes. Contained herein are the results from an initial scouting program during which carbon adsorption and reverse osmosis units were operated on two of the waste streams that will be treated in the Nonradiological Tareatment Facility (NRWTF).

2. WASTEWATER CHARACTERIZATION

Two process wastewater streams were examined in this study: (1) Building 3544 effluent (process waste treatment plant) and (2) 190 pond influent (process discharges from the 4500 area). Grab samples were taken from these streams at the beginning of the program for detailed characterization. In addition, total organic carbon (TOC), nitrate, sulfate, total suspended solids (TSS), and total dissolved solids (TDS) were followed daily while operating the carbon adsorption (CA) and reverse osmosis (RO) units. Results of the detailed analysis of the grab samples are presented in Table 1. For comparison, the "best available treatment economically achievable" (BATEA) required at other

Table 1. Characterization of Building 3544 effluent and 190 Pond influent

(obtained by analysis of a grab sample; all concentration in mg/L except as noted)

Parameter	3544 effluent	190 pond influent
Ag	0.0008	0.0008
Al	0.126	0.191
B	<0.018	<0.018
Ba	<0.02	0.0308
Be	0.00243	0.0097
Ca	<0.002	27.7
Cd	0.0004	0.0005
Co	0.0128	0.0307
Cr	0.002	0.006
Cu	0.003	0.105
Fe	0.027	1.43
Ga	0.163	0.196
Mg	<0.01	8.21
Mn	<0.023	0.176
Mo	0.022	0.0216
Na	<0.01	4.9
Ni	0.0242	0.438
Pb	0.01	0.114
Sb	0.025	0.004
Se	<0.001	<0.001
Si	2.52	2.03
Sr	<0.0021	0.0812
Ti	0.0106	0.0167
V	0.0127	0.0262
Zn	<0.01	0.0491
P	0.301	<0.26
As	<0.001	<0.001
Li	0.109	0.185
SO_4	28	23
NO_3	330	<5
NO_2	5	<1
F	1	1
Cl	14	7
Br	<1	<1
PO_4	<5	<5
Hg	0.0006	0.0025
CN	0.007	<0.002
Oil & grease	3	3
Phenol	<0.001	<0.001
pH[a]	7.54	7.87
Alkalinity as $CaCO_3$	72.2	95.5
TSS	<5	<5
TDS	577	160
COD (unfiltered)	8.0	8.0
TOC (unfiltered)	12	12

[a]Standard pH units.

government installations (Y-12 and ORGDP) is presented in Table 2, and the proposed effluent quality standards are given in Table 3.[1] Although the discharge limits have not been set, a combination of Tables 2 and 3 served as the design guidelines for the NRWTF.[1]

As can be seen in Tables 1 and 2, the 3544 effluent violates the proposed BATEA limits daily average for TDS, mercury, nitrate, and phosphorous and also exceeds the daily maximum for TDS, nitrate, and phosphorous. The 190 influent violates the daily average for beryllium, chromium, copper, iron, lead, mercury, nickel, and zinc and exceeds the daily maximum for copper and iron.

TOC was present in both the 3544 and 190 streams at a concentration of ~12 mg/L. At the beginning of the program samples from each source point were subjected to gas chromotography/mass spectrometry (GC/MS) analysis to determine the major constituents that comprised the TOC. No major peaks were observed for the 3544 stream, but two major peaks were observed for the 190 stream. Because of the low resolution of the mass spectra, the elemental composition of these two compounds could not be determined. The results indicate that one compound had an apparent molecular weight of 236 and could be an unsaturated (or cyclic) alcohol or ether, a simple 17-carbon alkene, or a cycloalkane. The second compound had an apparent molecular weight of 256 and could be an alcohol, ether, or ester.[2]

At a later date, another sample of 190 wastewater was analyzed by GC/MS. One major peak was observed which appeared to be a dimethyl ether of a glycol, such as tri- or tetramethyl glycol. Several minor peaks were also observed. The majority of these compounds were alkanes and unsaturated (or cyclic) hydrocarbons. Some oxygen-containing compounds were observed, including several phthalates, acids, and a compound that appeared to be an isomer of caffeine. Naphthalene and methylnaphthalene were also observed.[3]

Table 2. Proposed BAT effluent limits[a]

Parameters	Daily average (mg/L)	Daily maximum (mg/L)
Aluminum, total	0.50	1.0
Beryllium, total	0.0053	0.0130
Cadmium	0.00025	0.003
Chromium, total	0.0029	0.021
Copper, total	0.0056	0.022
Dissolved solids, total	250.0	300.0
Iron, total	0.30	0.60
Lead, total	0.0038	0.17
Mercury	0.00002	0.0041
Nickel, total	0.096	1.80
Nitrate (as N)	20.0	25.0
Phosphorous (as P), total	0.0001	0.0002
Oil and grease	10.0	15.0
Phenols, total	0.001	0.002
Silver	0.014	0.027
Suspended solids, total	30.0	50.0
Temperature, °C (°F)	30.5 (86.9)	
Zinc, total	0.047	0.32
Volatile organics		
Chloroform	0.01	0.02
Chlorobenzene	0.01	0.02
Benzene	0.01	0.02
Chlorodibromomethane	0.01	0.02
Methylene chloride	0.03	0.035
Trichloroethylene	0.01	0.02
Toluene	0.01	0.02

Additional Constraints

- The pH shall not be less than 6.5 standard units nor greater than 8.5 standard units.
- There shall be no discharge of floating solids or visible foam in other than trace amounts.
- The effluent shall not leave a visible sheen on the receiving waters.

[a]Source: Division of Environmental Management Guidelines, Draft Report, August 6, 1984.

Table 3. Proposed effluent quality standards

Parameter	Concentration (mg/L)
BOD_5	5 (max)
COD	10 (max)
Cr	0.5 (max)
DO	5 (min)
pH	6–9 (range)
Total suspended solids	5 (max)
Nitrates	25
Total dissolved solids	500

3. ACTIVATED CARBON

The granular activated carbon (GAC) process was included in the NRWTF design for the removal of organics, particularly chlorinated hydrocarbons, as well as possibly acting as a pretreatment for RO. The literature also indicates GAC, under the right conditions, can adsorb both organic and inorganic forms of mercury from water.[4]

The flow diagram of the GAC process used in this study is presented in Fig. 1. The process water (3544 effluent or 190 pond influent) was fed through a prefilter to remove suspended solids larger than 10 μm, doped with acidified mercuric nitrate to give a mercury concentration of ~0.020 to 0.040 mg/L, and stored in a surge tank. The water was pumped from the tank at a nominal flow rate of 3.79 L/min (gal/min) (1 gpm) through a series of three columns filled with Calgon Filtrasorb 300 granular activated carbon. These columns were 1.52 m (5 ft) high, each with an inside diameter of 26.4 cm (10.4 in.). The influent to and the effluent from each column were sampled (either daily or every other day) and analyzed for pH, TOC, TSS, nitrate, sulfate, and mercury. The GAC treatment results (mercury and TOC) for both the 3544 effluent and the 190 pond influent are given in Table 4.

During GAC processing of the 3544 effluent, feed to the system had mean concentrations of 0.0195 mg/L mercury and 4.6 mg/L TOC. The mean removal for mercury was 98.8%, with 96.6% being removed in the first

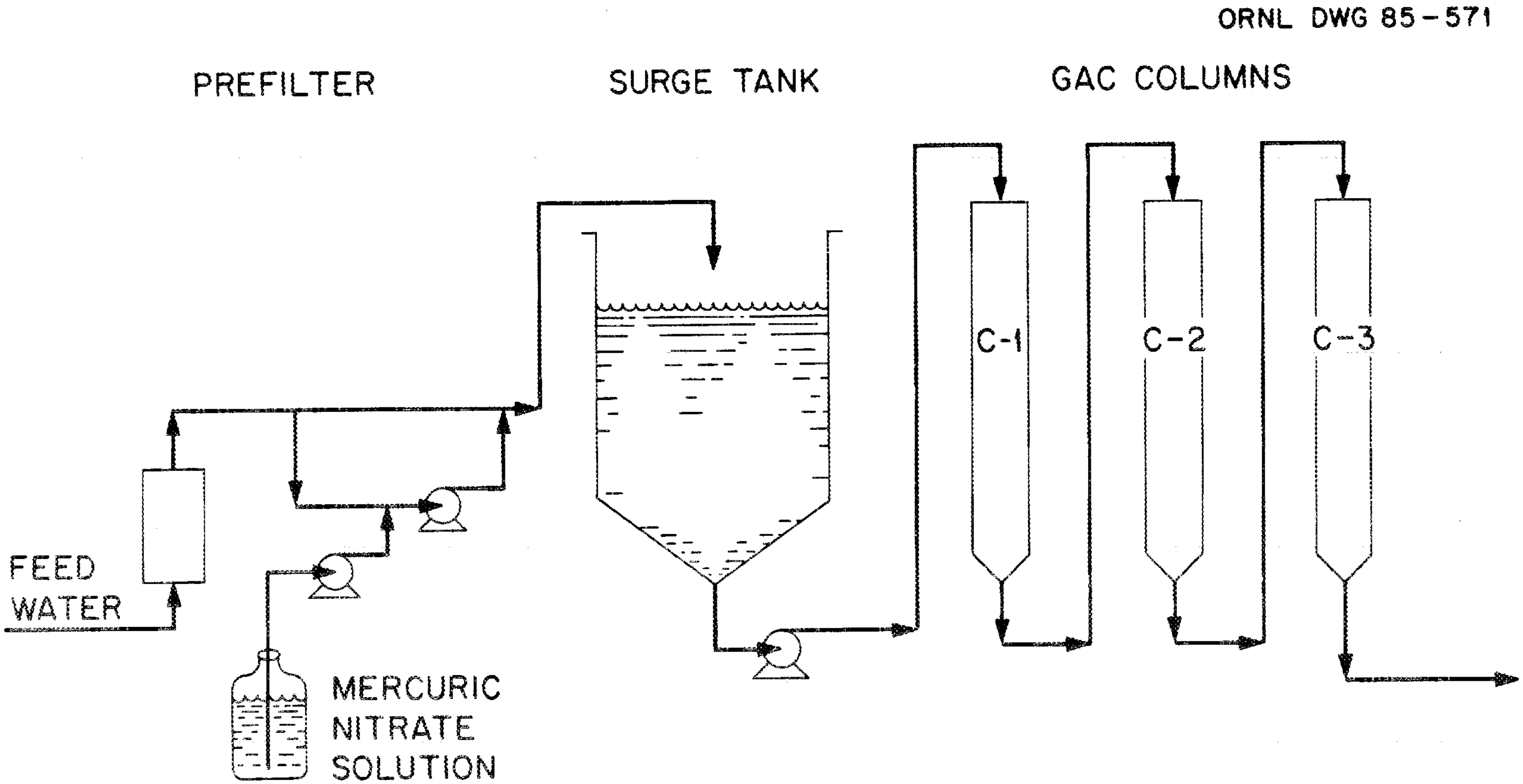

Fig. 1. Flow diagram of GAC system.

