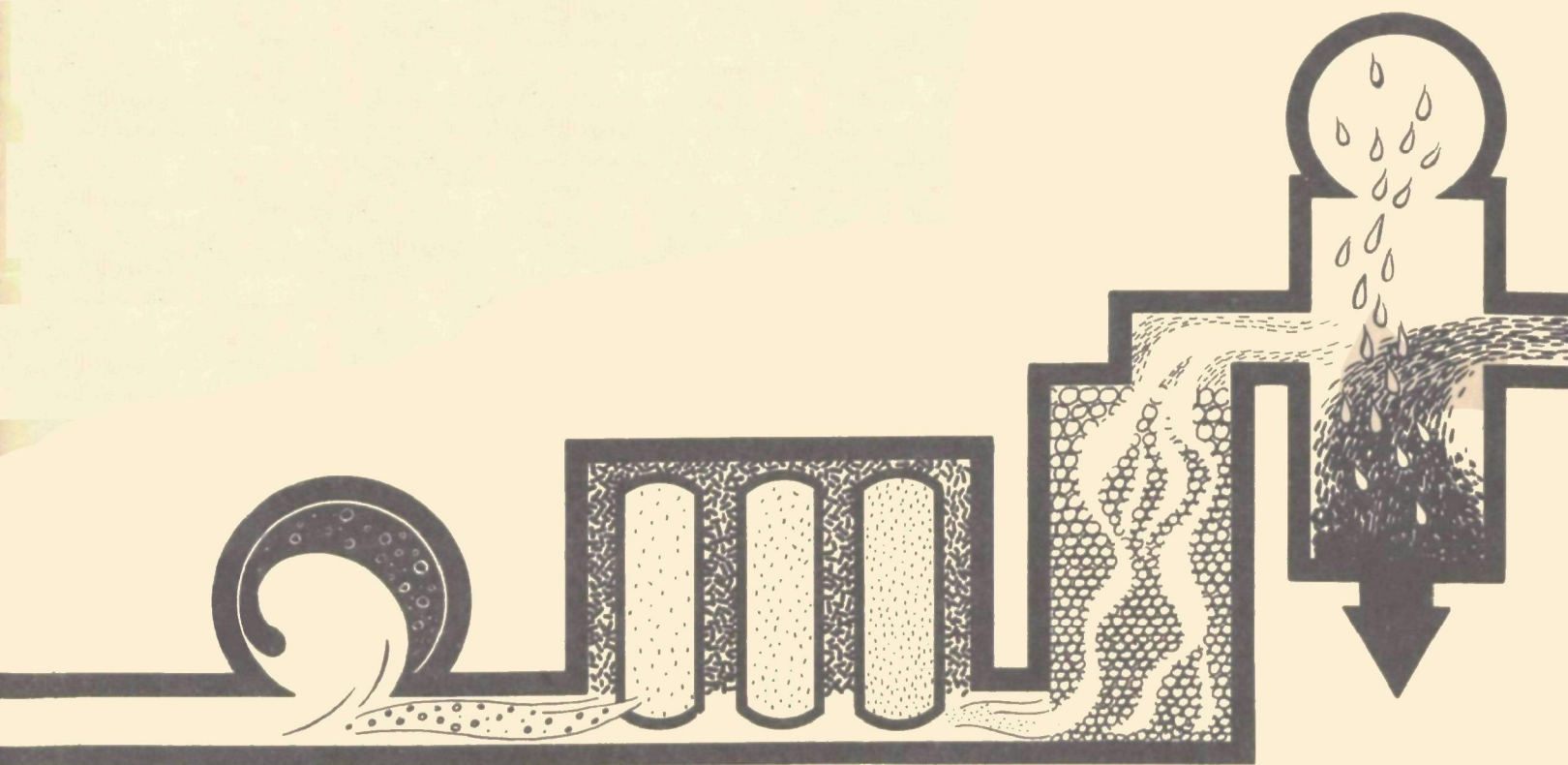CLEAN WATER

STUDY AND EXPERIMENTS
IN WASTE WATER RECLAMATION
BY REVERSE OSMOSIS

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STUDY AND EXPERIMENTS IN
WASTE WATER RECLAMATION BY REVERSE OSMOSIS

by

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for the

FEDERAL WATER QUALITY ADMINISTRATION

DEPARTMENT OF THE INTERIOR

Contract
May, 1970

FWQA Review Notice

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ABSTRACT

The basic objective of this program was to apply current reverse osmosis technology to the treatment and demineralization of secondary effluents. The development of commercial modules and systems has made it possible to determine operational problems that might be encountered with secondary and activated-carbon-processed secondary effluents and to seek solutions for these problems. Two parallel reverse osmosis systems were operated with 50 sq ft spiral-wound reverse osmosis modules. A comparison was made of results obtained with activated sludge effluent versus activated-carbon-treated activated sludge effluent, standard flux membrane modules versus high-flux membrane modules, and large (45-mil) brine spacer modules versus small (22-mil) brine spacer modules.

Severe fouling problems were encountered almost immediately upon starting operation with both feeds. Previously developed cleaning procedures proved generally ineffective. A technique utilizing an enzyme-based detergent was developed, which restored performance. Rejection of organic carbon, nutrient, and salt with high-flux membranes was very good, and the product water quality was not greatly different than that of the product water produced with standard-flux, high-selectivity membranes. At the same time, the quantity of product water produced over an extended period such as three years can be expected to be substantially more.

Except for a greater pressure drop across modules made with small brine spacers, there was no appreciable difference in performance between modules made with large or small brine spacers.

CONTENTS

INTRODUCTION

This is the final report by Gulf General Atomic Incorporated on
Federal Water Pollution Control Administration (FWPCA), U. S. Department
of the Interior, Contract 14-12-181, "Waste Water Reclamation by Reverse
Osmosis", covering the one-year period from July 1, 1968, through
June 30, 1969.

Reverse osmosis appears to have great potential for removing water
of potable or near-potable quality from secondary waste-water effluents
and industrial wastes. Pollution control, by itself, will generally not
require water of the quality that can be produced by this method, but the
fact that the product water may be suitable for direct reuse, or reuse
with minor additional treatment, could be important in making this process
economically feasible. The high membrane packing densities available in
the spiral-wound module concept and the economies attainable with factory
fabrication of modules should make this design a desirable approach.

Gulf General Atomic undertook a program to support and extend the
pilot-plant work on water renovation that had been initiated at the
Los Angeles County Sanitation Districts Pomona facility. The specific
aims of the program were (1) to evaluate the capability of the state-of-
the-art, desalination-oriented, reverse osmosis technology to treat
waste water, (2) to achieve modest extensions of the present technology,
as required, to accommodate waste-water treatment and to achieve a rapid
payoff with respect to demonstrated capability, and (3) to gather the
data necessary to allow a subsequent rapid introduction of the technology
into the fields of waste-water treatment and reclamation.

It was recognized that a complete investigation of the possibilities offered by reverse osmosis would require a broad program, including the study of completely new membrane materials and configurations, and it was not proposed to venture into these fields at this time. The effort was to be directed at adapting the best of present saline conversion technology to the waste-water field rather than to develop an entirely new technology. This approach, with the expenditure of some additional effort, offered the possibility of accelerating the usefulness of a new, advanced concept of waste-water treatment.

The studies previously conducted at Pomona have served to define some of the limitations of the direct application of the desalination module to waste-water treatment. The earlier experiments had a low level of funding support and proceeded quite slowly since progress was further complicated by mechanical difficulties of the early systems. Improvements in the modules and solution of mechanical problems made it possible for the County Sanitation Districts of Los Angeles County to conduct an extended reverse osmosis experiment on activated-carbon-treated secondary effluent. This, in turn, made it possible to consider the proposed study.

Essentially, the program consisted of the following: (1) design, construction, and installation of additional field-test facilities at Pomona, (2) a comprehensive series of short-term (500 to 700 hr) experiments in the new test facilities, and (3) direct and laboratory support of the short-term field experiments and of the longer-term testing that the County Sanitation Districts would be conducting in the 5000-gpd reverse osmosis pilot plant at Pomona. The program was directed toward an assessment of the state of the art of reverse osmosis technology and of operational problems that might be encountered. A computer program available at Gulf General Atomic could be used to assist in the analysis and interpretation of test results. Laboratory and test facilities were available at Gulf General Atomic for detailed evaluations

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of module and membrane parameters and for experiments in support of the field evaluation. Any new components or techniques developed from the laboratory support program were to be considered for incorporation under field conditions in the proposed new field-test program.

It was not expected that this program, because of the relatively short runs and because a number of variations in modules and operating conditions were included, would do more than set up the parameters for an extended program to provide reliable data upon which to base design, construction, and operation of full-scale reverse osmosis water renovation systems. The economics of large plants can be proven only by large-scale tests. Although much information along these lines could be gained from the operation of brackish water plants, the special problems associated with processing waste water require that a waste-water program should ultimately include the design and construction of full-scale plant modules, in the range of 0.1 to 0.5 mgd, of a plant having a capacity of 1 to 10 mgd.

EXPERIMENTAL FIELD OPERATION

The site selected for this study of the application of reverse osmosis to waste water reclamation or tertiary treatment was the Pomona, California, Water Reclamation Plant of the County Sanitation Districts of Los Angeles County. This plant has become the location for several important studies in advanced waste treatment by the Sanitation Districts and the Federal Water Pollution Control Administration. The facility at Pomona has long played a significant role in water reclamation studies.

The plant itself is basically a conventional activated-sludge plant into which has been built some flexibility that permits introduction of variations in operation that may make the effluent more suitable for subsequent processing. It is located adjacent to the major trunk sewer that conducts the wastes of the surrounding community to the central Los Angeles County system.

Raw sewage is pumped from the trunk sewer and treated at the activated sludge water reclamation plant, the effluent from which is used in a number of pilot plant studies. This permits the treatment facilities to operate under virtually constant hydraulic loading and with minimum variations in organic and nutrient loadings compared with conventional systems. This in turn enables the Pomona plant to operate under relatively constant and probably optimum loading. Primary and waste secondary sludge are returned to the trunk sewer and, in case of deterioration in treatment for any reason, operation can easily be controlled to assure a rapid return to satisfactory conditions. The feeds for the reverse osmosis units consisted of secondary clarifier effluent from the activated-sludge facility and the same effluent after it had been processed through a granular-activated-carbon adsorption system. Typical characteristics of the feeds are shown in Tables 1, 2, and 3.

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TABLE 1

MINERAL ANALYSIS OF REVERSE OSMOSIS STREAMS FROM ACTIVATED-CARBON-TREATED SECONDARY EFFLUENT FEED

	Feed[*]	Brine	Product
Mineral Content, mg/1			
Calcium (Ca)	68	196	0.8
Magnesium (Mg)	12	34	1.5
Sodium (Na)	128	328	14
Potassium (K)	11	35	1.3
Carbonate (CO_3)	0	0	0
Bicarbonate (HCO_3)	41	67	22
Sulfate (SO_4)	85	245	0
Chloride (Cl)	260	720	15
Nitrate (NO_3)	1.7	4.2	0.8
Orthophosphate (PO_4)	22	56	0.56
Total phosphate (PO_4)	27	76	0.6
Fluoride (F)	0.4	5.7	0.3
Boron (B)	0.5	0.7	0.4
Silica (SiO_2)	33	85	3.0
Iron (Fe)	0.02	0.07	0
Manganese (Mn)	0	0	0
Hardness ($CaCO_3$)	220	630	8
Total alkalinity ($CaCO_3$)	34	35	18
Total dissolved solids			
At 105°C	756	2152	24
At 180°C	672	1756	16
Electrical conductivity, micromhos/cm at 25°C	1140	2860	104
pH	5.8	6.2	5.7
Turbidity, Jackson units	0.55	0.83	0.27

[*]Acidified feed.

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TABLE 2

SUMMARY OF CHEMICAL ANALYSES OF FEED (F), PRODUCT (P), AND BRINE (B) AT POMONA

(Unit I, Phase III; operated on activated-carbon-treated secondary effluent)

Date	Total COD (mg/l)			Dissolved COD (mg/l)			NO_3-N (mg/l)			NH_3-N (mg/l)			PO_4 (mg/l)			TDS (mg/l)		
	F	P	B	F	P[a]	B	F	P	B	F	P	B	F	P	B	F	P	B
1/21/69	10.1	0.0	20.8	8.7	---	16.3	5.2	0.6	6.6	10.6	2.3	18.5	18.5	0.2	36.5	578	63	1047
1/23/69	9.8	1.0	26.3	9.4	---	25.7	2.1	1.0	4.6	13.7	2.9	33.6	29.0	0.12	85.0	635	39	979
1/28/69	13.0	0.8	28.0	11.0	---	26.4	9.4	4.2	17.0	2.2	0.5	5.4	29.0	0.12	63.0	674	96	1605
1/30/69	11.7	0.0	27.9	9.5	---	24.6	13.3	4.5	25.5	1.2	0.4	6.0	26.5	0.23	69.0	594	18	888
2/4/69	---	---	---	---	---	---	0.8	---	1.1	---	---	---	35.5	2.0	53.0	620	79	956
2/6/69	16.7	0.0	26.0	12.9	---	22.0	2.5	0.3	0.6	19.2	2.8	24.0	27.0	0.33	49.0	492	40	562
2/11/69	15.4	1.0	23.9	13.8	---	23.3	1.8	1.2	1.9	20.2	3.0	28.4	34.0	0.4	54.0	616	104	976
2/13/69	---	---	---	---	---	---	0.7	0.2	0.3	17.8	1.2	29.6	27.0	0.1	43.5	675	52	1051
2/20/69	14.4	1.0	21.2	13.2	---	18.6	19.3	6.5	26.2	1.8	0.1	2.4	24.0	0.12	48.0	599	44	1003
2/25/69	---	---	---	---	---	---	21.8	7.1	34.8	---	---	---	---	---	---	502	28	680
2/27/69	5.5	0.0	18.5	6.0	---	12.0	---	---	---	---	---	---	---	---	---	722	106	1500

NOTE: Samples were taken and analyzed by LACSD personnel at their Pomona facility.

[a] Product water COD samples run for total COD only.

TABLE 3

SUMMARY OF CHEMICAL ANALYSES OF FEED (F), PRODUCT (P), AND BRINE (B) AT POMONA

(Unit II, Phase III; operated on secondary effluent)

Date	Total COD (mg/l)			Dissolved COD (mg/l)			NO_3-N (mg/l)			NH_3-N (mg/l)			PO_4 (mg/l)			TDS (mg/l)		
	F	P	B	F	P[a]	B	F	P	B	F	P	B	F	P	B	F	P	B
1/21/69	38.5	1.8	79.7	21.6	---	51.2	8.1	1.9	15.2	9.3	1.4	20.1	17.0	0.7	40.0	603	---	1333
1/23/69	37.6	0.4	84.7	25.1	---	59.4	6.7	2.0	13.0	11.0	1.4	25.9	31.0	0.18	76.0	525	69	1570
1/28/69	40.4	5.8	69.2	28.2	---	53.6	9.4	5.7	16.9	1.4	0.5	3.8	29.0	0.6	54.3	784	99	1248
1/30/69	42.0	0.4	72.3	23.0	---	45.2	16.5	5.3	23.0	1.7	0.2	3.1	27.3	0.15	48.5	321	74	668
2/4/69	---	---	---	---	---	---	---	---	---	---	---	---	36.2	1.4	49.2	549	72	974
2/6/69	39.5	1.8	52.7	25.6	---	33.4	1.2	0.5	1.4	16.4	2.0	21.1	22.0	0.03	29.5	452	38	687
2/11/69	40.5	2.0	53.1	27.1	---	32.3	3.9	1.6	4.6	18.2	2.8	24.1	36.0	0.4	48.0	646	60	864
2/13/69	---	---	---	---	---	---	2.0	1.3	2.7	17.4	13.8	21.4	26.5	0.1	35.5	703	33	910
2/25/69	---	---	---	---	---	---	18.7	10.8	17.5	0.4	0.8	1.2	24.0	0.2	35.0	530	63	659
2/27/69	53.0	0.5	61.5	30.4	---	37.9	22.3	8.1	25.8	---	---	---	---	---	---	713	160	608