Table 4. Results of the granular activated carbon adsorption testing

3544 effluent				190 pond influent			
Volume processed [L(gal)]	Sample[a]	TOC (mg/L)	Hg (mg/L x 10^{-3})	Volume processed [L(gal)]	Sample[a]	TOC (mg/L)	Hg (mg/L x 10^{-3})
4,678 (1,236)	C-1 f	5.3	21	4,314 (1,140)	C-1 f	7.6	30
	C-1 e	2.9	0.5		C-1 e	3.1	0.7
	C-2 e	3.9	0.4		C-2 e	2.9	0.2
	C-3 e	2.7	0.4		C-3 e	3.5	0.1
21,166 (5,592)	C-1 f	6.2	16	14,989 (3,960)	C-1 f	5.8	18
	C-1 e	5.6	0.2		C-1 e	3.3	0.8
	C-2 e	5	0.1		C-2 e	1.8	0.4
	C-3 e	--	0.1		C-3 e	3.5	0.2
26,548 (7,014)	C-1 f	7.6	15	31,340 (8,280)	C-1 f	5.0	36
	C-1 e	8.2	0.4		C-1 e	2.5	2.0
	C-2 e	6.6	0.2		C-2 e	2.5	1.4
	C-3 e	--	0.2		C-3 e	3	0.9
32,112 (8,484)	C-1 f	8.3	18	42,241 (11,160)	C-1 f	7.9	*b*
	C-1 e	7.3	0.6		C-1 e	3.2	*b*
	C-2 e	7.7	0.1		C-2 e	3.0	*b*
	C-3 e	6.4	0.1		C-3 e	3.4	*b*
37,335 (9,864)	C-1 f	7.9	17	52,914 (13,980)	C-1 f	7.5	42
	C-1 e	7.1	0.5		C-1 e	4.9	2.3
	C-2 e	6.5	0.2		C-2 e	4.1	1.3
	C-3 e	6.7	0.5		C-3 e	5	0.9
42,899 (11,334)	C-1 f	3.5	24	74,716 (19,740)	C-1 f	4.3	36
	C-1 e	0	*b*		C-1 e	2.4	1.4
	C-2 e	0	0.1		C-2 e	2.5	0.9
	C-3 e	0	0.1		C-3 e	2.0	0.7
48,281 (12,756)	C-1 f	1.5	21	85,617 (22,620)	C-1 f	4.8	32
	C-1 e	0.3	1.0		C-1 e	2.2	1.2
	C-2 e	0	0.3		C-2 e	2.4	0.9
	C-3 e	0	0.2		C-3 e	2.6	0.6

Table 4. (continued)

3544 effluent				190 pond influent			
Volume processed [L(gal)]	Sample[a]	TOC (mg/L)	Hg (mg/L x 10^{-3})	Volume processed [L(gal)]	Sample[a]	TOC (mg/L)	Hg (mg/L x 10^{-3})
53,732 (14,196)	C-1 f	1.2	23	96,518 (25,500)	C-1 f	3.7	61
	C-1 e	0.3	0.5		C-1 e	3.2	1.6
	C-2 e	0	0.2		C-2 e	2.9	1.0
	C-3 e	0	0.05		C-3 e	2.7	0.7
59,477 (15,714)	C-1 f	2.1	20	112,869 (29,820)	C-1 f	4.5	32
	C-1 e	*b*	1.2		C-1 e	2.6	2.0
	C-2 e	*b*	0.3		C-2 e	3.0	1.5
	C-3 e	1.2	0.2		C-3 e	2.9	1.2
70,242 (18,558)	C-1 f	2.7	23	123,770 (32,700)	C-1 f	4.4	31
	C-1 e	1.2	0.8		C-1 e	2.8	3.9
	C-2 e	0.3	0.3		C-2 e	3.0	3.2
	C-3 e	0	0.3		C-3 e	2.1	2.7
81,143 (21,438)	C-1 f	*b*	18	134,670 (35,580)	C-1 f	4.6	31
	C-1 e	*b*	0.7		C-1 e	3.3	4.5
	C-2 e	*b*	0.4		C-2 e	3.1	2.8
	C-3 e	*b*	0.3		C-3 e	3.1	1.8
97,494 (25,758)	C-1 f	*b*	18	151,022 (39,900)	C-1 f	4.4	45
	C-1 e	*b*	0.8		C-1 e	2.6	1
	C-2 e	*b*	0.4		C-2 e	2	0.9
	C-3 e	*b*	0.3		C-3 e	2.6	0.8
				161,922 (42,780)	C-1 f	3.9	34
					C-1 e	1.8	2.4
					C-2 e	2.5	1.8
					C-3 e	2.5	1.1

[a]Samples: f = feed sample (ex: c-1 f = influent to column 1); and e = effluent sample.

[b]No data available.

column. Mean removal of TOC was 69.6%, with 48.5% being removed in the first column. While processing the 3544 stream, the GAC system had average inlet concentrations of 39.6 mg/L nitrate-nitrogen (175 mg/L nitrate), 46.0 mg/L sulfate, and <5 mg/L TSS. The GAC system removed none of the nitrate and sulfate.

During GAC process of the 190 pond influent, the feed contained mean concentrations of 0.0357 mg/L of mercury and 5.3 mg/L of TOC. The mean removal of mercury was 97.1%, with 94.4% being removed in the first column. The mean removal for TOC was ~43%, with essentially all of this being removed by the first column. While processing the 190 stream, the GAC system had average inlet concentrations of 1.1 mg/L nitrate-nitrogen (4.9 mg/L nitrate), 17.8 mg/L sulfate, and <5 mg/L TSS. Again, the GAC system removed no nitrate or sulfate.

The performance of the GAC column is depicted graphically in Figs. 2 and 3 for mercury and TOC respectively. In each figure, for both the 190 and 3544 process streams, the percent of contaminant remaining in the effluent of column one is plotted as a function of the volume of waste processed. The inlet concentrations of mercury and TOC as a function of the volume of water processed is presented in Figs. 4 and 5, respectively. As shown in Fig. 2, the first column consistently removed >93% of the mercury in both the 3544 and 190 process water, except for a spike in the 190 water which occurred between ~120,000 and ~133,000 L. During this period, none of the operational parameters followed showed any significant change, and the reason for this spike is not known. It is also indicated in Fig. 2 that the mercury wavefront had not broken through the first column at run termination for either the 3544 or 190 stream. Since the 190 water had higher inlet mercury concentrations and was processed for a longer period of time, this stream was used to determine that the <u>minimum</u> mercury capacity obtained in column one was 0.16 mg Hg/g carbon. For comparison, in jar tests run by Logsdon and Symons,[5] with mercury concentrations of ~0.009 mg/L, the data show that in achieving a concentration of 0.002 mg/L mercury, each

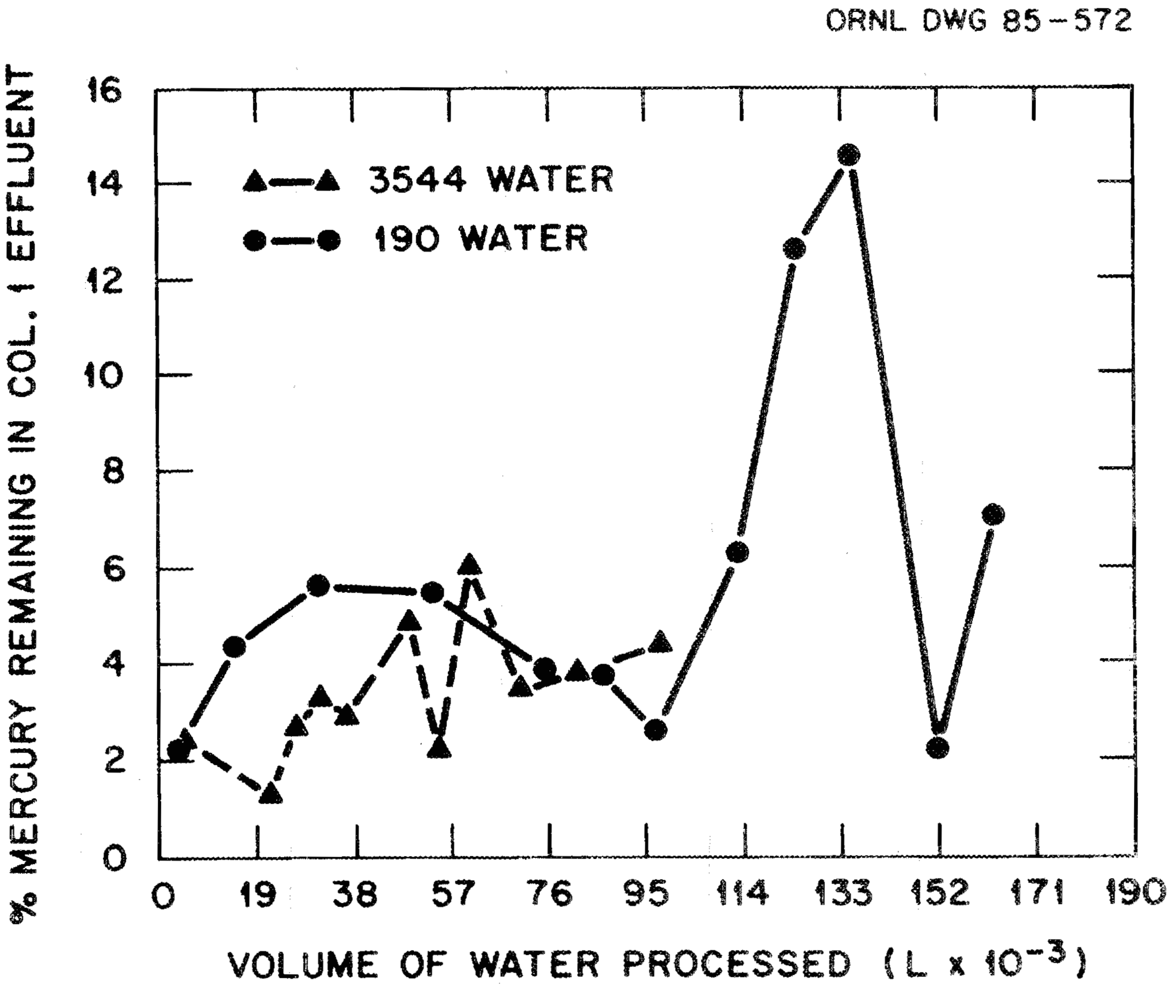

Fig. 2. Mercury removal by granular activated carbon.

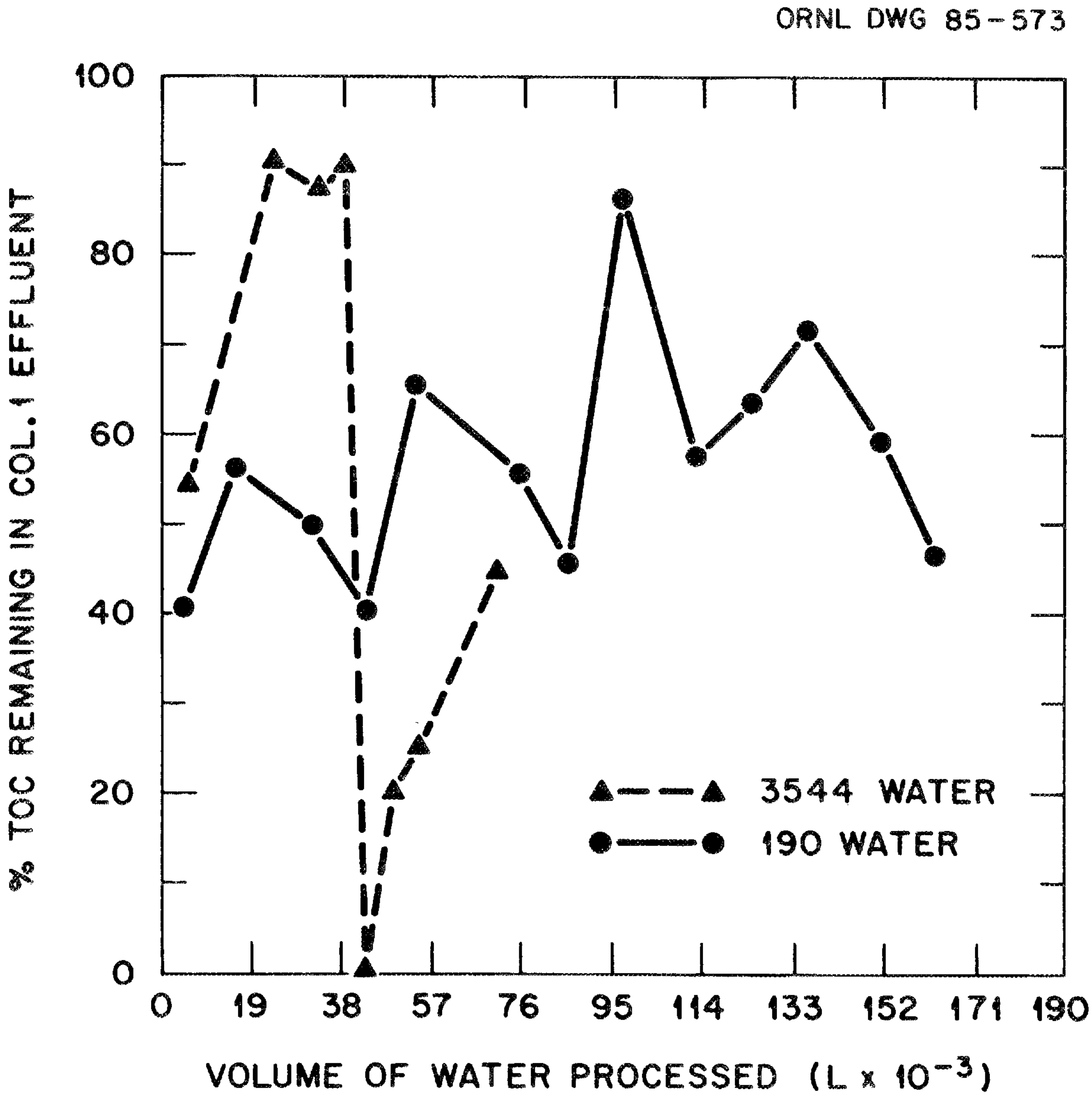

Fig. 3. TOC removal by granular activated carbon.

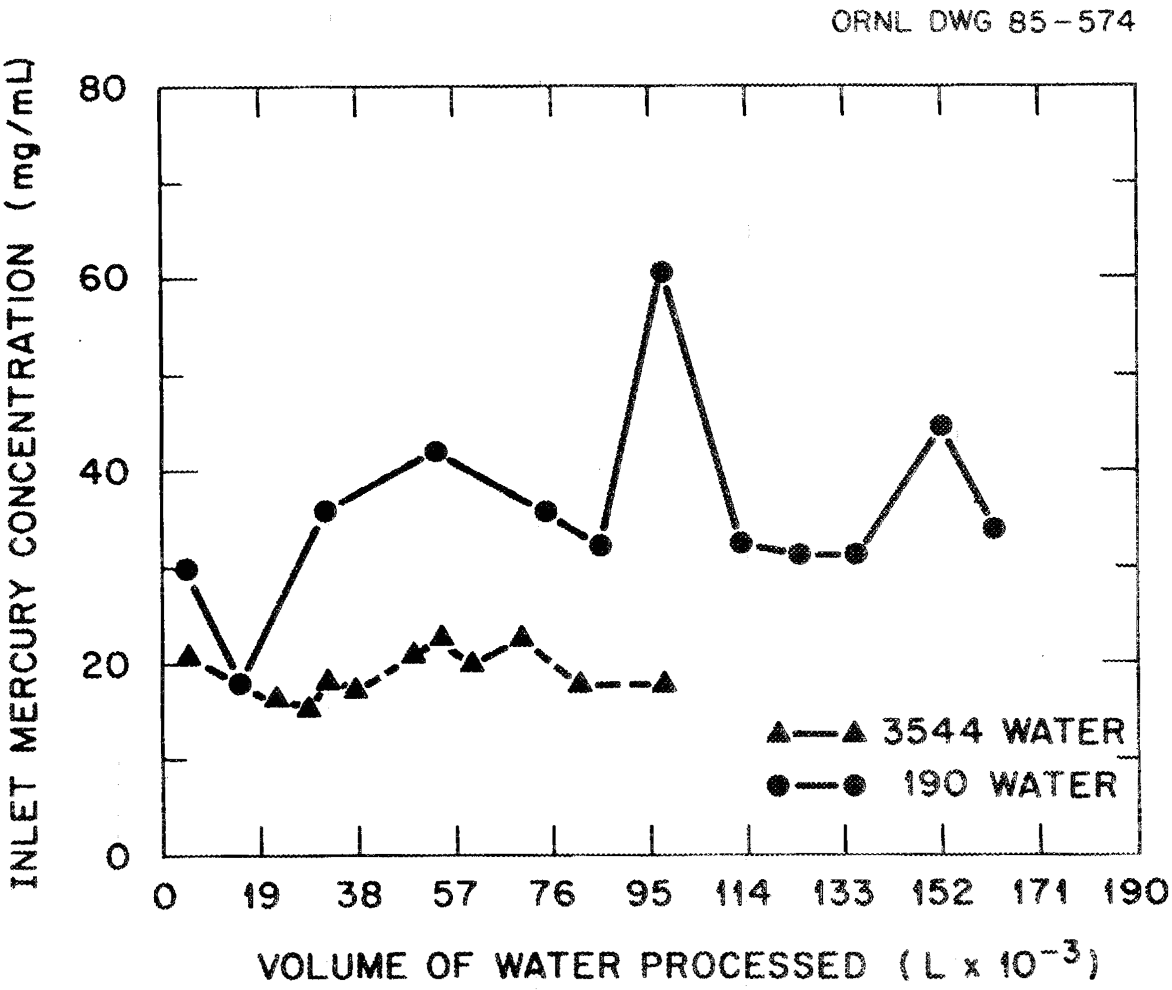

Fig. 4. Inlet mercury concentration as a function of the volume of water processed.