NOTE: Samples were taken and analyzed by LACSD personnel at their Pomona facility.
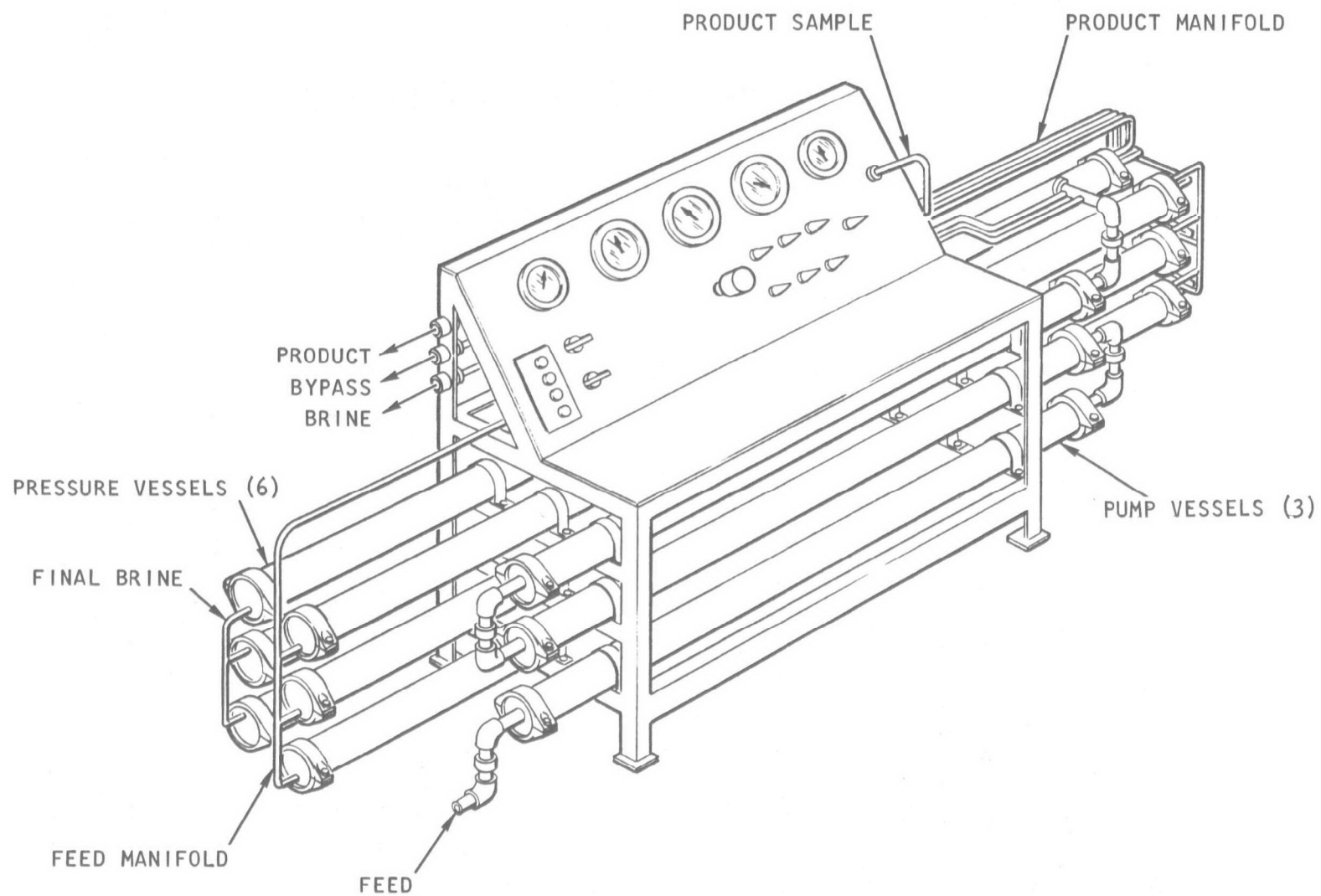
[a] Product with COD samples run for total COD only.

TEST EQUIPMENT

The reverse osmosis equipment used in the study was essentially a production model; this nominally rated 10,000 gpd unit is shown pictorially in Fig. 1 and schematically in Fig. 2. Additional instrumentation and piping were installed in order to permit gathering as much information as possible. Two 10,000 gpd units (Units I and II) were provided, each identically equipped and piped so that secondary effluent or carbon-column effluent could be supplied to either one unit or to both units at the same time. Each system was equipped with six 4-in.-diameter Schedule 40 pressure vessel (tubes); each vessel could hold up to three of the current 3-ft-long spiral-wound modules, each containing a nominal 50 sq ft of membrane area. Pressure and flow were provided by three submersible multistage centrifugal pumps connected in series. The pumps were housed within 4-in. Schedule 40 pressure vessels and mounted on the same frame as the reverse osmosis module vessels. The pumps provided a 9 gpm feed at 800 psi. Provision was made to obtain product and brine samples and flow measurements from each pressure vessel, as well as total samples for the whole unit. Pressure differentials could be measured across each tube. Gas feed chlorinators and chemical proportional feeders for feeding acid and pretreatment additives were provided. A pH controller was used on each unit to control the acid used for pH adjustment of the feed. The loops were also piped so that it was possible to flush the modules easily with an air-water mixture.

Initially (Phase I), the pressure vessels were arranged in a parallel-series combination, i.e., the feed flowed through three tubes in parallel, to two tubes, to one tube ($3\rightarrow2\rightarrow1$). This configuration was used with the high-selectivity, standard-flux membrane modules, which had an initial (1 hr) water permeation coefficient A of about 1.5×10^{-5} g/sq cm-sec-atm.* (See Appendix.)

_____

*Water permeation coefficient A of 1.0×10^{-5} g/sq cm-sec-atm = 8.64 gal./sq ft-day at 600 psi net pressure.

PRODUCT SAMPLE

PRODUCT MANIFOLD

PRODUCT

BYPASS

BRINE

PRESSURE VESSELS (6)

PUMP VESSELS (3)

FINAL BRINE

FEED MANIFOLD

FEED
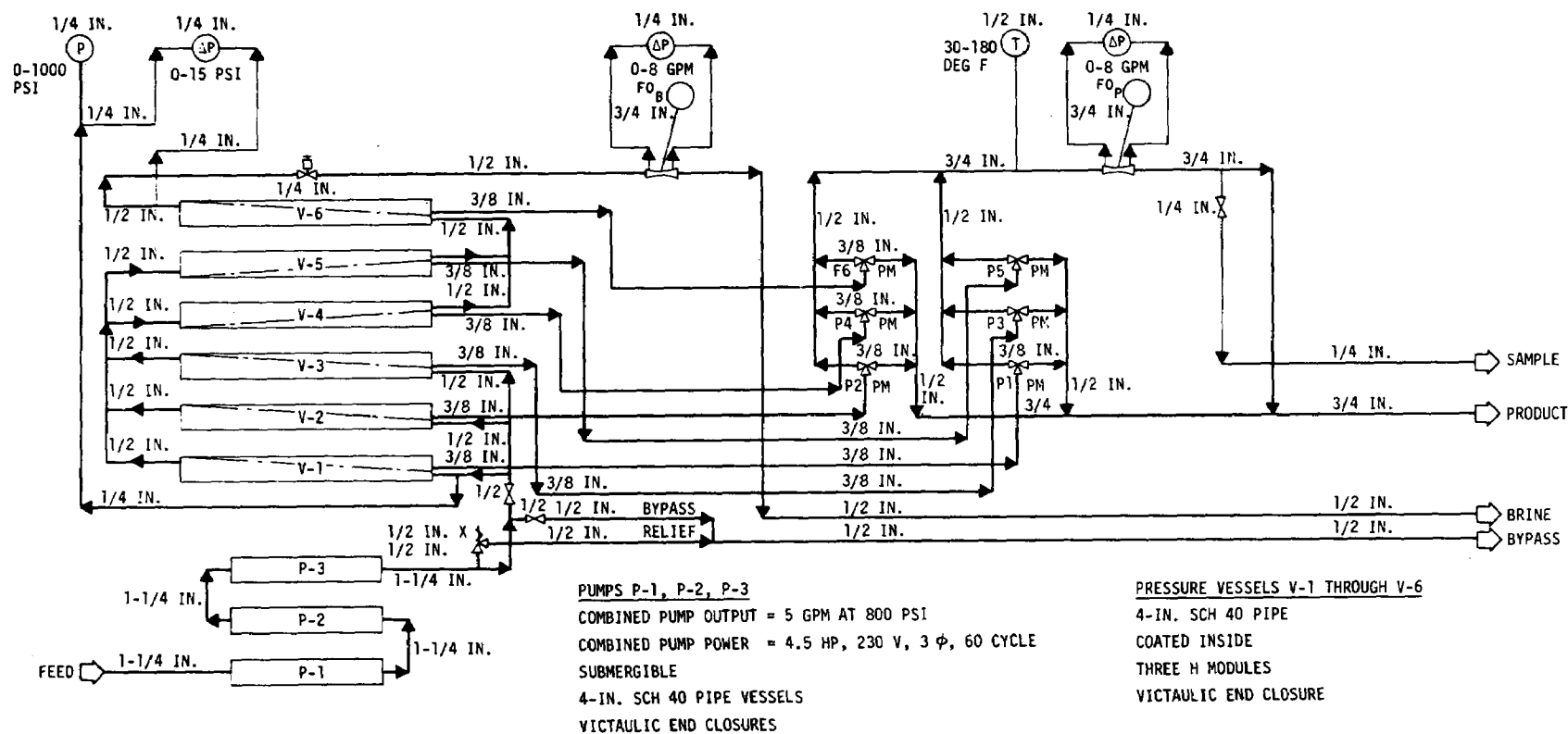
LC59771

Fig. 1. 10,000-gpd ROGA reverse osmosis system

Fig. 2. Process and instrumentation diagram

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During Phase II, the reverse osmosis units were loaded with high-flux modules [A (1 hr) = 2.25 x 10^{-5} g/sq cm-sec-atm]. Only four of the module pressure vessels were used, and the array was changed to 2→1→1 since the desired nominal flow could be produced with only twelve modules rather than the eighteen required by the 3→2→1 array. The tubes are placed in a parallel series arrangement in order to maintain the fluid flow and turbulence through the modules great enough to minimize concentration polarization at the membrane. (See Appendix, p. 109.)

Following the third field experiment, Unit I was modified so that a portion of the brine or concentrate could be recycled through the unit (see Fig. 3). Studies at the laboratory of Gulf General Atomic had shown that a brine flow of 3 to 4 gpm through the modules was required in order to minimize concentration polarization and maintain flow conditions through the modules which would produce favorable performance. With flows of less than 3 gpm through the modules, the net effect is to impair product-water quality and to increase the probability of membrane fouling and pre-cipitation of marginally soluble salts. This is further aggravated with high-flux-membrane modules, which require 4 gpm brine flow. In order to maintain 3 gpm through the 10,000 gpd units, as originally equipped at Pomona, the water recovery rate for the initial phases of the study was limited to 67% or less. This is short of the project goal of 80 to 90% water recovery. By recycling a portion of the final brine to the feed to maintain brine-channel turbulence, it was possible to attain water recoveries approaching 90%. It should be recognized that recycling of the brine increases the dissolved solids concentration of the feed, thus raising the osmotic pressure slightly and changing the dissolved solids content of the product water slightly. In other words, once recycling is introduced into a small reverse osmosis pilot plant of the type utilized here, the results do not correspond exactly with what can be expected overall from a large reverse osmosis plant; however, the experi-mental results do simulate what can be expected from the downstream one-half or one-third of a large plant. (See Appendix, pp. 83-86.) At the end of the fourth field experiment, Unit II was also modified by adding a brine recycle pump.
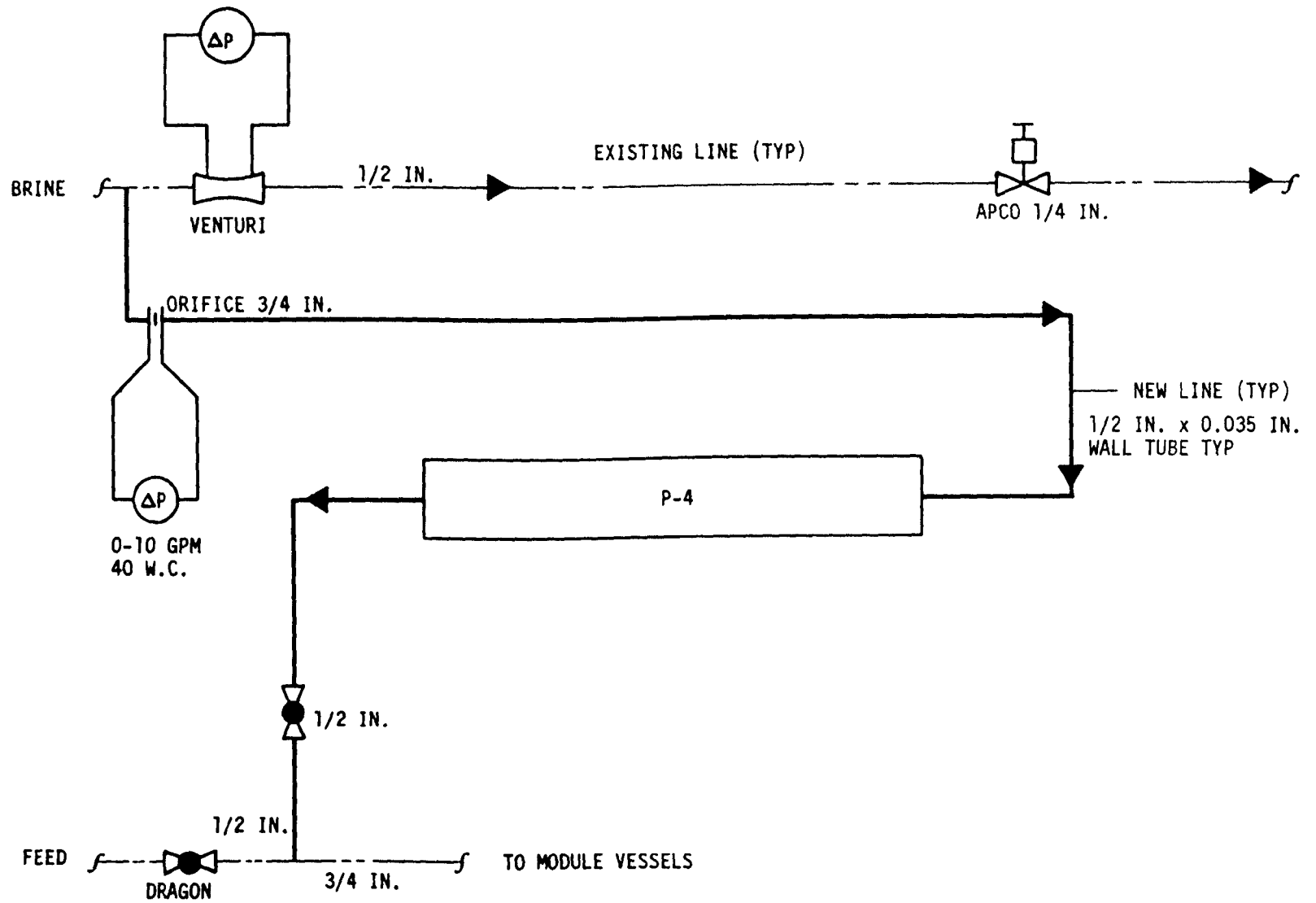
Fig. 3. Schematic diagram of brine recycle system

The operating pressure selected for the field experiment was 600 psi. This pressure is the normal operating pressure for which Gulf General Atomic reverse osmosis loops operating on brackish water have been rated. The equipment, as designed, can be operated at a pressure as high as 1400 psi, however. Based on previous operational experience, 600 psi represents the best compromise of system efficiency and membrane properties for extended life and operation of the system on water containing less than 10,000 mg/l TDS (total dissolved solids). Flux decline, due to compaction of the cellulose acetate membrane substructure at 600 psi, has been shown to be low enough so that economical water fluxes can be maintained for periods in excess of three years.

At the beginning of the fifth field experiment, the pressure vessels of Unit II were changed from a horizontal to a vertical orientation. This variation was introduced because from examination of modules after cleaning studies, there was reason to believe that some advantage both in cleaning fouled modules and in controlling fouling might be realized from placing the modules in a vertical operating position. Sediment dropped out rapidly from modules removed from the loop and placed in a vertical position in water. Postmortemed modules that had been subjected to air-water flushing in a horizontal position showed bands of dirty and clean membrane which were related to position. The dirty bands were at the bottom of the module and the clean bands at the top; separation of the air and water was occurring, which limited the cleaning effectiveness. In addition, although the anti-telescoping devices also act to center the modules, there is some evidence to show that when a seal failure occurs, it does so at the top of the seal when the module is placed horizontally.

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PRETREATMENT

The two feeds available for study at the Pomona Water Reclamation
Plant, as noted already, are the effluent from a standard municipal
activated-sludge waste-treatment plant and the same effluent after it
had been processed through the granular-activated-carbon-column pilot
plant at Pomona. The carbon columns produced an essentially well-filtered
feed for the reverse osmosis study. During earlier studies at Pomona,
markedly reduced fouling of the modules and membranes was observed when
the feed had been treated by granular activated carbon. This had originally
been attributed primarily to filtration, but data obtained during the
course of this study show a correlation between the chemical oxygen
demand (COD) of the carbon-treated feed and membrane fouling.