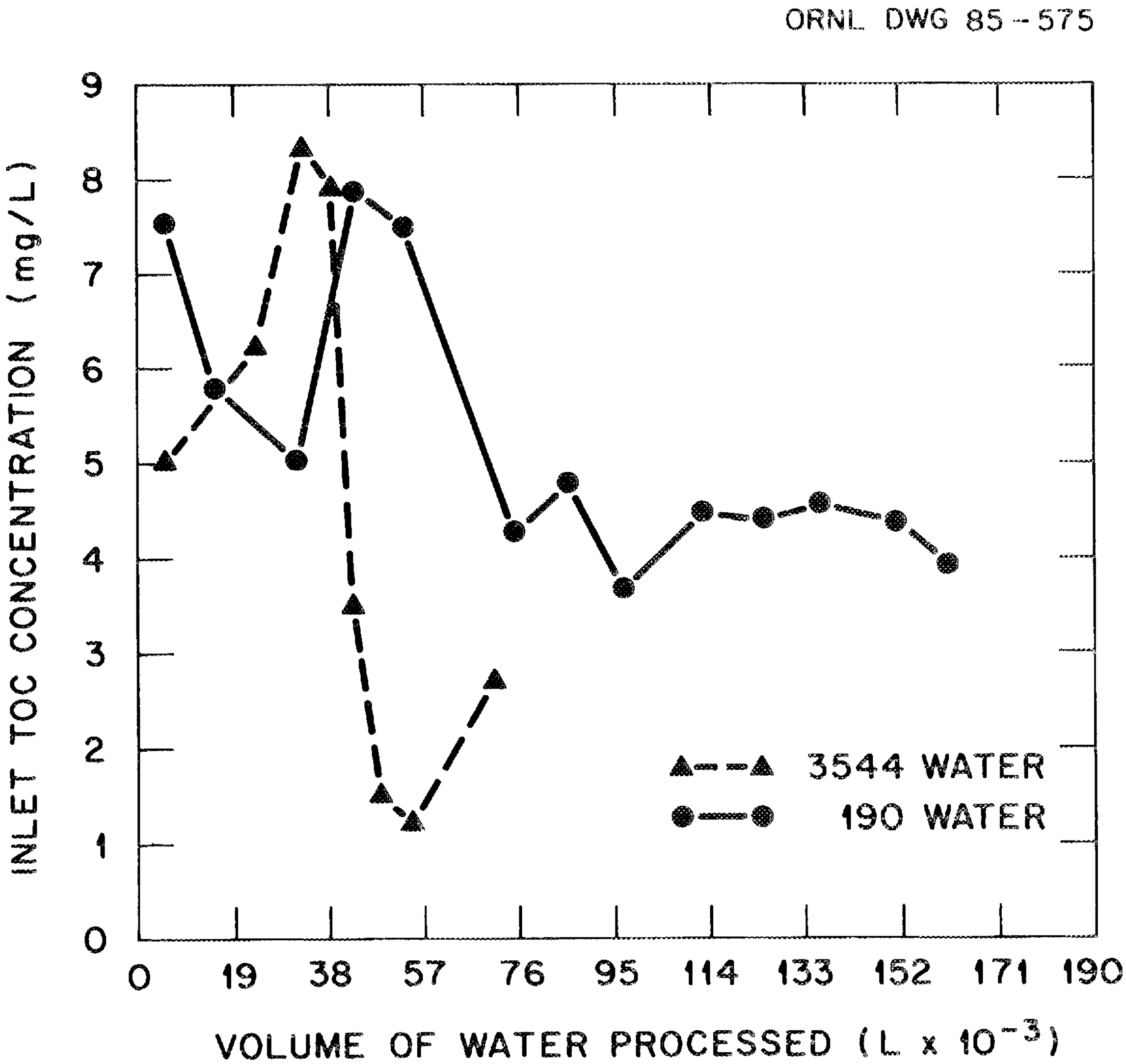

Fig. 5. Inlet TOC concentration as a function of the volume of water processed.

g/L of powdered activated carbon removed 0.1 mg/L of mercury, a loading of 0.1 mg Hg/g.[5] In column tests with average influent concentrations from 0.020 to 0.029 mg/L mercury and a 3.5-min contact time, mercury capacities of ~0.21 mg Hg/g carbon and ~0.4 mg Hg/g carbon were obtained for inorganic mercury and organic mercury, respectively, at 80% removal.[5] In column tests at Westvaco labs, virtually complete adsorption of 0.025 to 0.050 mg/L Hg as CH_3HgCl in tap water over a three-month period was obtained.[6] The literature indicates mercury adsorption by GAC is pH dependent and that sulfurizing and/or chelating agents could possibly be used to improve mercury removals.[5,7] Isotherm studies should be conducted to determine the effects of pH, sulfurizing agents, chelating agents, and carbon types on the ultimate carbon capacity for mercury. Column studies should then be run for the most promising set of operating data. Note that GAC adsorption is wastewater specific; therefore, these studies should be run on waters that are representative of the actual wastewater to be treated in the NRWTF.

As indicated in Fig. 3, the removal of TOC from the 3544 and 190 wastewaters varied from 100% to <10%. This variation means that the CA unit cannot be properly evaluated because the degree of removal is substrate dependent and cannot be predicted except on a case-to-case basis. Studies should be performed on waters that are representative of the actual wastewater that will be treated by the NRWTF and the regulated organics followed individually. Also by comparing Figs. 3 and 5 it can be seen that the fall to 0% TOC in the effluent corresponds to a drop in the inlet TOC concentration.

A radioactivity analysis was performed on the inlet and effluent water samples while processing both the 3544 and 190 wastewaters. A sample of the GAC was also taken from the middle of the first column after processing each waste stream and compared with an analysis of a sample of the virgin carbon. The initial analysis of the GAC at the close of each run indicates significant concentration of radioactive species by the carbon. A recheck of the same carbon samples a few weeks later, however, indicated very little radioactive accumulation by the carbon. No radioactive species which decayed at that rate could be found; therefore, an error in the analysis was assumed. More work should be done to clarify this conflicting data.

4. REVERSE OSMOSIS

Reverse osmosis (RO) was included in the NRWTP design for the removal of TDS, nitrate, and possibly mercury. The flow diagram of the RO unit used in this study is given in Fig. 6. The process water (3544 effluent) was doped with mercuric nitrate, giving an inlet mercury concentration of ~0.020 mg/L, to allow measurement of mercury rejection. The mercuric nitrate was fed into a recycle loop to ensure that it was completely mixed with the process water before entering the surge tank. In the surge tank the pH was adjusted to ~6 to 7, and in some runs sodium sulfide solution was added. From the surge tank the wastewater was first pumped through a filter to remove suspended solids larger than 5 μm and then through one of the two RO membranes examined in this study.

The first membrane tested was a model SEPA-97-CA cellulose acetate membrane manufactured by Osmonics, Inc. The design specifications for the membrane are 555 mL/min (0.15 gal/min) of permeate flow with 90 to 95% rejection of conductivity when operated at standard test conditions of 2.72 MPa (400 psig), 1000 mg/L NaCl, 25°C, and 10% feed recovery. The second membrane was a model BW30 thin-film composite membrane manufactured by FilmTec Corporation. The design specifications for this membrane are 4730 mL/min (1.25 gal/min) of permeate flow with a minimum Cl^- rejection of 96% when operated at standard test conditions of 1.6 MPa (225 psi), 2000 mg/L NaCl, 25°C, and a maximum recovery of 30%. Both of these membranes met the manufacturer's specifications.

The average operational parameters for the two membranes during the test period are summarized in Table 5, and a chronology of the operations is given in Tables 6 and 7.

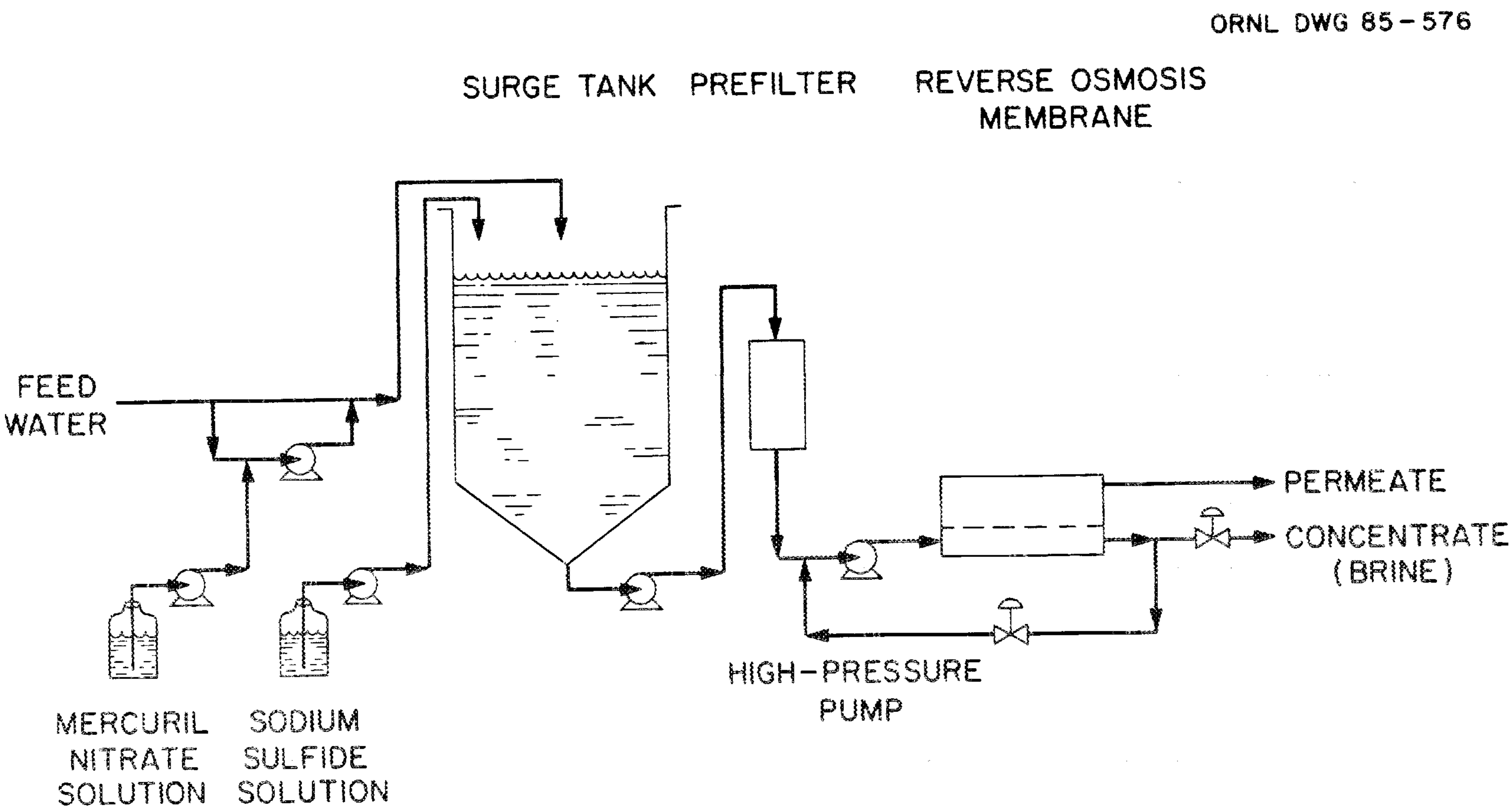

Fig. 6. Flow diagram of reverse osmosis system.

Table 5. Summary of the average operational parameters for the Osmonics and FilmTec membranes during the test period

Parameter	Osmonic membrane value (σ)[a]	FilmTec membrane value (σ)[a]
Feed temperature, °C	26.60 (0.78)	25.70 (1.25)°C
Feed pH	6.44 (0.92)	6.19 (0.12)
Circulation flow rate (LPM)	7.57	17.00 (1.40)
Membrane feed (MPa) pressure, (psig)	3.010 (0.175) 421.79 (10.73)	1.671 (0.148) 277.75 (6.80)
Membrane (MPa) ΔP[b] (psig)	0.042 (0.010) 6.08 (1.41)	0.159 (0.032) 23 (4.66)

[a] σ = standard deviation.
[b] ΔP = feed pressure − concentrate pressure.

Table 6. Operational chronology with Osmonics membrane

Date	Time (0–2400 h)	Event
8/1/84	~1700	Unit startup on tap water spiked with NaCl for initial membrane baseline check at ~50% recovery.
8/2/84	~1500	Membrane baseline completed and unit shut down.
8/6/84	~1500	Unit startup on 3544 effluent which had been pretreated by GAC at ~50% recovery.
8/7/84	~1500	Recovery increased to ~75%.
8/9/84	~1500	Started mercuric nitrate addition to RO feed and decreased recovery to ~65%.
8/10/84	~1300	Unit shut down to repair feed pump.
8/10/84	~1800	Unit startup on 3544 effluent pretreated by GAC and spiked with mercuric nitrate at ~80% recovery.
8/11/84	~1400	Recovery increased to ~95%.
8/14/84	~1600	Unit shut down.
8/16/84	~1700	Unit startup on 3544 effluent which had been pretreated by GAC followed by mecuric nitrate and sodium sulfide addition at 95% recovery.
8/20/84	~1100	Unit shut down.
8/20/84	~1300	Unit startup on first-pass permeate at ~95% recovery.
8/22/84	~0900	Unit shut down.
8/22/84	~1000	Unit startup on raw 3544 effluent spiked with mercuric nitrate and sodium sulfide at ~85% recovery.
8/23/84	~1000	Recovery increased to ~95%.
8/24/84	~0900	Unit shut down.
8/27/84	~1100	Unit startup on the water spiked with NaCl to compare with results on initial membrane baseline check.
8/28/84	~1530	Added sodium nitrate to tap water, NaCl solution.
8/29/84	~1600	Unit shut down.

Table 7. Operational chronology with FilmTec membrane

Date	Time (0–2400 h)	Event
9/11/84	~1300	Unit startup on tap water spiked with NaCl for initial baseline check at ~50% recovery.
9/14/84		Results from baseline check indicate membrane is defective. Ordered new membrane.
9/17/84	~1500	Unit startup for NaCl baseline check of new membrane at ~50% recovery.
9/18/84	~0830	Discovered a controller had malfunctioned during the night causing the valve on the concentrate stream to close and the membrane to be fouled by mineral precipitation. Shut down unit.
9/18/84	~1500	Unit startup on phosphoric acid solution to clean mineral deposits from membrane.
9/18/84	~1530	Unit shut down.
9/19/84	~1400	Unit startup on NaCl solution for baseline check at ~50% recovery.
9/20/84	~1100	Added $NaNO_3$ to NaCl solution.
9/20/84	~1400	Unit shut down.
9/21/84	~1300	Unit startup on raw 3544 effluent spiked with mercury at ~60% recovery.
9/22/84	~1000	Recovery increased to ~80%.
9/23/84	~1100	Recovery increased to ~95%.
9/25/84	~1100	Na_2S was added to the RO feed stream.
9/26/84	~1600	Unit shut down.

A summary of the RO test results is presented in Table 8. As shown, the RO data can be divided into six operational groups. In groups a through d, the RO unit was operated with the Osmonics membrane; in groups e and f, the RO unit was operated with the FilmTec membrane.

In group a, the Osmonics membrane was operated using the 3544 effluent as feed. The feed was pretreated with GAC and spiked with mercuric nitrate. The percent recovery [(permeate flow rate/feed flow rate) $\times$ 100] was raised from ~64% to ~95% and the rejection [100- (permeate concentration/feed concentration) $\times$ 100] of TDS, nitrate, mercury, and sulfate followed. As shown in Table 8, as the recovery was raised from ~64% to ~95% the average rejection of nitrate fell from 66% to 22.5%, the average rejection of TDS fell from 74% to 45.5%, and the average rejection of sulfate fell from 92% to 85%. Mercury was not rejected at any recovery. This information is presented graphically in Fig. 7.

In an attempt to improve mercury rejection, sodium sulfide was added to the wastewater to obtain a concentration of 0.075 mg/L (0.2 g Na_2S/700 gal). It was postulated that sulfide would precipitate the mercury, in colloidal form, as HgS. The membrane would then reject the mercury. The results can be seen in group b of Table 8. After sulfide addition the membrane rejected an average of 97.4% of the mercury reaching it. Note that the 5-μm filters removed ~84% of the mercury before it reached the membrane, indicating HgS had precipitated. The membrane rejection above is based on the amount of mercury actually reaching the membrane and does not include the 84% removed by the filters. Also, material balances indicate much of the mercury was not actually rejected, but deposited, on the membrane.

The permeate from group b was collected and retreated by RO to observe how the membrane would handle materials at lower concentrations and to determine the mercury concentration after two passes through the RO membrane. The results can be seen in group c of Table 8. The average rejections were 29% TDS, 30% nitrate, 74.4% mercury, and >92%

Table 8. Summary of reverse osmosis test results[a]

Group	Av recovery (%)	Av inlet TDS conc. (mg/L)	Av TDS rejection (%)	Av inlet NO_3-N conc. (mg/L)	Av NO_3-N rejection (%)	Av inlet Hg conc. (ng/mL)	Av Hg rejection (%)	Av inlet SO_4 conc. (mg/L)	Av SO_4 rejection (%)
a	63.5	645	74.0	76.8	66	10	0	54.3	92
	79.1	517	64.5	71.6	54.5	31.5	0	55.9	87
	94.9	705	45.5	65.8	22.5	16	0	46.7	85
b	95.0	576	38.7	59.9	24.8	5.4	97.4	40.0	88.3
c	93.7	377	29.0	45.2	30.0	0.42	74.4	50	>92
d	84.8	638	55.5	70.0	50.0	11	98.2	48.5	>91.8
	93.5	642	44.0	64.3	16.0	9.9	97.6	51.8	98.1
e	59.0	264[b]	95.4[b]	41.5	95.5	15.5	54.9	21.0	100
	78.9	264[b]	89.4[b]	34.5	93.0	14.5	38.0	29.8	100
	93.3	314[b]	96.5[b]	31.6	69.9	9.0	33.0	79.8	>98.5
f	93.1	376	82.5	24.8	66.8	203[b] 52[b]	60.1[b] 48.1[b]	120	96.7

[a]Experimental conditions:

Group a: 3544 effluent spiked with mercury then treated with GAC then RO (Osmonics membrane).
Group b: 3544 effluent spiked with mercury and sodium sulfide, treated with CA and then RO (Osmonics membrane).
Group c: First-pass permeate from Group b treated with RO (Osmonics membrane).
Group d: Raw 3544 effluent spiked with mercury and sulfide, treated with RO (Osmonics membrane).
Group e: Raw 3544 effluent spiked with mercury, treated with RO (FilmTec membrane).
Group f: Raw 3544 effluent spiked with mercury and sulfide, treated with RO (FilmTec membrane).

[b]Actual concentrations and rejections (not average).