Two small, pressurized sand filters (Crystaleen Model C-6) with a
surface area of 3.1 sq ft, each, piped in parallel, were included for
removing gross particulate matter from the activated-sludge-plant effluent.
They were used for only a short interval since it was felt that the purpose
of the project was to investigate processing secondary effluent without
pretreatment. The use of gross screening filters requires further consideration,
however, because small particles resembling minute grease balls are to
be found in even the most well-treated secondary effluents and these particles
may cause plugging of the upstream face of the modules.

The effluent from the activated-sludge plant was delivered chlorinated
with about 2 mg/1 combined residual. Carbon-treated effluent had no chlorine
residual since it was rapidly dechlorinated by the activated carbon.
Accordingly, the carbon-column effluent was rechlorinated before introduction
into the reverse osmosis unit to give approximately 2 mg/1 combined residual.
Chlorination inhibited the growth of slimes within the modules as evidenced
by the postmortem examination of both chlorinated and unchlorinated modules.

The pH of the feed was adjusted to 5.0 ± 0.5 with hydrochloric acid. There are several reasons for adjusting the pH of the feed, the most important of which are prevention of precipitation of calcium carbonate in the modules and prolongation of membrane life. At pH 5.0, virtually all carbonate alkalinity has been removed, and the hydrolysis rate of the cellulose acetate ester from which the membrane is formed is at a minimum. The rate of hydrolysis increases exponentially above and below this range. Above pH 8 and below pH 2, the rate of hydrolysis of the cellulose acetate membrane is such that replacement of the module would probably be necessary in less than one year of operation, resulting in excessive costs (see Fig. A-10).

There is an additional requirement for pH adjustment to 6 or less when treated waste water is processed, particularly where the original water source is quite hard. The concentration of orthophosphate, PO_4, ion in secondary effluent can be expected to be of the order of 30 to 50 mg/l. $CaHPO_4 \cdot 2H_2O$ solubility is about 200 mg/l at 25°C. Even with only 67% water recovery, the concentration of calcium phosphate may exceed saturation in the boundary layer. Precipitates of calcium phosphate, $CaHPO_4$, and calcium phosphate double salts have been found in the modules when pH control has been lost. Calcium phosphate solubility increases rapidly below pH 6 when the equilibrium shifts toward monocalcium phosphate, $Ca(H_2PO_4)_2$, so that pH adjustment is an effective scale-control technique.

It was originally proposed that a threshold inhibitor (Cyanamer P-35) would be added to the feed to inhibit the precipitation of calcium sulfate and eliminate this source of interference to the project. After operating the equipment for a short period with the Cyanamer P-35, it was decided to eliminate its use since sulfate and calcium concentrations in the feed were low enough that saturation with calcium sulfate would not be reached at the water recoveries anticipated in this study. In Table 1 an analysis of a typical feed and brine at Pomona shows that it would require a more than 10X concentration of the feed to approximate saturation of calcium sulfate. Laboratory studies had already shown that neither sodium hexametaphosphate nor Cyanamer P-35 were effective in inhibiting the precipitation of dibasic calcium phosphate.

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FIELD EXPERIMENTS

The field experiments outlined in Table 4 represented the consensus of Gulf General Atomic and the County Sanitation Districts of Los Angeles County as the most meaningful steps that could be taken to develop information on the capability of reverse osmosis systems to treat waste waters of the types encountered at Pomona. The list of experiments was modified to that shown in Table 5 during the course of the work on the basis of the results of previous tests and by mutual agreement between the FWPCA, Gulf General Atomic, and the Sanitation Districts.

On the basis of earlier testing at Pomona, a daily air-water flush of each test unit was incorporated as a standard operating procedure. This consisted of a 2-min tap water flush at line pressure (60 to 75 psi) followed by a 3-min flush of tap water with compressed air (60 to 90 psi) added. This procedure was repeated three times in succession. The purpose of this flush was to minimize the buildup of any material within the module and thereby minimize fouling problems.

Early in the second phase of the test program, a cleaning technique was discovered that has had a significant impact on reverse osmosis performance. This was the demonstrated ability to clean the system using a solution of a commercial enzyme preparation. Initially, the units were flushed (closed loop) with a solution of 10,000 mg/l of BIZ* for 50 min at ambient temperature. After this flushing, during which time a considerable amount of particulate matter was removed from the system, each loop showed approximately 20% increase in product water flow. The development and results of the cleaning procedure are covered in a later section of this report.

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*BIZ is a Proctor and Gamble enzyme-containing laundry presoak product. Mention of commercial products does not imply endorsement by the Federal Water Pollution Control Administration.

TABLE 4

PROPOSED EXPERIMENTS

Experiment	Test Unit	Feed	Treatment[a]	Flushing	Membrane[b]	Spacers	Array	Comments
I	I	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	A	Large	Series	To evaluate relative system performance on carbon effluent and secondary effluent, using large spacers and highly selective membranes. Although each unit will be operated at high recovery (>80%) sampling ports will be provided to allow an evaluation of performance at lower recovery as well.
	II	Secondary effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	A	Large	Series	
II	I	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	A	Large	Series	To evaluate relative system performance operating on carbon effluent, using high- and intermediate-selectivity membranes. As before, the units will be operated at high recovery, with provision for monitoring performance at low and intermediate recovery.
	II	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	C	Large	Series	
III	I	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	A	Small	Series	To evaluate relative system performance on carbon effluent and secondary effluent, using small spacers and high-selectivity membranes. Again, operation will be at high recovery, with provision for monitoring lower-recovery performance.
	II	Secondary effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	A	Small	Series	
IV	I	Secondary effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	A	Large	Series	To evaluate relative system performance operation on secondary effluent when using high- and intermediate selectivity membrane. Again, high-recovery operations are planned, with provision for monitoring lower-recovery performance.
	II	Secondary effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	C	Large	Series	
V		--	--	--	--	--	--	Feed, treatment, membrane types, operating parameters, etc., to be selected on the basis of results of Experiments I through IV.

[a]Chlorine values are combined residuals.

[b]A = high-selectivity membrane; C = intermediate-selectivity membrane.

TABLE 5

FIELD EXPERIMENTS CONDUCTED

Experiment (Phase No.)	Test Unit	Feed	Treatment[a]	Flushing	Membrane[b]	Spacers	Module Array
I	I	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day	A	Large	Series
	II	Sand-filtered secondary effluent	Continuous Cl_2 at 2 mg/l; 10 mg/l Cyanamer P-35	Air/water 15 min/day	A	Large	Series
II	I	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning once a week	A	Large	Series
	II	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning once a week	C	Large	Series
III	I	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning once a week	C	Large	Series
	II	Secondary effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning twice a week	C	Large	Series
IV	I	Secondary effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning twice a week	C	Large	Series
	II	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning once a week	C	Small	Series
V	I	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning once a week	C	Large	Series
	II	Carbon-column effluent	Continuous Cl_2 at 2 mg/l	Air/water 15 min/day; BIZ cleaning once a week	C	Large	Series[c]

[a] Chlorine values are combined residuals.

[b] A = high-selectivity membrane; C = intermediate-selectivity membrane.

[c] Module tubes in vertical orientation.

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TEST RESULTS

The results of the five sets of field tests are described below, along with the objectives and conclusions.

PHASE I

This experiment was designed to compare system performance of reverse osmosis units operating with carbon-column effluent and with sand-filtered secondary effluents as feeds. The modules were fabricated with large (polypropylene Vexar) brine-side spacers to minimize system pressure drop and to further minimize potential fouling problems, and with high-selectivity, standard-flux membranes. A gross evaluation of the capability of reverse osmosis modules fabricated with highly selective membrane to treat both carbon-column effluent and secondary effluent was to be made from this experiment.

Unit I operated on clarified secondary effluent that had been passed through a carbon adsorption column. Unit II operated on sand-filtered secondary effluent. The pH on both units was adjusted to 5.5 ± 0.5 with hydrochloric acid. In addition, 10 mg/l of Cyanamer P-35 was added to minimize any possibility of calcium sulfate precipitation. It was decided that the addition of Cyanamer P-35 would not be necessary in future work as long as the recovery rates of 75 to 80% were not exceeded.

Because of the varying pressures employed during the first 300 to 400 hr of operation, it is difficult to interpret compaction and fouling data. Since the majority of membrane compaction takes place during the first few hundred hours of operation, a more meaningful flux decline slope can be drawn from the data available after 300 hr. In addition, the pressure was constant at 600 psi from that period on, and steady-state operation was achieved. This test, as well as all the succeeding ones, was operated at 600 psi.

Figures 4 and 5 are log-log plots of the water permeation coefficient A versus time for Units I and II. A line is plotted that shows a flux decline slope of -0.06. This is a reference slope. Data obtained from laboratory studies on compaction and from field installations on flux decline have shown that a flux decline of -0.06 is typical of what can be expected from modified cellulose acetate membranes subjected to feed waters free of undissolved solids at 600 psi and 25°C (see Appendix).

As shown by the curves, the flux decline slope for Unit I (carbon-column effluent) is equal to -0.16. Unit II exhibits a slope of -0.425 over the same period. Since this time period (400 hr to 800 hr) represents steady-state operation for the two systems and -0.06 is typical of the compaction slope, it can be seen that fouling causes the log-log slope of the water flux decline curve to be approximately three times greater than normal when carbon-column effluent is the feed and approximately seven times greater than normal when sand-filtered secondary effluent is the feed.

Water flux declines of this magnitude cannot be tolerated since at the end of one year a slope of -0.16 would represent a 50% loss in water flux and a slope of -0.425 would represent an 85% loss in water flux. A module with a flux decline slope of -0.06 would show a decline in water flux of 23% in the same time. The undissolved materials must either be removed upstream of the reverse osmosis unit or development of a procedure that would prevent fouling or enable rapid, economical cleaning was necessary.

Both units showed excellent rejections throughout this phase of the program. Unit I consistently gave 95% TDS rejection as measured by conductivity rejection, while Unit II was 93% or better. This lower rejection by Unit II can be explained by boundary-layer phenomena resulting from the higher degree of fouling.

The results of this phase did indicate, however, that it was feasible to operate reverse osmosis modules on both carbon-treated and secondary effluents and that further testing was warranted.
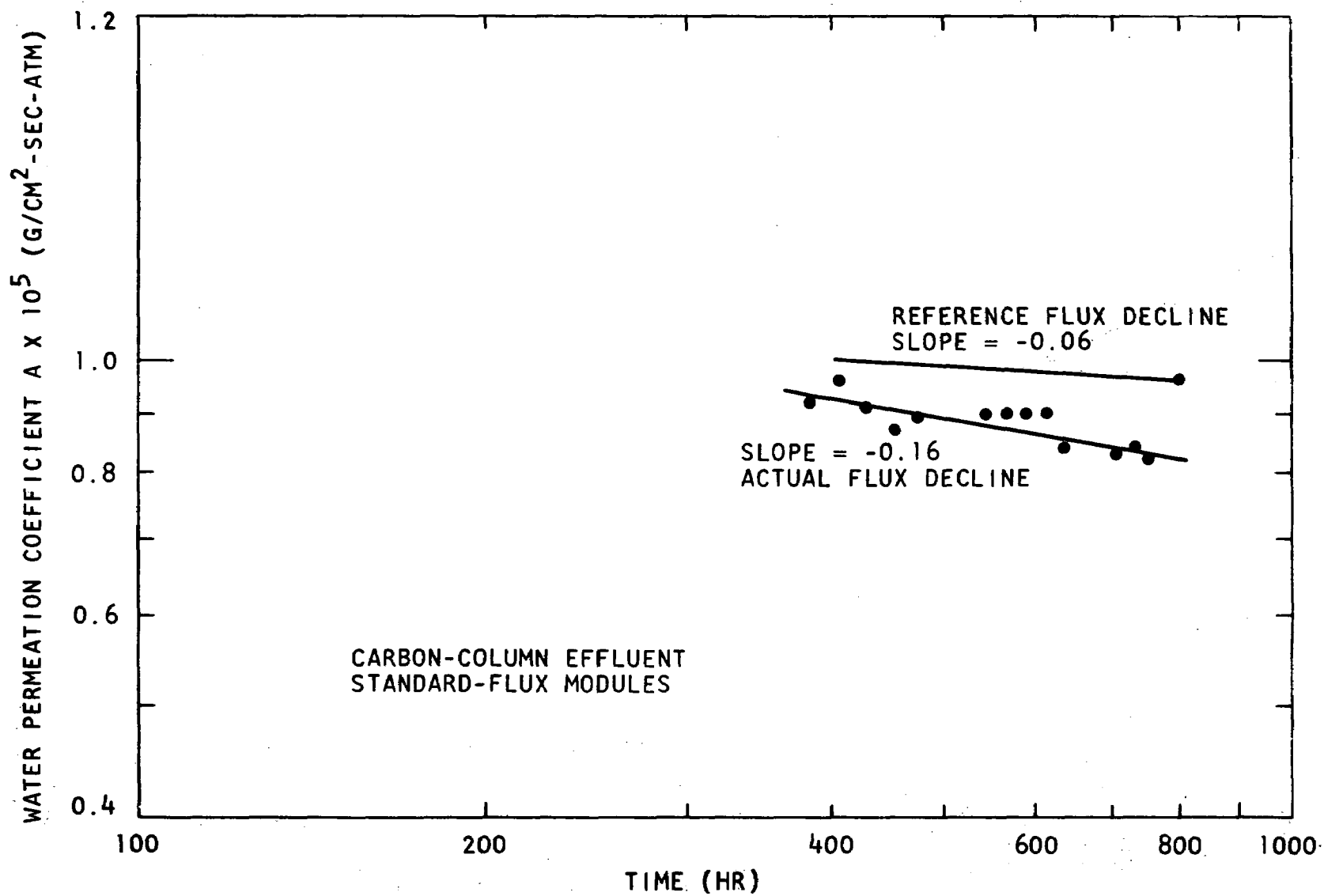
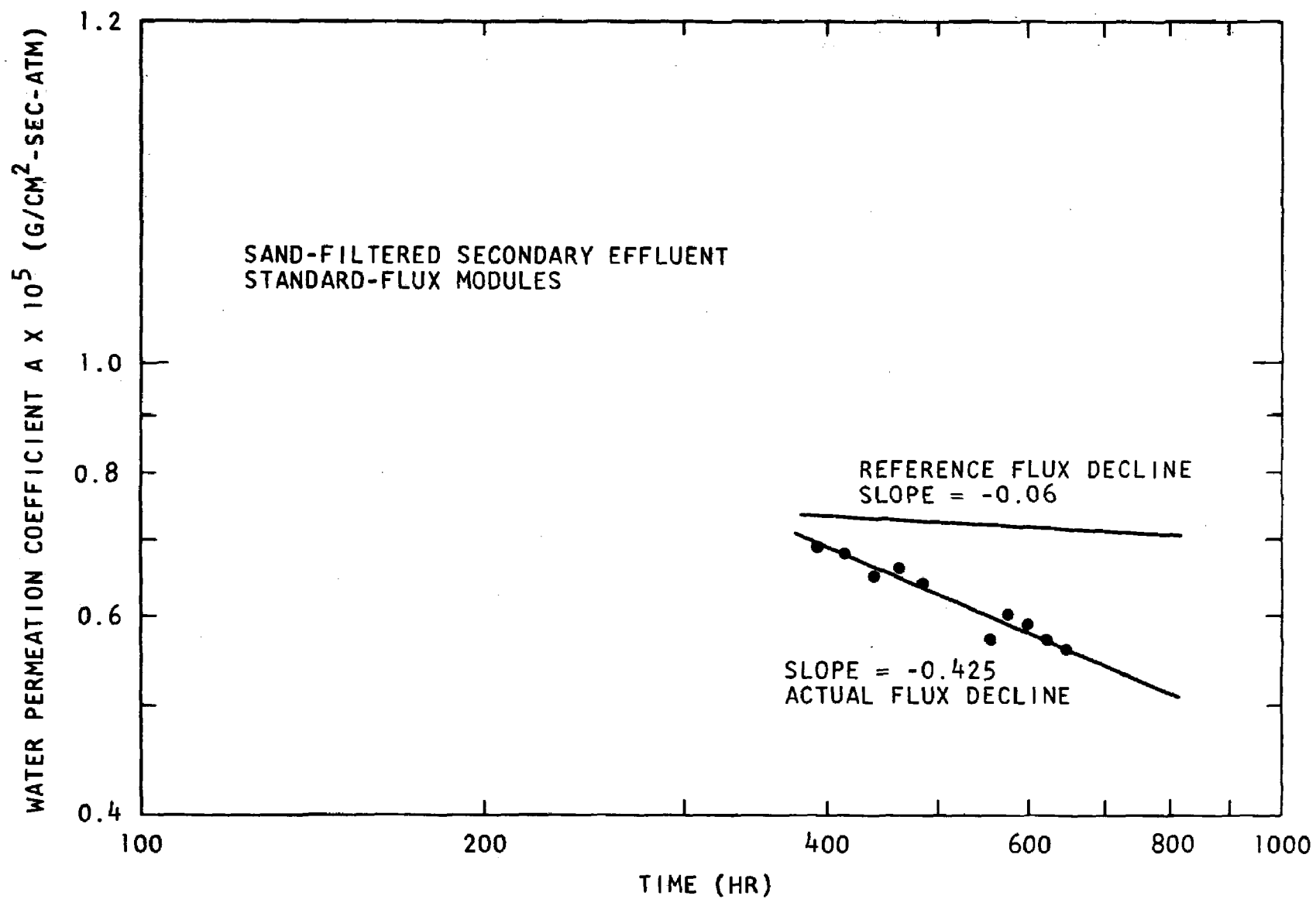Fig. 4. Water permeation coefficient A versus time; Unit I, Phase I

Fig. 5. Water permeation coefficient A versus time; Unit II, Phase I

PHASE II

This experiment was designed to compare the performance of modules
fabricated with high- and intermediate-selectivity membranes when they
were operated on carbon-column effluent. The formulation and casting of
high- and intermediate-selectivity modified cellulose acetate membranes
is identical; differences in performance in terms of water flux and
salt rejection are produced by varying the annealing temperature (see
Appendix). Since, in general, waste waters are not highly saline, there
would appear to be an advantage to using a higher-flux, less-selective
membrane to increase product water output and reduce treatment costs.
Earlier work had indicated that there might be a plugging problem with
intermediate-selectivity membranes, with a resulting rapid flux decline.
The purpose of this experiment was to examine the relative merits of the
high- and intermediate-selectivity membranes and to evaluate possible
plugging problems. Carbon-column effluent was selected as the feed because,
of the two feeds being evaluated, it seemed to offer the highest probability
of successful operation.