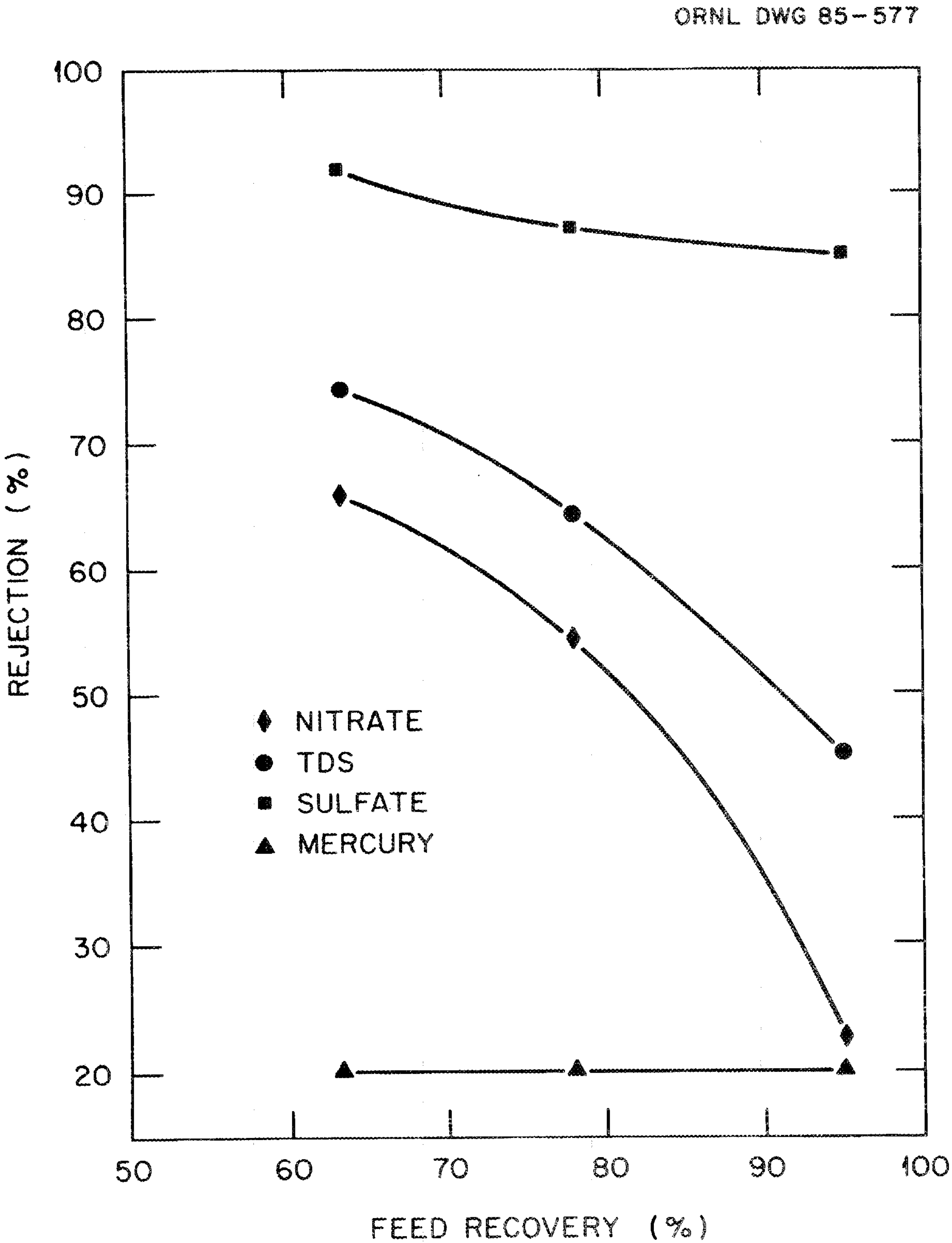

Fig. 7. Rejection measured with Osmonics membrane while processing 3544 effluent pretreated with GAC (group a).

sulfate. After the second pass through the RO membrane, the average mercury concentration in the permeate was ~0.0001 mg/L.

Group d in Table 8 summarizes the data for operation with the Osmonics membrane on raw 3544 effluent spiked with mercury and sulfide. Comparing these data with group b data at ~94% recovery it can be seen, at least in the short term, that RO is not enhanced by pretreatment with GAC.

Groups e and f in Table 8 summarize the data for operation with the FilmTec membrane. These data are presented graphically in Fig. 8. As shown in Fig. 8, as the recovery was increased from ~60% to ~94%, the average TDS rejection decreased from 95.4% to 82.5%, the average nitrate rejection decreased from 95.5% to 68.4%, the average mercury rejection decreased from 54.9% to 33.0%, and the sulfate rejection held essentially constant at >98.5%. Note that in several cases TDS analyses indicated no TDS in the permeate stream. When this occurred the rejection of the TDS was based on a material balance between the feed and concentrate streams, thus minimizing the error inherent in low-level TDS analyses. Also, the TDS rejection for group e at ~94% recovery was not included on Fig. 8 because only one data point was measured, and the data points at the same recovery in group f indicate a rejection of ~82%.

By comparing Figs. 7 and 8, it can be seen that in all cases the FilmTec membrane performed better than the Osmonics membrane. Also Fig. 8 indicates there is a sharp decline in the rejection of nitrate above a feed recovery of 72 to 80% with the FilmTec membrane. Communications with the FilmTec representative indicated this decline was normal and suggested operation of the membrane at a recovery with a high rejection of nitrate and treatment of the concentrate stream with a seawater membrane (requiring about twice the operating pressure). A flowsheet showing this mode of operation along with the expected nitrate rejections is presented in Fig. 9.

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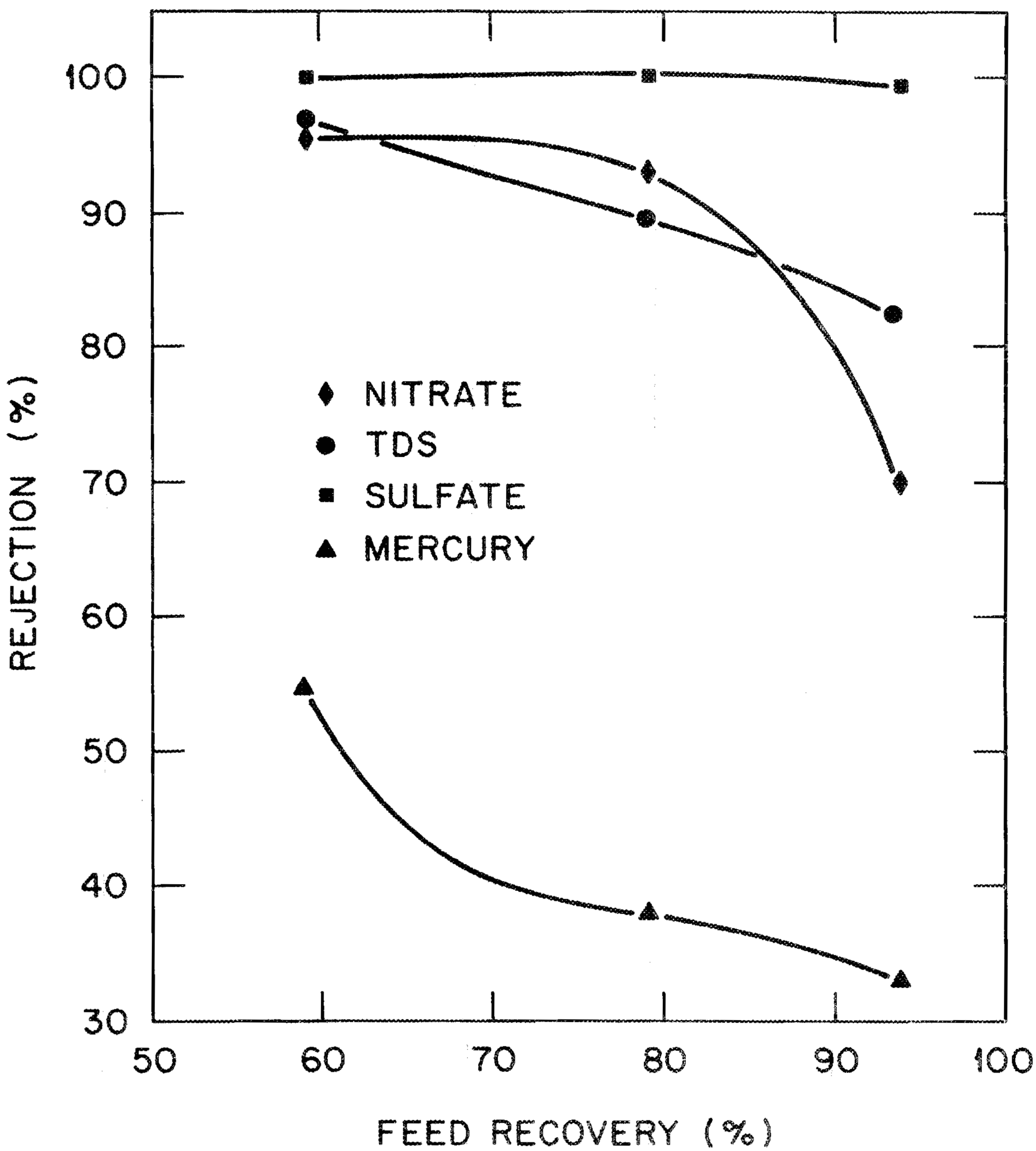

Fig. 8. Rejection measured with the FilmTec BW-30 membrane while processing raw 3544 effluent (groups e and f), group f mercury data not included.

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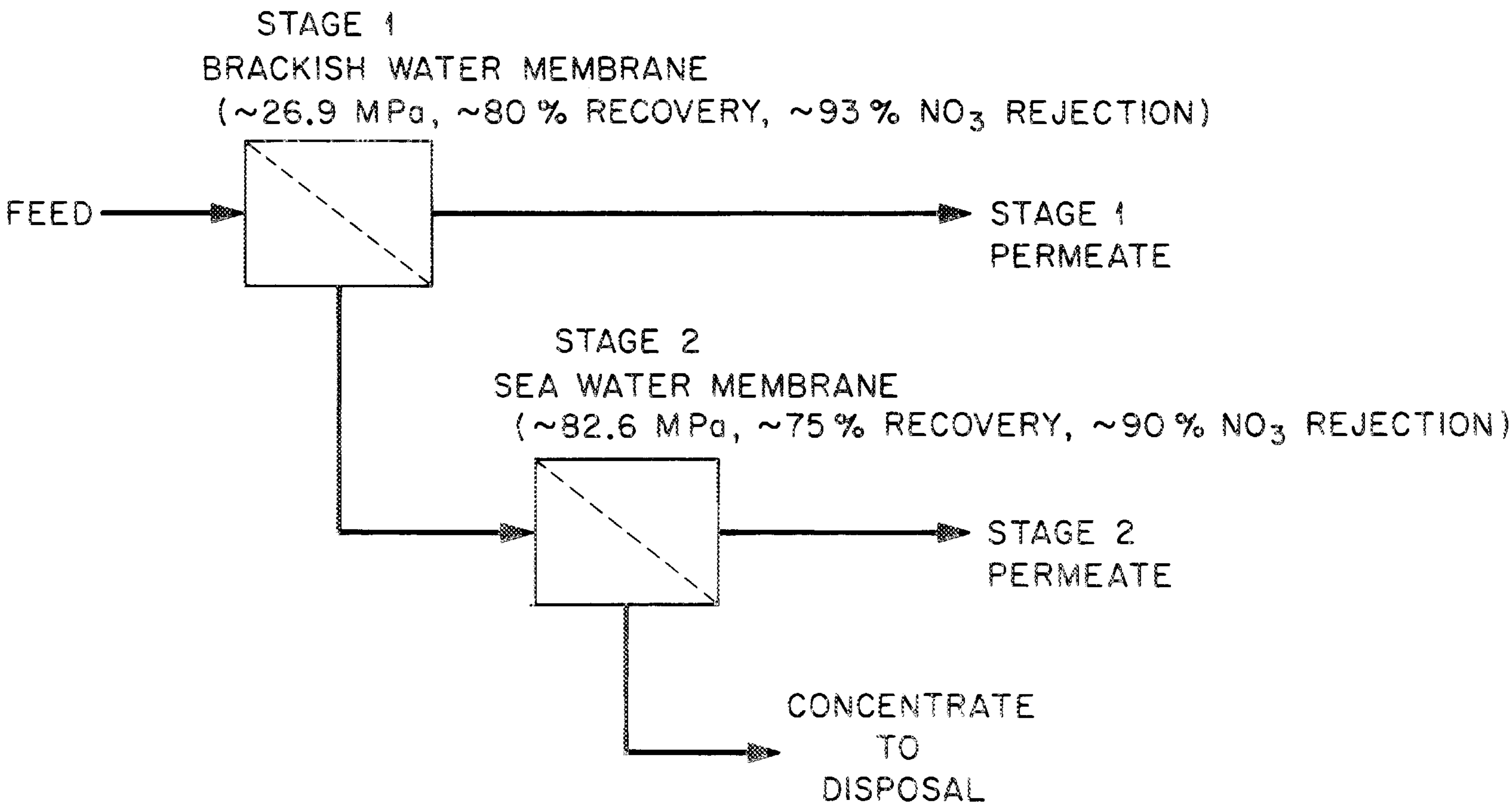

Fig. 9. Flowsheet for high nitrate rejection at high recovery.