Unit I was loaded with eighteen standard-flux modules (A $\sim$ 1.5) in
a 3$\rightarrow$2$\rightarrow$1 array. Unit II was loaded with twelve high-flux modules (A $\sim$ 2.0)
in a 2$\rightarrow$1$\rightarrow$1 array. Both systems were operated at 600 psi on carbon-column
effluent (pH 5.5 $\pm$ 0.5, adjusted with HCl). During working days, each
system was flushed with air and water at low pressures. In addition,
each unit was cleaned once a week with a solution of 10,000 mg/l of BIZ
for 50 min at ambient temperature.

Some pump problems were encountered during this run, especially on
Unit I. These problems were identified as being electrical in nature,
and modifications were made on the three pumps to solve these problems.
In addition, inadequate feed pressure was also a problem. This was
attributed to the chlorination system; plumbing changes that were made
solved this problem. As a result of this problem, the systems were not
chlorinated from approximately Hour 150 to the completion of the run.

Figures 6 and 7 represent the rejection performances for Units I and II, respectively. Unit I (standard-flux modules) dropped from an initial TDS rejection as measured by conductivity of greater than 96% to around 94.5% after 825 hr of operation. Unit II (high-flux modules) dropped from 94% to 91.5% after 1000 hr of operation. Decline in rejection of this magnitude over these periods of time cannot be explained by hydrolysis at pH 5.5. There are several possibilities that might explain this decline. The first is the fact that this was the period when BIZ cleaning was first utilized. The enzyme detergent (BIZ), at the concentrations used of 10,000 mg/l, exhibits a pH of 10. At this pH, the hydrolysis rate for the membrane is high and could feasibly explain the lower rejections. Also, in addition to the weekly BIZ cleaning, these modules were not chlorinated from Hour 150 to the completion of the run. There were also problems associated with conductivity equipment used which necessitated changing the meter and cell. The occurrence of these problems coincided rather closely with the noticeable decline in rejection, as shown in Figs. 6 and 7. When these variables are considered, it is difficult to project a meaningful explanation for the relatively rapid decline in rejection. In any event, the product quality was quite acceptable.

Figures 8 and 9 are log-log plots of the water permeation coefficient A versus time for Units I and II, respectively. On each figure, there are two straight lines; one of these is a conservative representation of flux decline, and the other, an optimistic representation.

The slope of each straight line is noted on each curve. The broken line curves clearly show a cyclic function. The peaks on both curves represent data that was taken approximately 20 hr after the weekly BIZ cleaning. The minimum points are representative of highly fouled values. By using the weekly BIZ cleaning procedure, reasonable flux decline slopes have been maintained. Even the conservative slopes are reasonable for clarified secondary effluent. Flux decline slopes on the order of -0.16 were noted for comparable membrane on this type of feed during the first phase of this program.
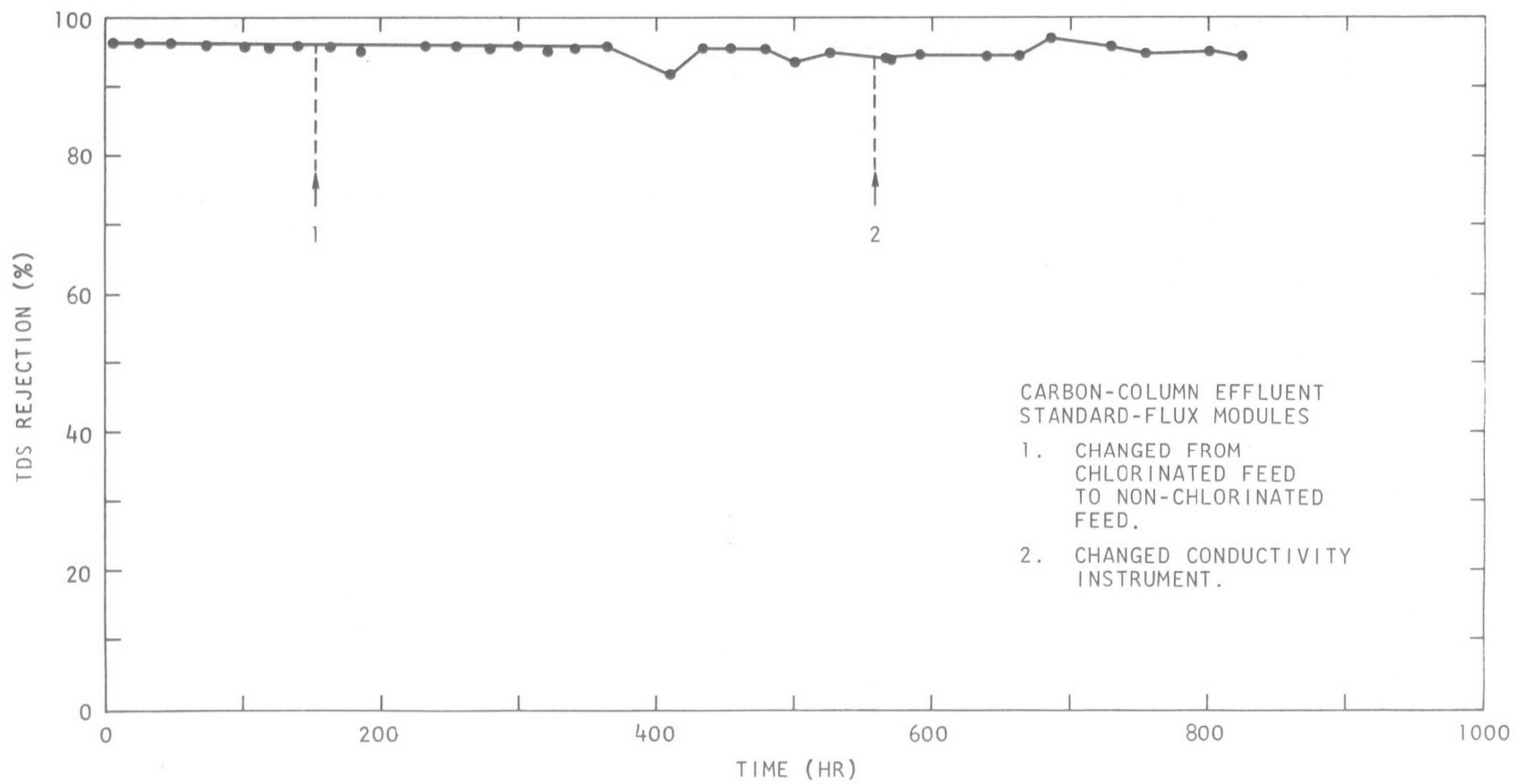
Fig. 6. Percent TDS rejection versus time; Pomona Unit I, Phase II

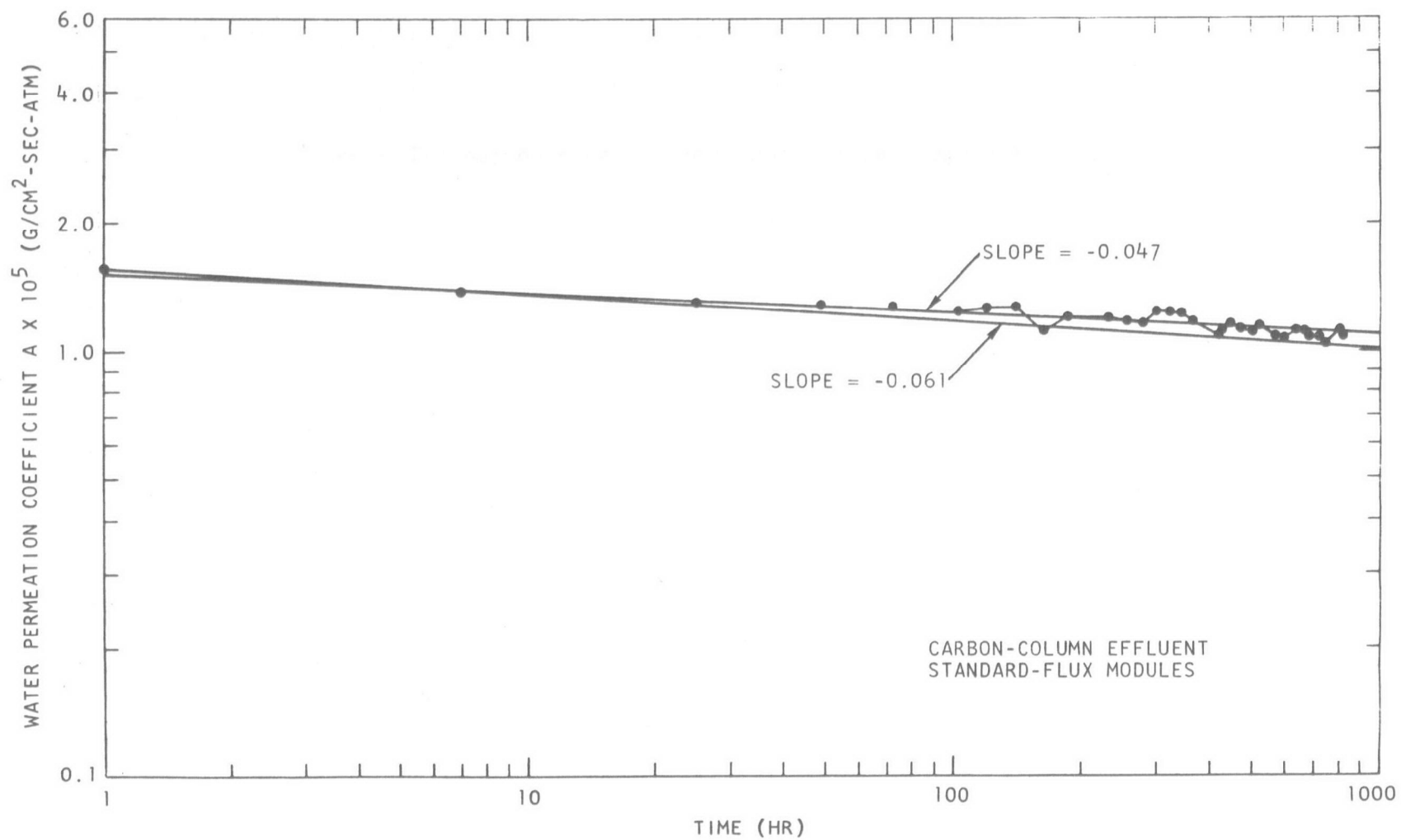Fig. 7. Percent TDS rejection versus time; Pomona Unit II, Phase II

Fig. 8. Water permeation coefficient A versus time; Unit I, Phase II
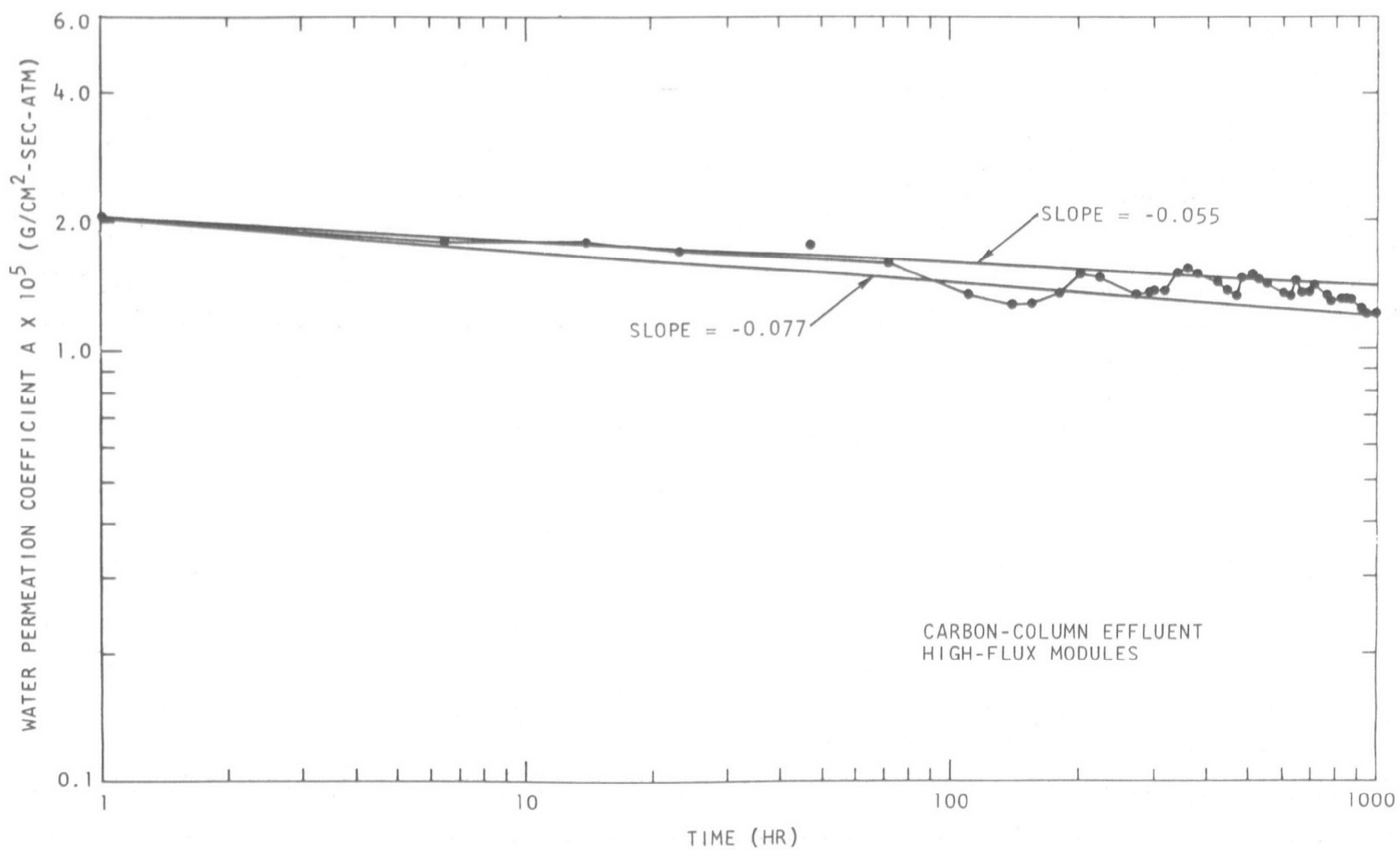
Fig. 9. Water permeation coefficient A versus time; Unit II, Phase II

As anticipated, the higher-flux modules have a slightly greater flux decline slope (-0.055 to -0.077) than the standard-flux modules (-0.046 to -0.061). The differences are not abnormal and are in fact reasonably close to the values obtained in controlled laboratory experiments. Figure 10 is a log-log plot of the expected ranges of A versus time for the high-flux modules. If the extrapolation is valid (and past experience has shown this to be the case for pure compaction, i.e., no fouling) and the data are representative of compaction with little or no fouling, then an evaluation can be made of the merits of high-flux versus standard-flux systems. The poorest situation would be to take the optimistic flux decline slope for standard-flux membrane and the conservative slope for high-flux modules. If this is done, it can be seen (Fig. 10) that the two curves cross at approximately 10,000 hr (about 1.2 yr). Based on these considerations, it appears that a significant increase in water flux may be obtained over a 25,000-hr (3-yr) operating period using high-flux modules with a slight decrease in product water quality. However, additional work comparing the results for the high- and standard-flux membranes over longer periods of time is required before a judgment can be made.

PHASE III

This phase, by mutual agreement of participating agencies on technical grounds, deviated slightly from the proposed program. In view of what had been learned in prior phases, it was agreed that an evaluation of high-flux modules on secondary effluent and on carbon-column effluent was in the best interest of the research program. After minor plumbing changes and upgrading of some components, both units were loaded with twelve high-flux modules. The respective feedwaters were adjusted to a pH of 5.5 ± 0.5, and each unit received a daily air-water flushing.

Unit I (carbon-column effluent) was loaded with high-flux modules having an initial A of 2.6, while Unit II (secondary effluent) was loaded with high-flux modules having an initial A of 2.5. Both systems were
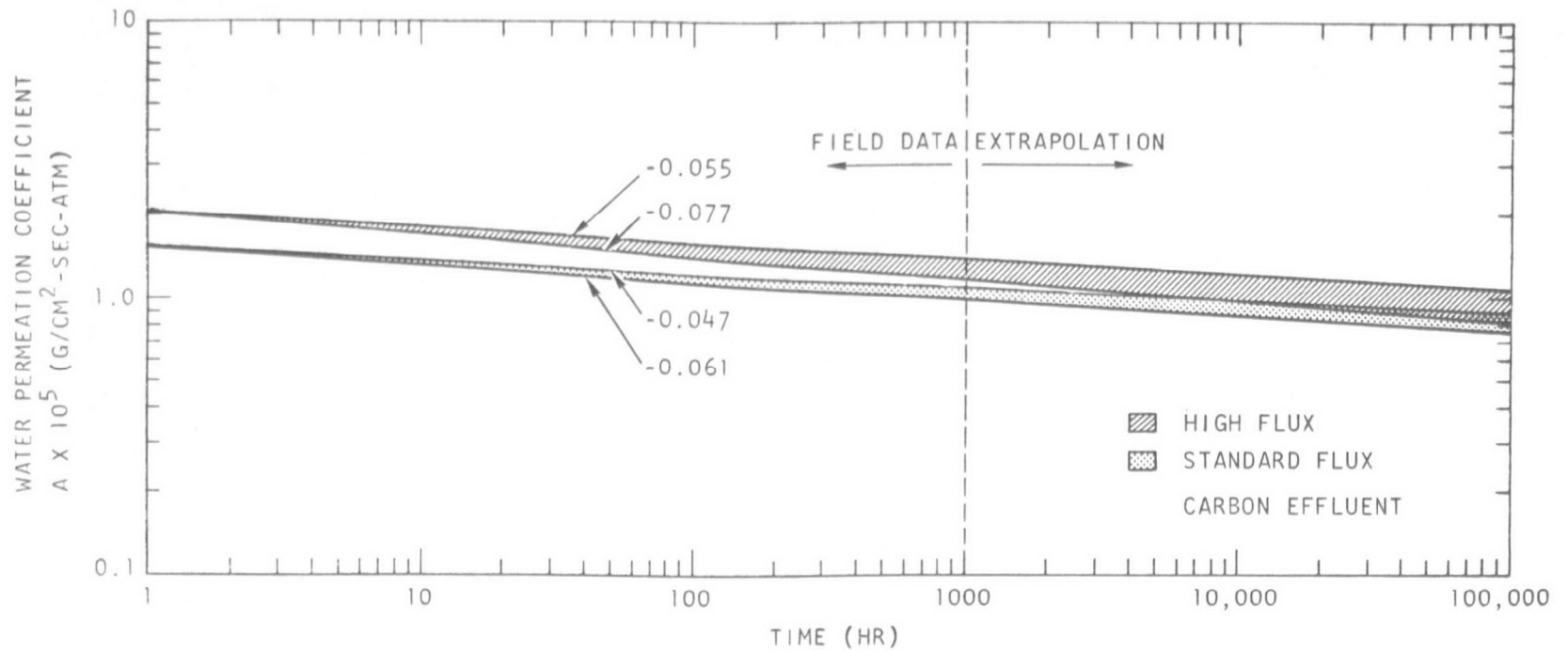
Fig. 10. Water permeation coefficient A versus time; extrapolated compaction data based on Phase II

30

operated at 600 psi in a 2→1→1 array and with an exit brine flow rate of 3 gpm. Unit I received a once-weekly BIZ cleaning, while Unit II was cleaned with 10,000 mg/l of BIZ twice a week. Recoveries varied between 40 and 70% during the length of the run.

TDS rejection versus time is plotted in Fig. 11 for Unit I and in Fig. 12 for Unit II. As indicated, the rejection remained essentially constant at 92%. Figure 13 is a log-log plot of the water permeation coefficient A versus time for Unit I. The flux decline slope is -0.14. This is approximately twice the value found for this type of system (high-flux modules, carbon-column effluent) during Phase II. It appears that the carbon-column effluent quality may have an effect on the rate of fouling. Phase II was started immediately after the activated-carbon column had been regenerated. At that time, effluent from the carbon columns contained an approximate chemical oxygen demand (COD) of 3 mg/l.

Phase III was started after the carbon columns had been in operation for some time. The carbon-column effluent gradually declines in quality over a 2-1/2 to 3 month period, from COD = 3 to COD = 15 mg/l (see Table 2). During Phase II the unit operated on an effluent with a COD of between 3 and 9 mg/l. During Phase III, the COD was between 9 and 15 mg/l. The flux decline slopes were -0.07 and -0.14 for Phases II and III, respectively. A definite correlation could be seen from the feed qualities and flux decline slopes during these two phases; this indicated that cleaning schedules should be adjusted to changing feed conditions.

Unit II was plagued with frequent unscheduled shutdowns due to loss of feedwater. During these shutdowns, the modules experienced severe pressure shocks. In addition, the diameters of several of the modules were found to be slightly small. As a result of these problems, brine seal failures were observed in this unit. Several of the modules were removed, the diameters built up, and new seals applied. When the modules were reinstalled, the rejection improved (see Fig. 12, Hour 300). More
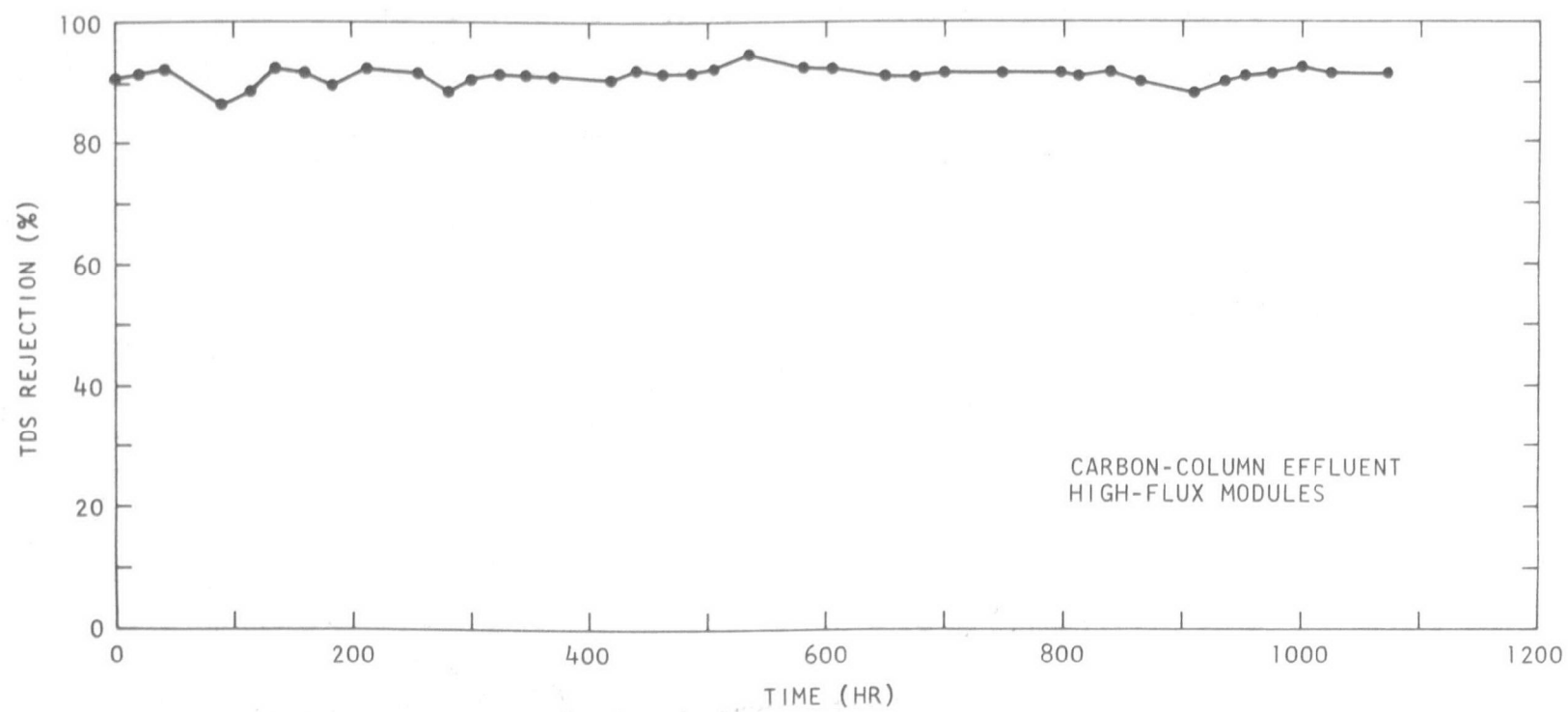
31

100

TDS REJECTION (%)

80

60

40

20

0

CARBON-COLUMN EFFLUENT
HIGH-FLUX MODULES

0   200   400   600   800   1000   1200

TIME (HR)

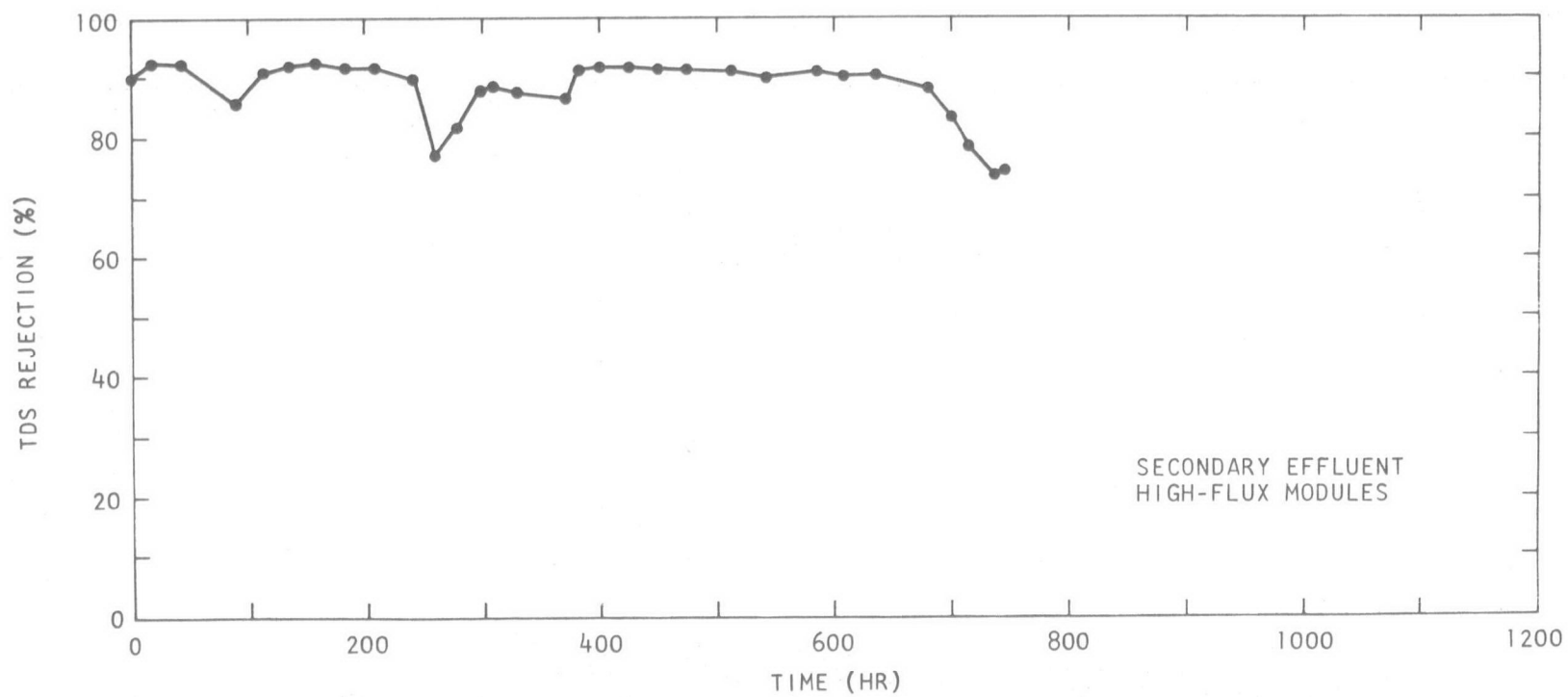Fig. 11. Percent TDS rejection versus time; Pomona Unit I, Phase III

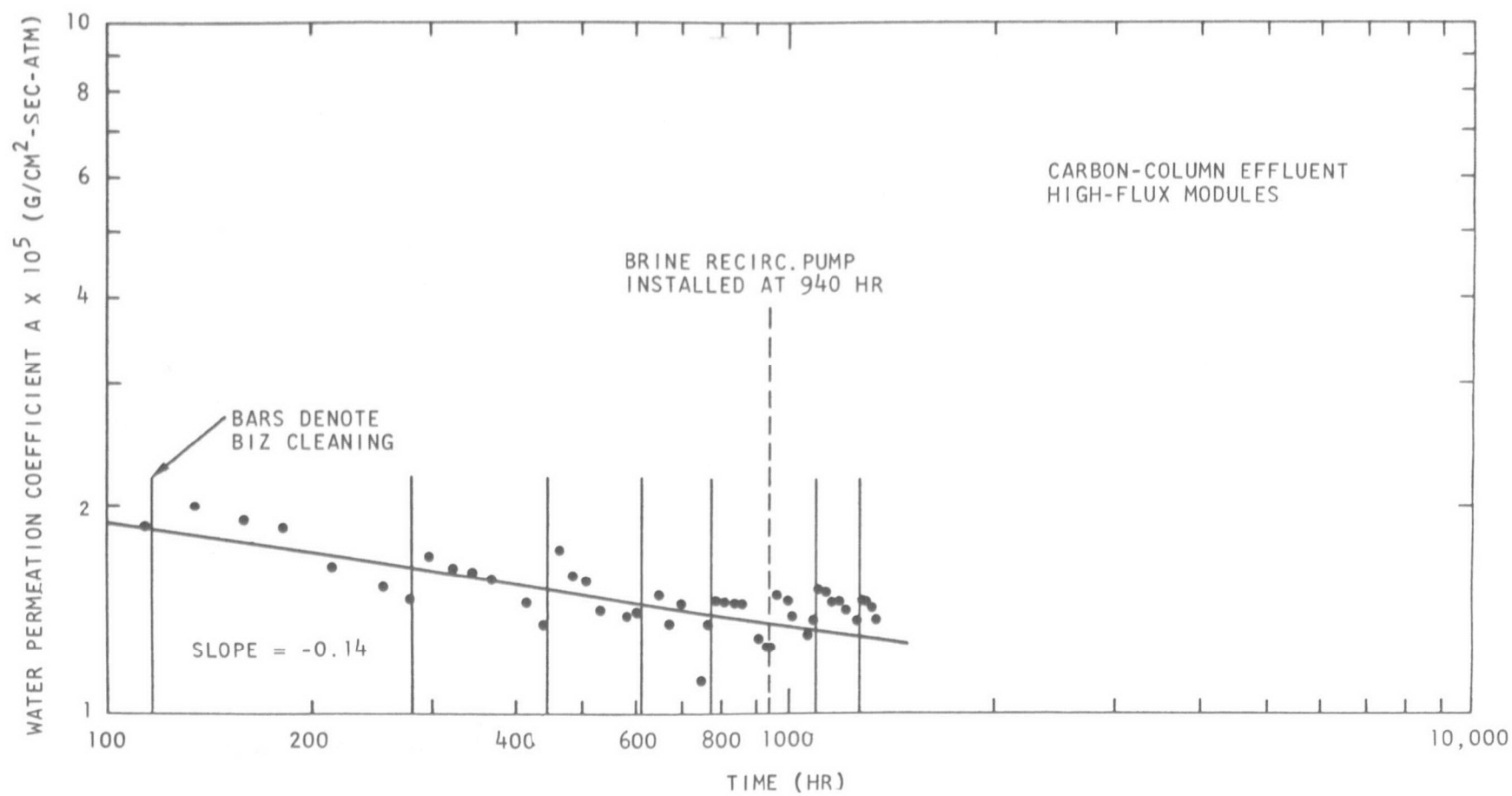Fig. 12. Percent TDS rejection versus time; Pomona Unit II, Phase III

33

Fig. 13. Water permeation coefficient A versus time; Unit I, Phase III with extension

shutdowns were experienced during the remainder of the run. Three modules were removed at the termination of the experiment; each had a brine seal failure, even though the diameters were within specification.