In comparing the mercury rejection of the Osmonics and FilmTec membranes, the Osmonics membrane rejected no mercury before sulfide addition and the FilmTec membrane rejected between 33 and 54%. After sulfide addition the Osmonics membrane rejected ~97% of the mercury at ~95% recovery, and the FilmTec membrane rejected between ~48 and 60% (an increase of ~46 to 82%). Note that after the sulfide was added in the FilmTec operation, very little mercury was removed by the prefilters. This observation indicates the probable absence of the HgS precipitate which was postulated earlier when operating with the Osmonics membrane.

A summary of mass balance closures for the various operational groups is presented in Table 9. A negative value indicates the material was held by the membrane. As can be seen, most of the material balances closed within ~12%, with the exception of TDS and mercury. Before operational group c, the balance used to perform TDS assays was located in an area where building vibration made accurate measurement difficult. After moving the balance to a location where it was unaffected by vibration, the material balances (groups c, d, e, and f) generally closed within ~15%. The small amount of TDS present in the permeate stream made accurate TDS determination difficult with the sample volume being used. In future analyses, the volume of liquid used in the TDS analyses should be greater than the current value of 100 mL.

By observing the mercury mass balance closure, it can be seen that the addition of sulfide to the wastewater (groups b, c, d, and f) caused most of the mercury to be deposited on the membrane. Again, this phenomenon is postulated to be due to the formation of a colloidal HgS precipitate.

Data on the flow rates of the feed, permeate, and concentrate streams vs operating time are presented in Figs. 10 and 11 for the Osmonics and FilmTec membrane, respectively. From Fig. 10 it can be seen that the flow rate of the permeate remains essentially constant for the Osmonic membrane, indicating no fouling during the operation period. The slight increase in the permeate flow from ~280 to 310 h can probably be

Table 9. Summary of the material balance closures for RO operation

Group	Recovery (%)	Mass balance closure (%)			
		TDS	NO_3	SO_4	Hg
a	62.9	-19	6.9	7.7	*a*
	64.1	-12.3	5.6	1.6	4.8
	79.1	-1.7	-2.9	8.4	12.3
	79.1	-9.9	-1.0	18.6	-27.1
	94.9	-50.6	1.6	5.0	*a*
	94.9	-46.4	-11.9	6.2	-48.1
b	93.8	12.5	*a*	7.7	
	95	23.3	-14.5	-10.9	-92.3
	95	-35.2	11.4	-9.5	-91.8
	95	-45.2	3.8	-14.4	-95.3
c	93.7	-13.6	-8.6	*a*	-49
	93.7	-1.3	*a*	*a*	-69.7
d	85	-14.2	-8.5	*a*	-83.7
	84.5	-15.4	-13.6	*a*	-79.9
	93.6	-27.8	25.3		-91.9
	92.9	6.9	*a*		-88.2
e	57.0	-8.5	-1.5	16.0	1.8
	60.9	13.7	-4.1	*a*	-12.0
	80	>1	-1.1		-7.5
	77.8	-21.2	3.8	*a*	-31.2
	93.3	-3.5	6.5	-14.9	
f	93.4	11.6	-3.2	10.0	-83.5
		-6.5	*a*	-12.1	-65.7

[a] No data available.

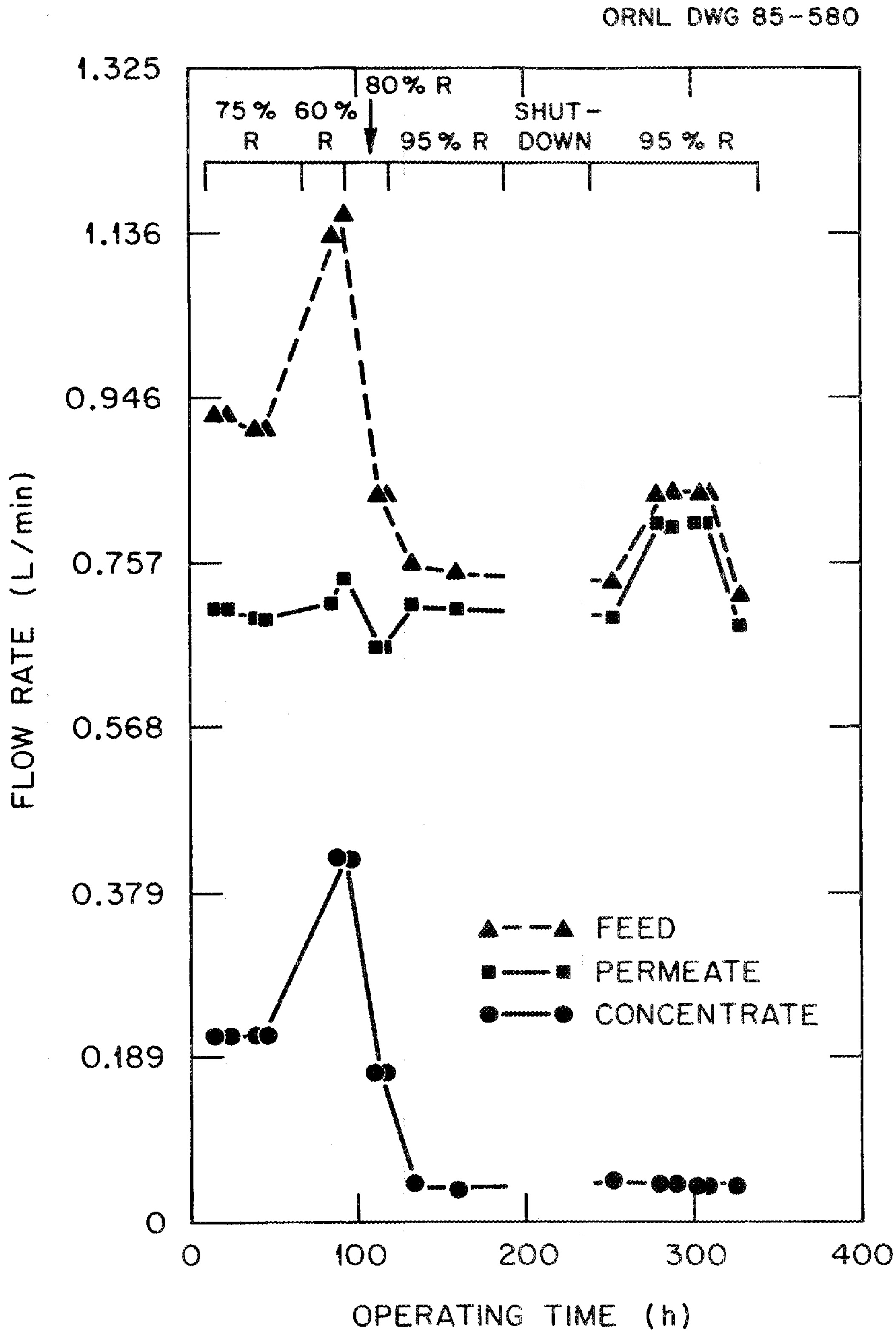

Fig. 10. Feed, permeate, and concentrate flow rates vs time with the Osmonics membrane while operating on 3544 effluent pretreated with granular activated carbon.