Figure 14 is a log-log plot of A versus time for Unit II with a flux decline slope of -0.24. This is a severe decline in water flux, even though the system was cleaned twice each week with 10,000 mg/l of BIZ. The results of this experiment were almost certainly perturbed by the seal failures. Efficient cleanings could not be conducted if the brine seals were bypassing brine, and fouling during operation would be more rapid and severe.

Investigations of modules removed after Phase II and of several removed during and after Phase III indicated some form of attack on the rubber and possibly on the Silastic RTV adhesive. The adhesive deterioration looked more pronounced in the system running on secondary effluent. The brine seals are made of Buna-N rubber, and oxidative attack on the rubber by the chlorine in the effluent was a strong possibility. A survey of available compounds indicated that ethylene-propylene is not subject to this chlorine attack, and a sample lot of the copolymer brine seals was procured. All the molecules from the two systems were removed, checked for dimensions, diameters built up with tape, and new ethylene-propylene brine seals installed using vinyl tape. Figures 15 and 16 show the appearance of several of the brine seals upon removal. One module was removed 120 hr after the new seals were installed, and the brine seal was visibly unaffected at that time.

It was planned to correct the brine seal situation before Phase IV was started, and this was accomplished.

A short-term run, designated Phase III extension, was conducted to evaluate seal performance. This brought to light further seal problems, which were successfully corrected.
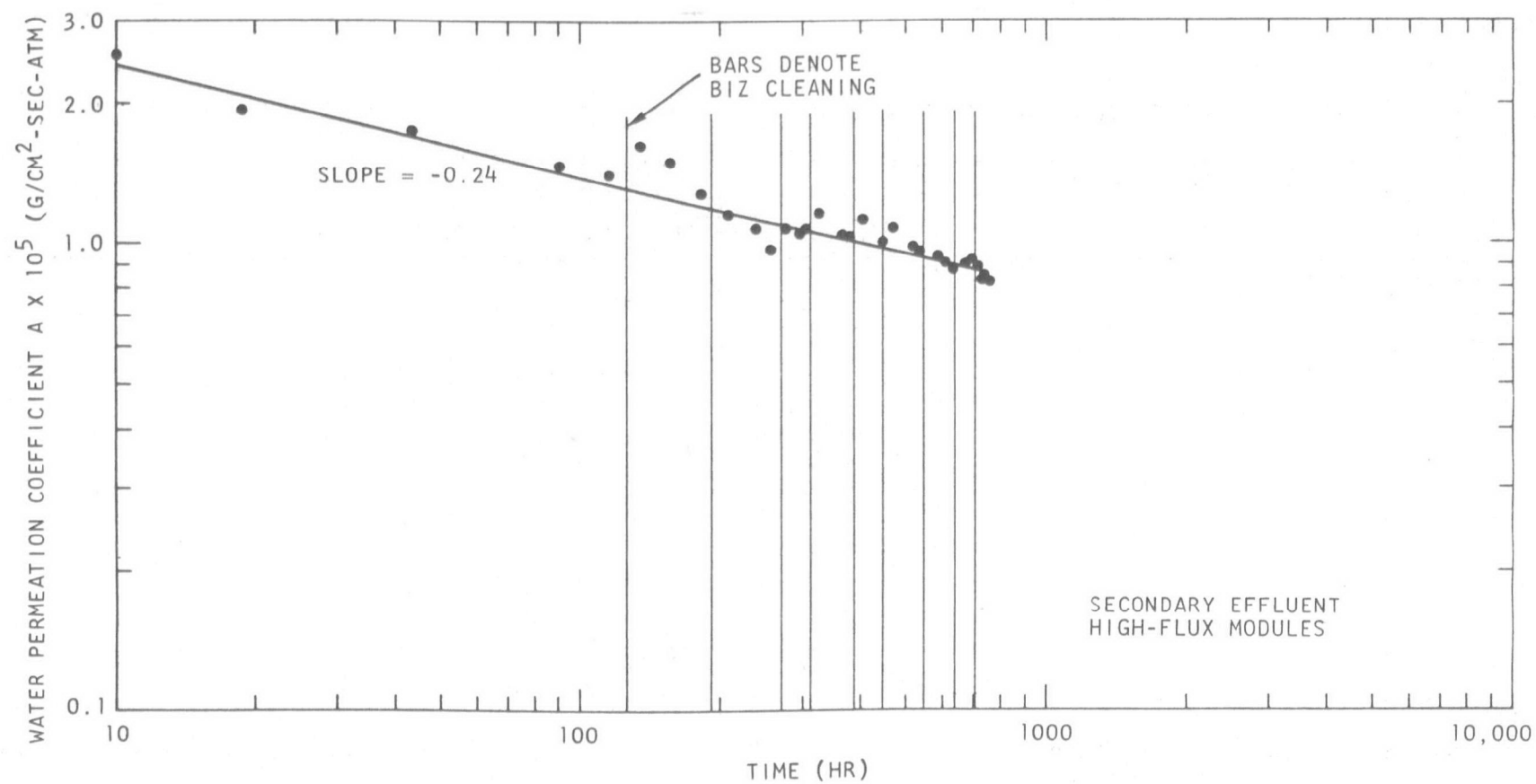
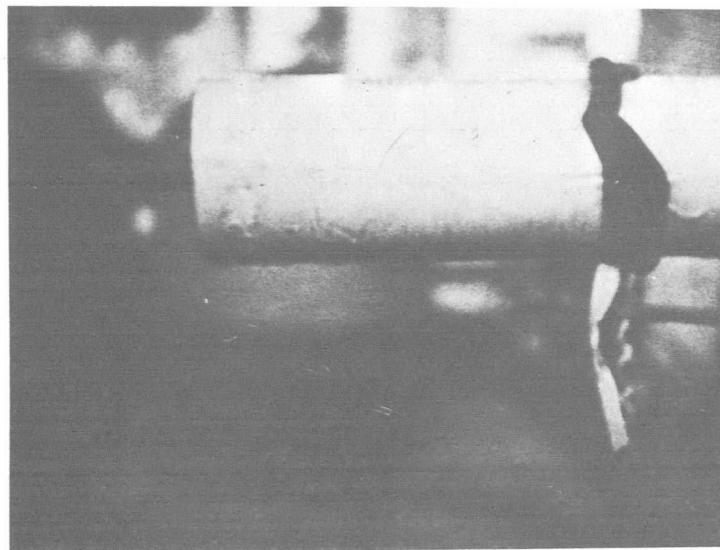Fig. 14. Water permeation coefficient A versus time; Unit II, Phase III
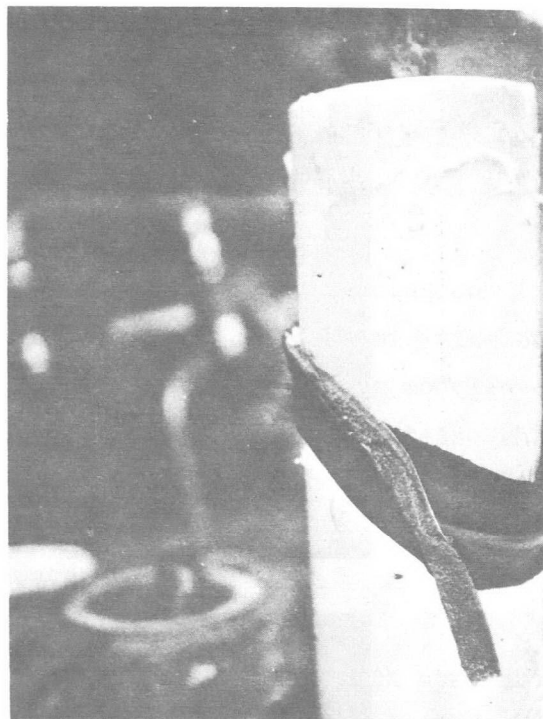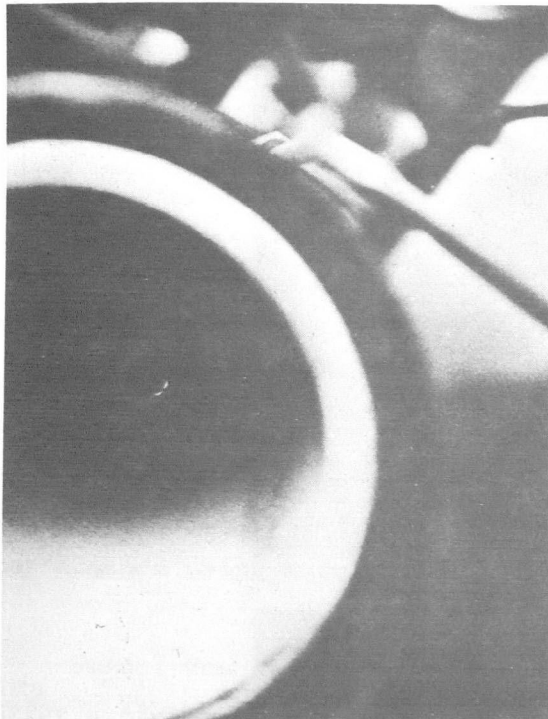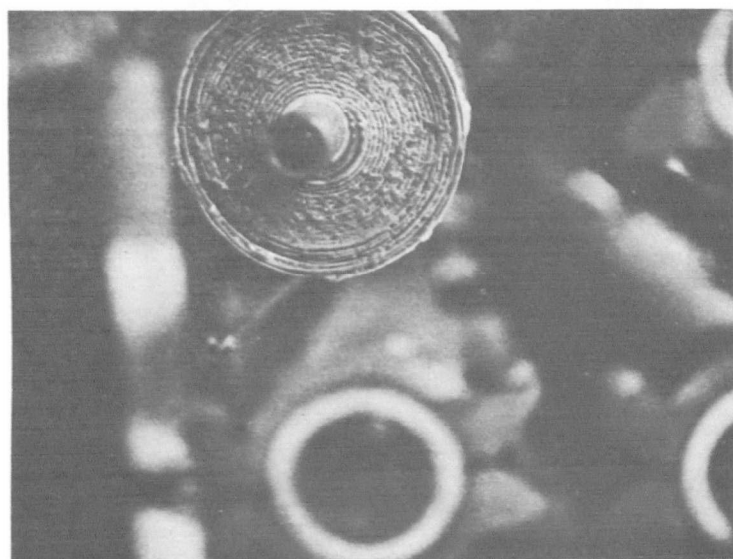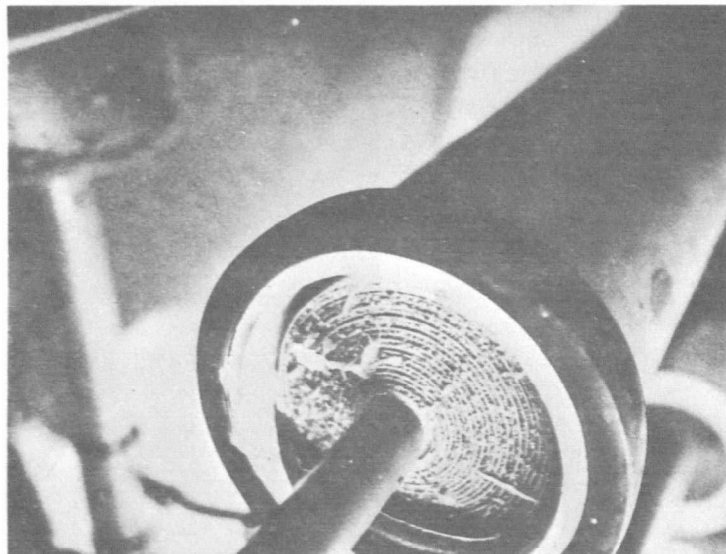
36

Fig. 15. Photographs of displaced brine seals (Phase III)

K75558

Fig. 16. Additional views of displaced brine seals (Phase III)

Brine recirculation was also investigated during this short-term run but no meaningful conclusion was drawn at that time.

PHASE IV

Previous experiments (Phases I, II, and III) were conducted on modules using standard polypropylene Vexar brine spacers to minimize overall system pressure drop and possible fouling problems. By using modules with small brine spacers, however, it would be possible to increase the active membrane area per unit volume of the system and thus increase the product water output. Experiment IV was designed to evaluate system performance using modules with small spacers.

Unit I was loaded with twelve high-flux modules made with standard brine spacers and operated on secondary effluent feed. Unit II was also loaded with twelve high-flux modules. These, however, were fabricated with special Chicopee polypropylene brine spacers. The special brine spacers have less open area and thickness, with resulting higher (but acceptable) system pressure drops; they were studied to provide further enlightenment with respect to the relationship between brine channel geometry, turbulence, and fouling. Unit II was operated on carbon-column effluent.

All of the modules had the more resistant brine seals and carefully checked diameters. Unit I operated for 1550 hr; at the end of this time, there was no evidence of brine seal attack or failure.

Both systems were plumbed in a 2→1→1 array and initially operated at the same system conditions as those of the previous run, i.e., 600 psi with 3 gpm brine flow and pH of 5.5 ± 0.5 adjusted with HCl. Unit I (secondary effluent) was cleaned twice a week with 10,000 mg/l of BIZ, while Unit II (carbon-column effluent) was cleaned once a week. Each system was flushed daily with tap water and air. Recoveries range from 55 to 75% in both units during this run.

Rejection versus time is plotted in Fig. 17 for Unit I and in Fig. 18 for Unit II. As shown, the rejection remained essentially constant at 95 ± 1% for the first 1000 hr. Figure 19 is a log-log plot of the water permeation coefficient A versus time for Unit I. Since the unit was cleaned with 10,000 mg/l of BIZ twice a week, it was not possible to obtain a single flux decline curve. An envelope that contains most of the points for the first 1000 hr is shown with a slope of -0.090. This is by far the best sustained performance obtained on secondary effluent. The effect of the cleaning is evident on this figure as well as on Fig. 20, a linear plot of product flow (in gpm) versus time. Brine recirculation to increase brine flow to the level recommended for the modules was initiated at 625 hr, and system pressure was increased to 625 psi to offset the increased ΔP. This enabled the recovery to be increased from 60 to 75% at 760 hr while brine flow was maintained. The unit operated at 625 psi and 4.5 gpm brine flow (3.0 being recirculated). The modules were flushed individually with tap water at 623 and at 980 hr. One of the pumps failed at 855 hr and was replaced with a spare.

Unit I operated for 1550 hr during Phase IV. The length of this run was dictated by several reasons. First, there was time available before the Phase V modules were available, and there were also some additional parameters of BIZ cleaning, i.e., concentration and temperature, that warranted investigation. The cleaning procedures were altered beginning at about 1000 hr and continued during the final 500 hr of operation, during which time the unit was cleaned seven times.

Note in Fig. 17 that during the final few hundred hours, when high temperature (~115°F) and higher concentrations of BIZ (pH 10, 20,000 mg/l) were used, there was some indication that rejection was decreasing.

Figure 21 shows the water permeation coefficient A versus time for Unit II, as well as the effects of the altered BIZ cleaning procedures. There is a marked increase in water flow; in fact, the flow is as good as was observed in the first several hundred hours.
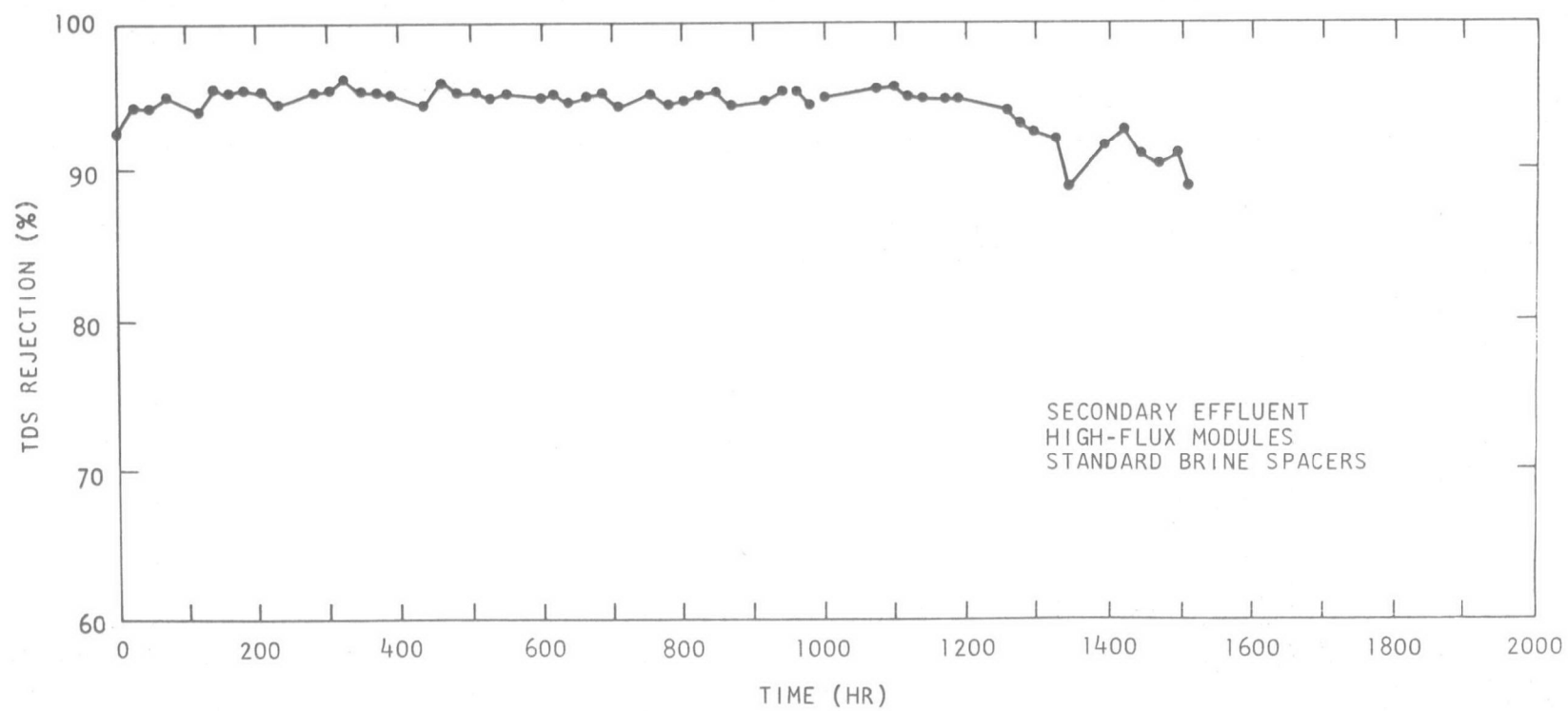
40

Fig. 17. Percent TDS rejection versus time; Pomona Unit I, Phase IV
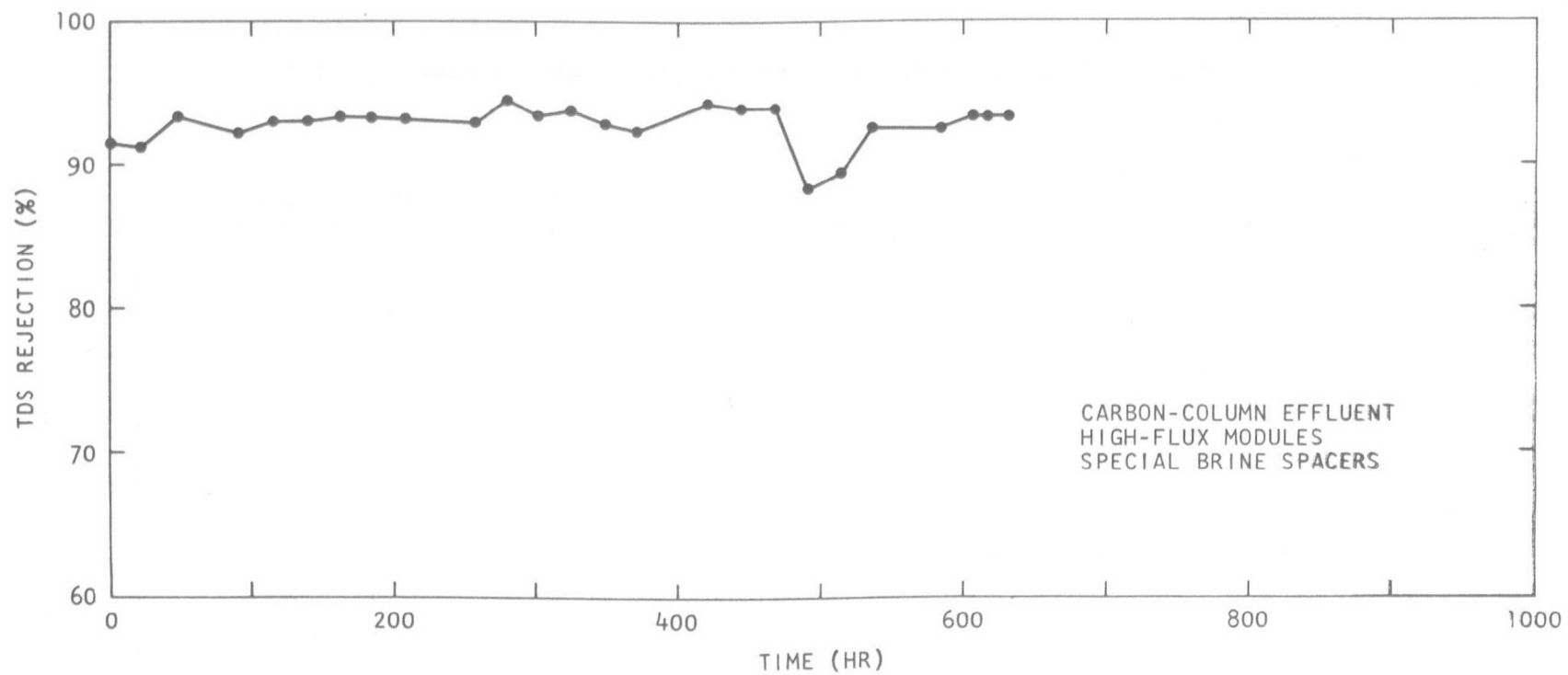
47

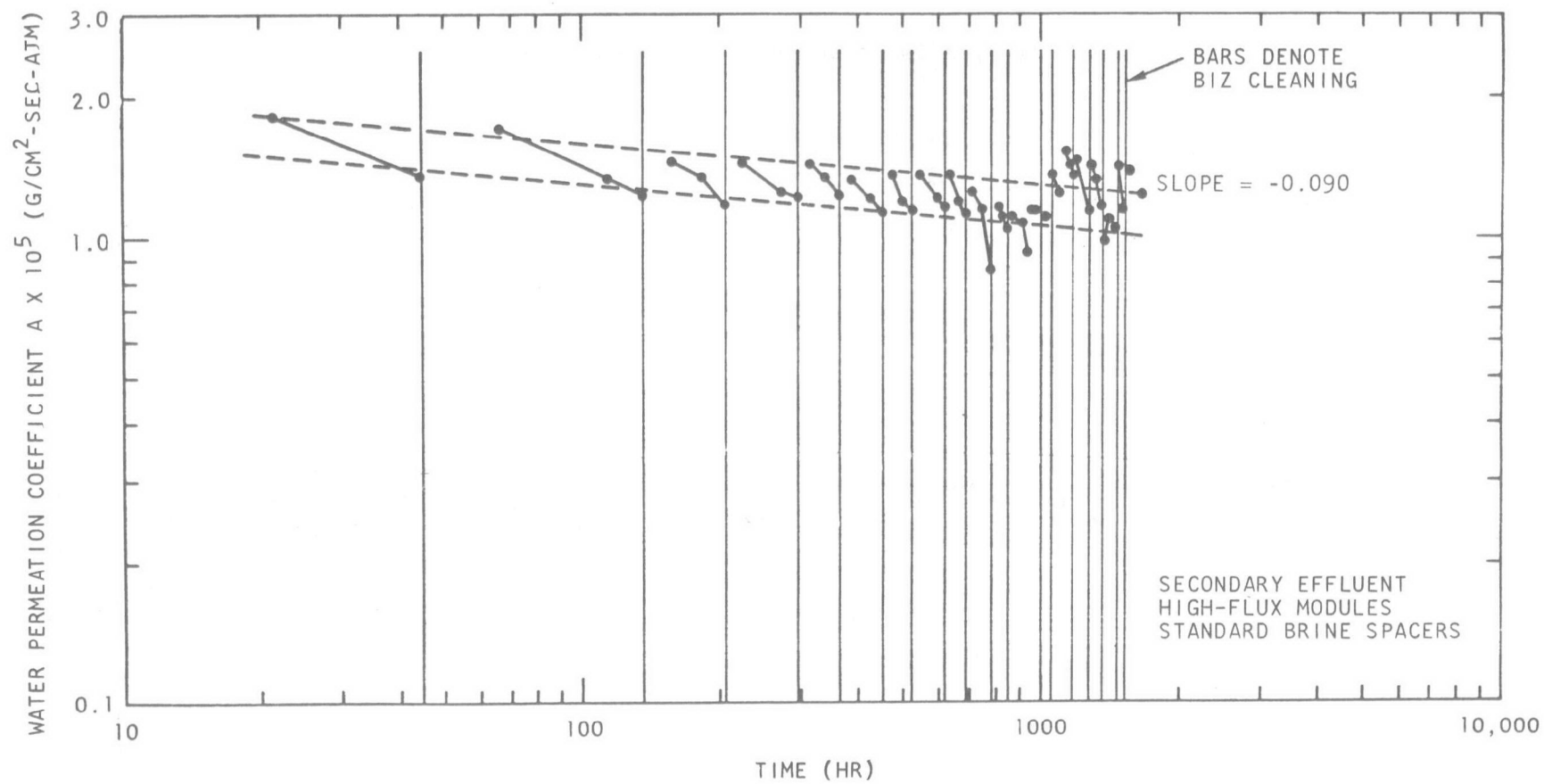Fig. 18. Percent TDS rejection versus time; Pomona Unit II, Phase IV

Fig. 19. Water permeation coefficient A versus time; Unit I, Phase IV
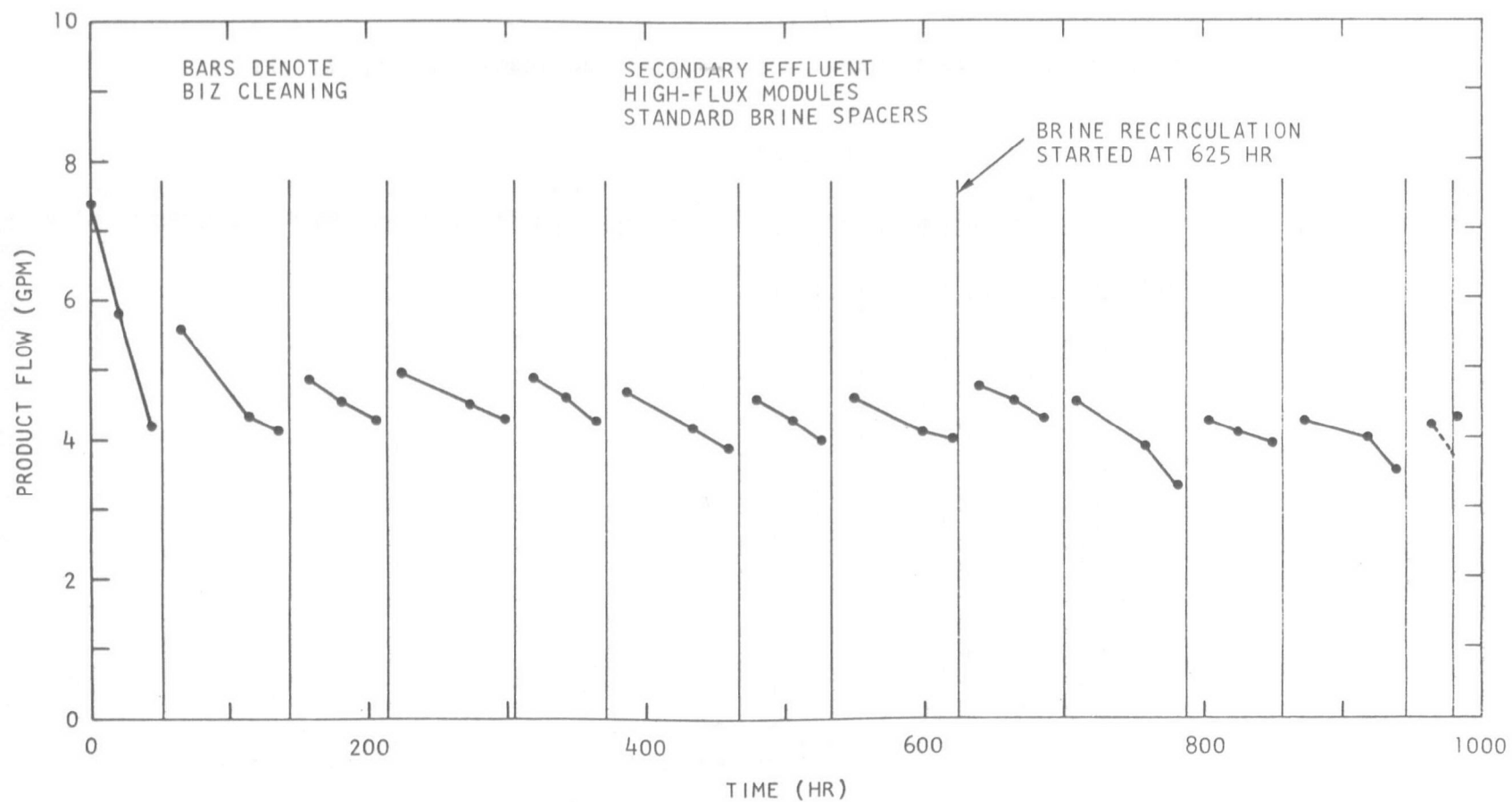
Fig. 20. Product water flow versus time; Unit I, Phase IV
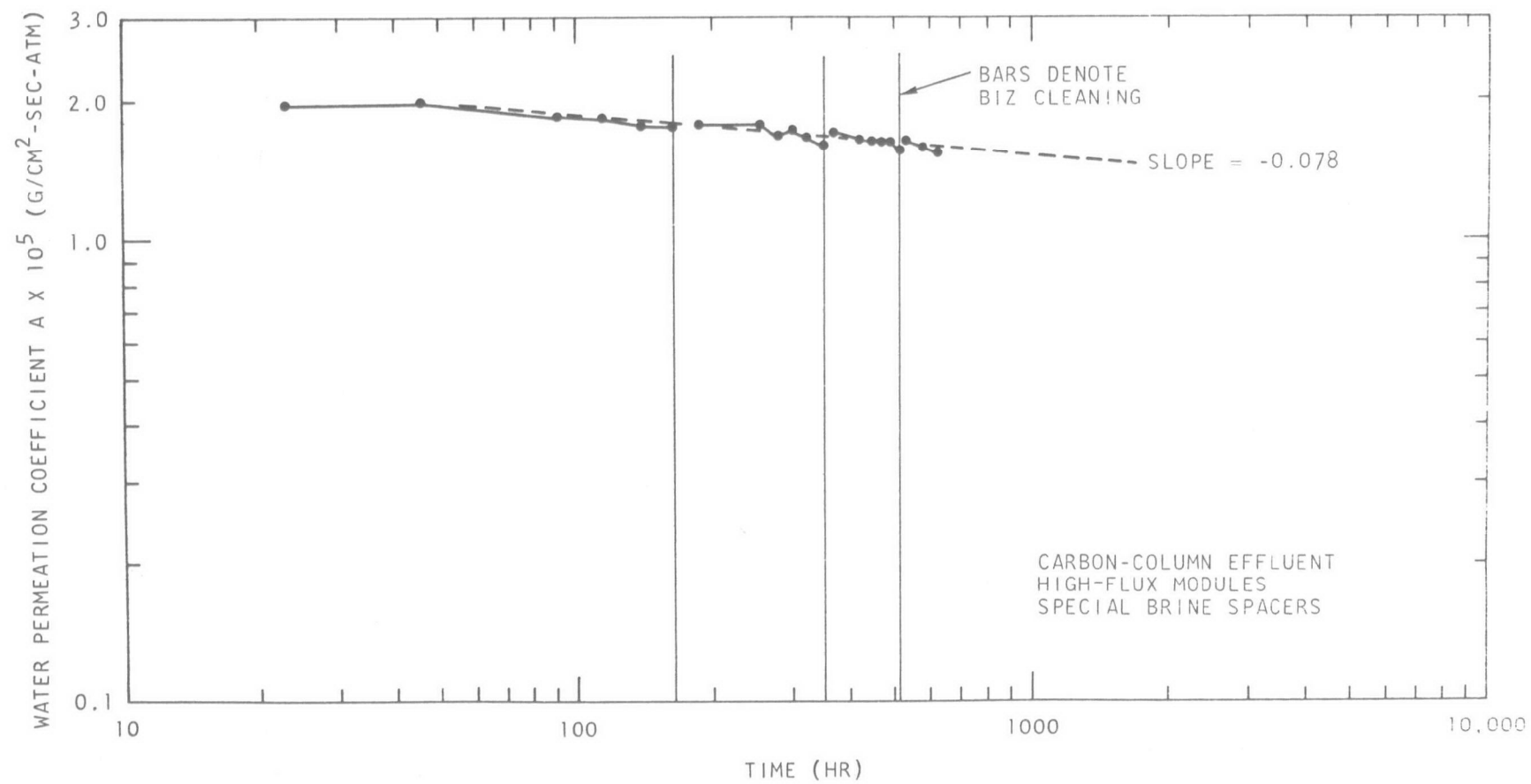
44

Fig. 21. Water permeation coefficient A versus time; Unit II, Phase IV

Thus, indications are that there is still much to be gained by further investigations of BIZ cleaning parameters and the mechanisms of fouling.