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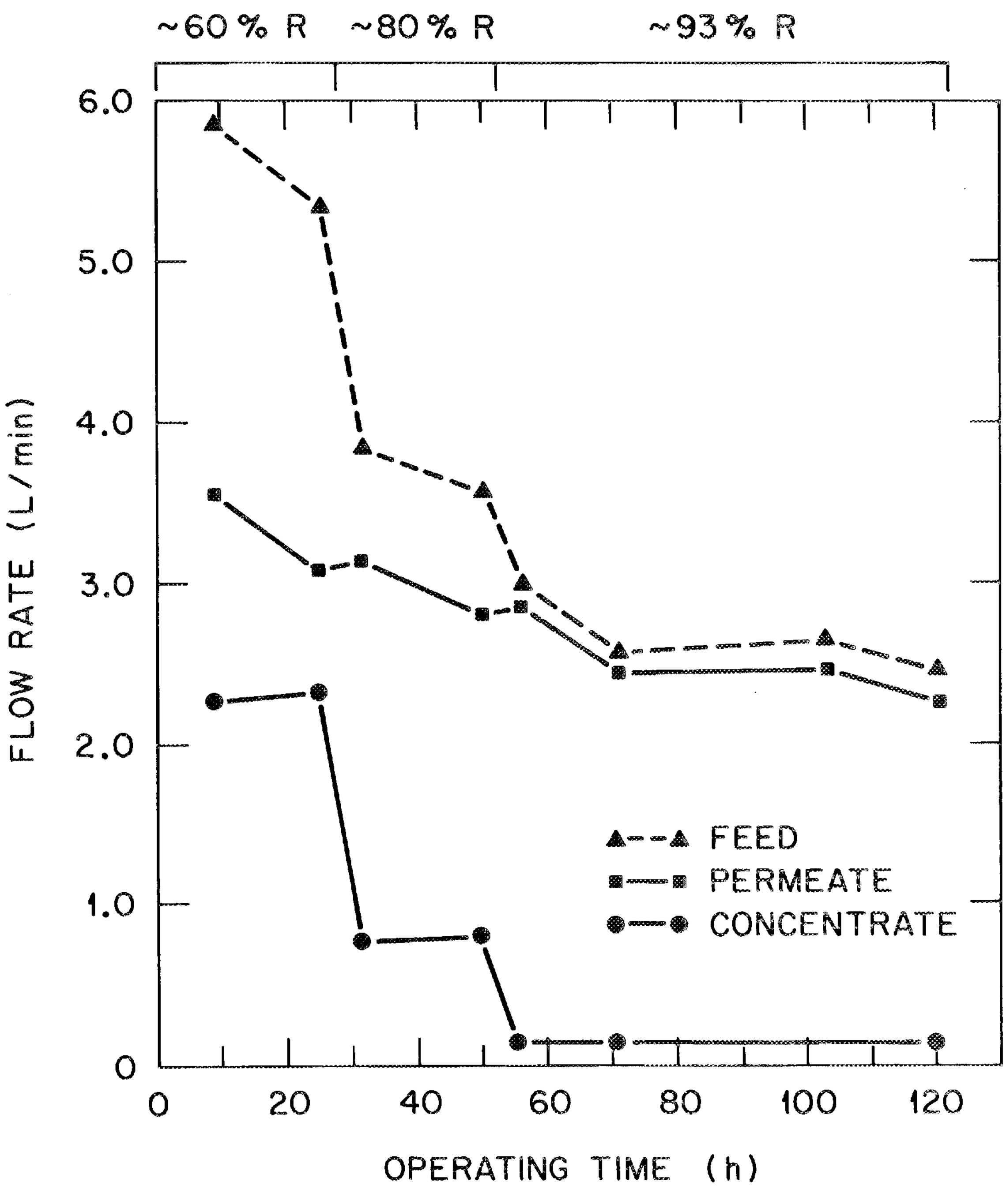

Fig. 11. Feed, permeate, and concentrate flow rates vs time with the FilmTec BW-30 membrane while processing raw 3544 effluent.

attributed to a slight increase in the membrane pressure from 2.896 mPa (420 psi) to 2.965 mPa (430 psi). As shown in Fig. 11, the FilmTec permeate flow rate decreased with operating time. This decrease is as expected because of the increase in recovery from 60% to 93%.

Conductivity rejection by the FilmTec membrane while processing raw 3544 effluent at 95% recovery vs operating time is shown in Fig. 12. As can be seen, no deterioration in performance was measured, rather a slight increase in rejection from ~80% to 86% occurred over the ~70 h of operation at ~95% recovery.

The results of the radioactivity analyses on the 3544 effluent processed by RO are given in Table 10. As can be seen, in all cases the RO membranes concentrated the radioactive species. Enough data are not available, however, to adequately evaluate the membrane performance for the removal of the radioactive species.

5. SUMMARY

Two process streams to be treated in the proposed NRWTF were characterized by grab samples in which several key parameters were monitored daily. This characterization indicated that several parameters may violate the possible discharge limits.

GAC was used to treat these two streams for the removal of organics, mercury, and as a possible pretreatment for RO. The first stream treated by GAC, the 3544 effluent, had average feed concentrations of 0.0195 mg/L Hg and 4.6 mg/L TOC. It was found that the GAC system had a mean Hg removal of 98.8%, with 96.6% being removed in the first column. The mean removal for TOC was 69.6%, with 48.5% removed in the first column. The GAC removed no nitrate or sulfate.

The GAC system, when fed with the 190 wastewater, had a mean mercury inlet concentration of 0.0357 mg/L Hg and a mean TOC concentration of 5.3 mg/L. The GAC system had a mean removal of 97.1% Hg, with 94.4%

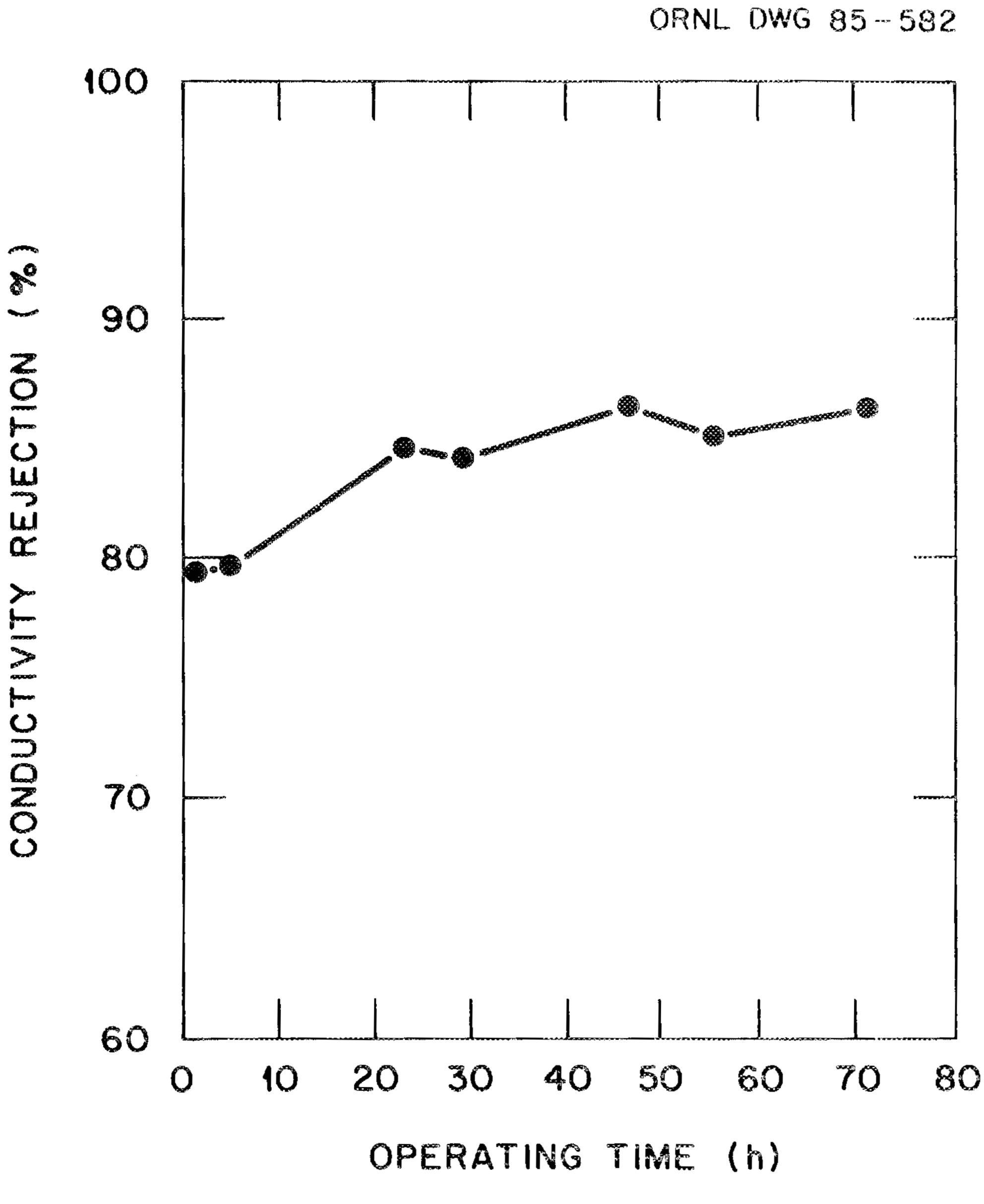

Fig. 12. Conductivity rejection with the FilmTec BW-30 membrane while processing raw 3544 effluent at ~95% recovery vs operating time.

Table 10. Results of radioactivity analyses on 3544 effluent stream processed by reverse osmosis[a]

Membrane	Sample	G-α	^{90}Sr	^{137}Cs	G-β	^{134}Cs	^{60}Co
Osmonics	RO Feed	3.4 ± 9.8	0.31 ± 0.19	49 ± 4	50 ± 24	--	--
	Permeate	3.4 ± 9.8	0.20 ± 0.16	27 ± 2	35 ± 23	--	--
	Concentrate	23 ± 17	0.47 ± 0.22	350 ± 20	320 ± 50	4.6 ± 0.8	--
FilmTec	RO Feed	2.7 ± 1.8	2.0 ± 2.0	25 ± 3	43 ± 5	25 ± 3	23 ± 3
	Permeate	<0.7	0.55 ± 0.80	4.7 ± 1.4	7.6 ± 2.7	4.7 ± 1.4	1.4 ± 1.2
	Concentrate	50 ± 9	5.5 ± 5.5	340 ± 20	510 ± 20	340 ± 20	260 ± 20

[a]All concentrations in Bq/L.

removed by the first column. The mean removal of TOC was ~43%, with essentially all of this being removed by the first column. Again the GAC had no effect on the nitrate and sulfate.

Results indicate that the adsorption wave front had not broken through in any of the runs for either TOC or mercury, and the minimum mercury adsorptive capacity was 0.16 mg Hg/g carbon. Radioactive species accumulation on the GAC was measured.

The removal of TDS, nitrate, sulfate, and mercury from the 3544 effluent was examined by RO with a cellulose acetate membrane (Osmonics) and a thin-film composite membrane (FilmTec). In operating the Osmonics membrane, as the feed recovery was increased from ~64% to ~95%, the average rejection of nitrate decreased from 66% to 22.5%, the TDS rejection from 74% to 45%, and the sulfate from 92% to 85%. Mercury was not rejected at any recovery. With the FilmTec membrane, as the recovery was increased from 60% to 94%, the nitrate rejection decreased from 95.5% to 68.4%, the TDS rejection from 95.4% to 82.5%, the mercury from 54.9% to 33%, and the sulfate held constant at >98.5%. In all cases, the FilmTec membrane performed better than the Osmonics membrane. It was also found that the addition of sulfide improved the rejection of mercury in both membranes. This phenomenon was postulated to be due to the formation of a colloidal HgS precipitate. Both membranes concentrated radioactive species.

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