Unit II had operated for 632 hr when the run was terminated. High product conductivity values were observed at 490 hr for one of the first two parallel tubes. When the modules were removed, the outer tape wrap of the lead module in the bad tube was found to be split for about one half its length. This failure could have been caused by a too rapid pressurization of the loop. Also, the lead module in the other initial tube was badly deformed as a result of slippage of the brine seal adapter ring. These rings were used to adjust the module diameter since the modules were fabricated with the small Chicopee brine spacer. There was no evidence of brine seal failure in either loop during this run.

Figure 18 shows TDS rejection versus time for Unit II, which averaged about 93% until module failure. Figure 21, the log-log plot of A versus time for Unit II, indicated a flux decline slope of -0.078. During the period of this run, the carbon-column effluent contained between 10 and 15 mg/l COD. The effects of the once-a-week BIZ cleaning is shown in Fig. 22.

In an attempt to further identify the fouling agents, samples were scraped from a module that was removed from Unit II, which operated on carbon-treated effluent; these samples were submitted to two independent laboratories for analysis. Results of these analyses are listed in Tables 6 and 7.

PHASE V

Phase V of the contract was selected to demonstrate a "best effort" based on feed, treatment, membrane type, spacers, and other operating parameters. In addition, there was some evidence that warranted a systematic study of the value of vertical-oriented pressure vessels to minimize fouling and/or enable more effective cleaning.
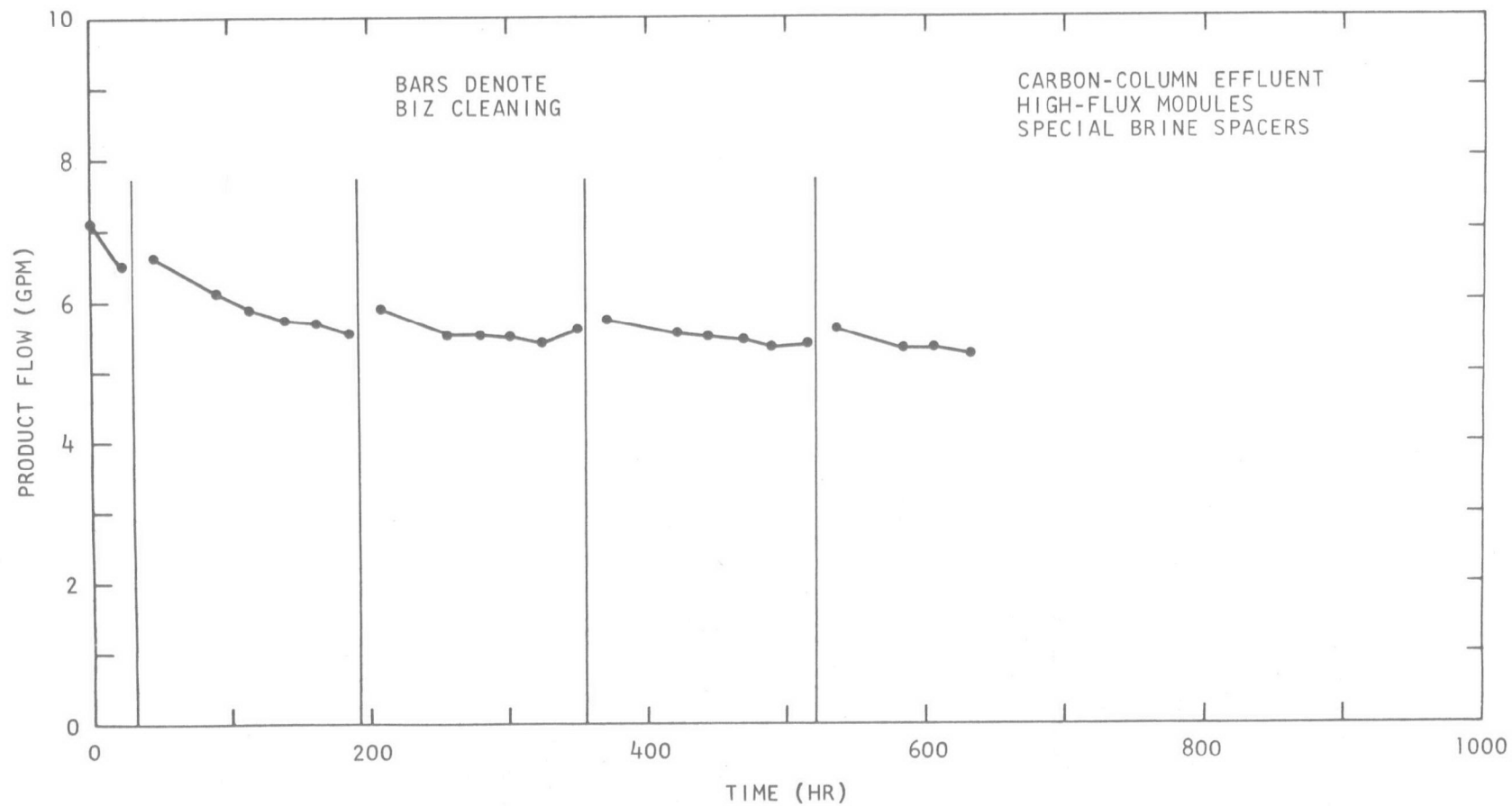
Fig. 22. Product water flow versus time; Unit II, Phase IV

TABLE 6

ELEMENTAL ANALYSIS
(In %)

SLIME FROM POMONA REVERSE OSMOSIS UNIT II (5/21/69)

Carbon 45.33

Hydrogen 6.61

Nitrogen 6.04

Oxygen 34.27

Sulfur . . . . Not detected (<0.1)

Phosphorus 2.31

Ash 11.02

EMISSION SPECTROGRAPHIC ANALYSIS OF ASH
(% of Element in Ash)

Sodium . . .	7.1	Copper . . .	0.42
Silicon . . .	5.0	Nickel . . .	0.09
Calcium . . .	12	Molybdenum .	0.09
Manganese . .	0.31	Tin	0.49
Iron	1.4	Silver . . .	0.002
Magnesium . .	2.9	Zinc	0.20
Chromium . .	0.58	Titanium . .	0.19
Aluminum . .	1.5	Zirconium . .	0.10
Cobalt . . .	0.002	Potassium . .	1.4
Boron	0.06	Strontium . .	0.06
Lead	0.21	Gallium . .	0.02

TABLE 7

ANALYSIS OF SLIME FROM POMONA REVERSE OSMOSIS UNIT II (5/21/69)

Gross Composition, %

Moisture 97.0

Total Solids 3.0

Solids Composition, %

Crude protein 32.3

Crude fat 1.8

Crude fiber + carbohydrate . . . . 57.3 (by difference)

Ash 8.7

Subculture and Growth

Growth in thioglycollate medium . . . . Very heavy, 24 hr

Growth on Sabourauds medium . . . . Heavy, 72 hr

Growth on wort agar . . . . None

Growth on Difco Micro Assay agar . . . . Extensive; favors
                                                   aerobic conditions

Growth on potato dextrose agar . . . . Extensive

Cultures did not sporulate or change color of media.

Thus, both systems were plumbed in a 2→1→1 array, with Unit I
horizontal as before and Unit II having vertical pressure tubes. Both
systems were to be operated as nearly identically as possible. Both
units were loaded with high-flux modules with standard Vexar brine channel
spacing and operated at 600 psi, with 4.5 gpm brine flow (3 gpm being
recirculated) and pH of 5.5 ± 0.5 adjusted with HCl. Both units operated
initially on carbon-column effluent with weekly BIZ cleanings and daily
air-water flushing.

Figures 23 and 24 are graphs of TDS rejection versus time for Units
I and II, which averaged about 93% for both units.

Figures 25 and 26 are log-log plots of A versus time for both units.
The rather severe flux declines experienced in the first 100 hr were
caused by lack of acid addition and by effluent of extremely poor quality
due to the excessive suspended solids. Both units were flushed with
acidified tap water (pH 3 to 6) for several days before operation was
continued.

Water recoveries as high as 87% were attained in Phase V with no
apparent operating problems.

The flux decline slopes indicate that there is no advantage in
vertical orientation over horizontal orientation, but this may warrant
another investigation under a larger range of testing conditions.

Further testing, utilizing these units and modules, was undertaken
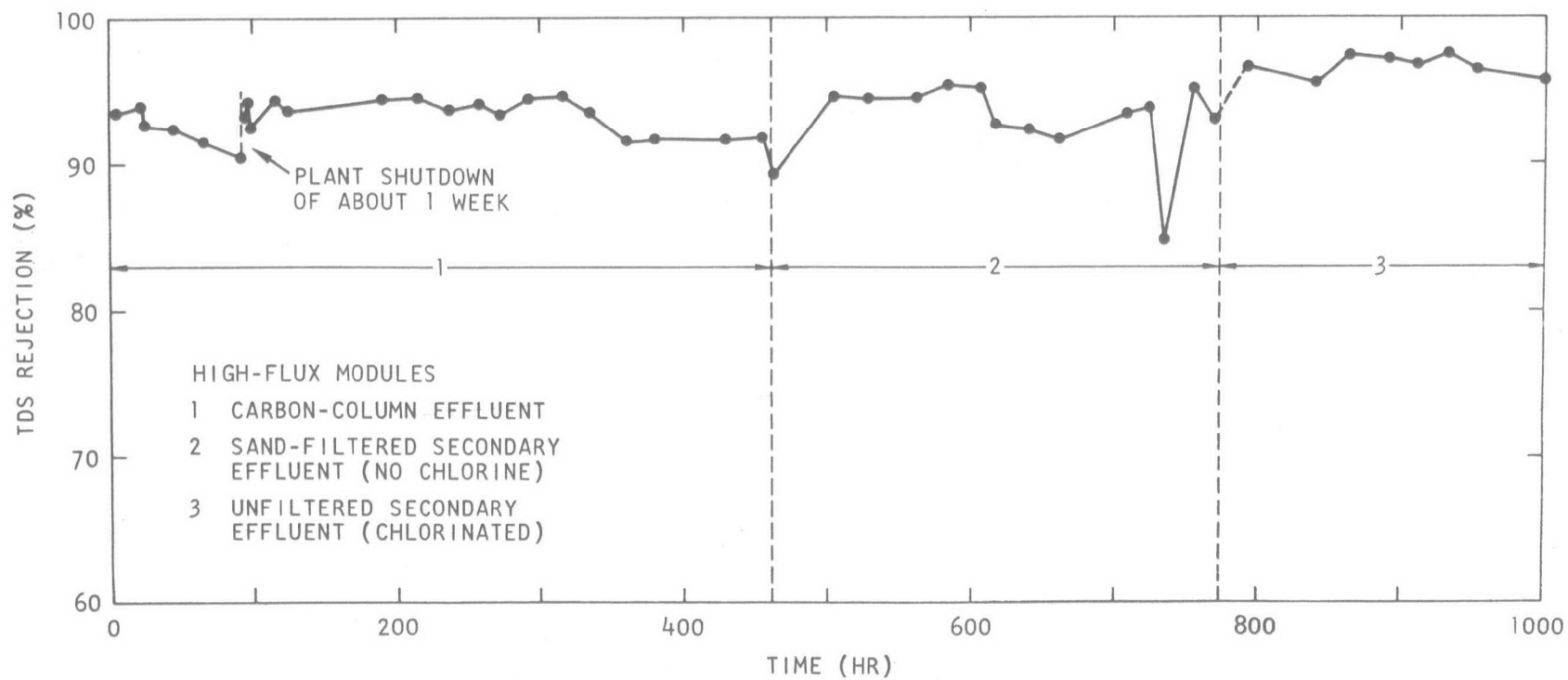by the FWPCA and the County Sanitation Districts of Los Angeles County.

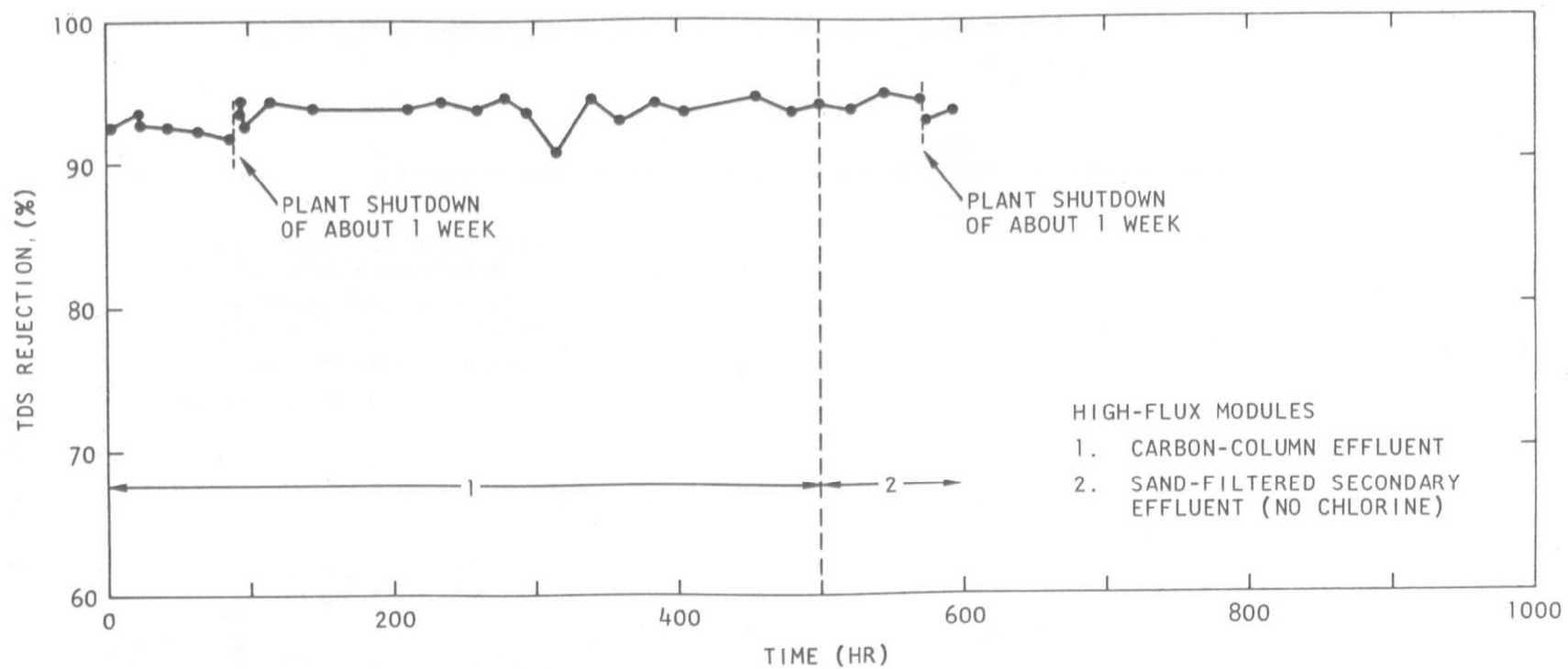Fig. 23. Percent TDS rejection versus time; Pomona Unit I, Phase V

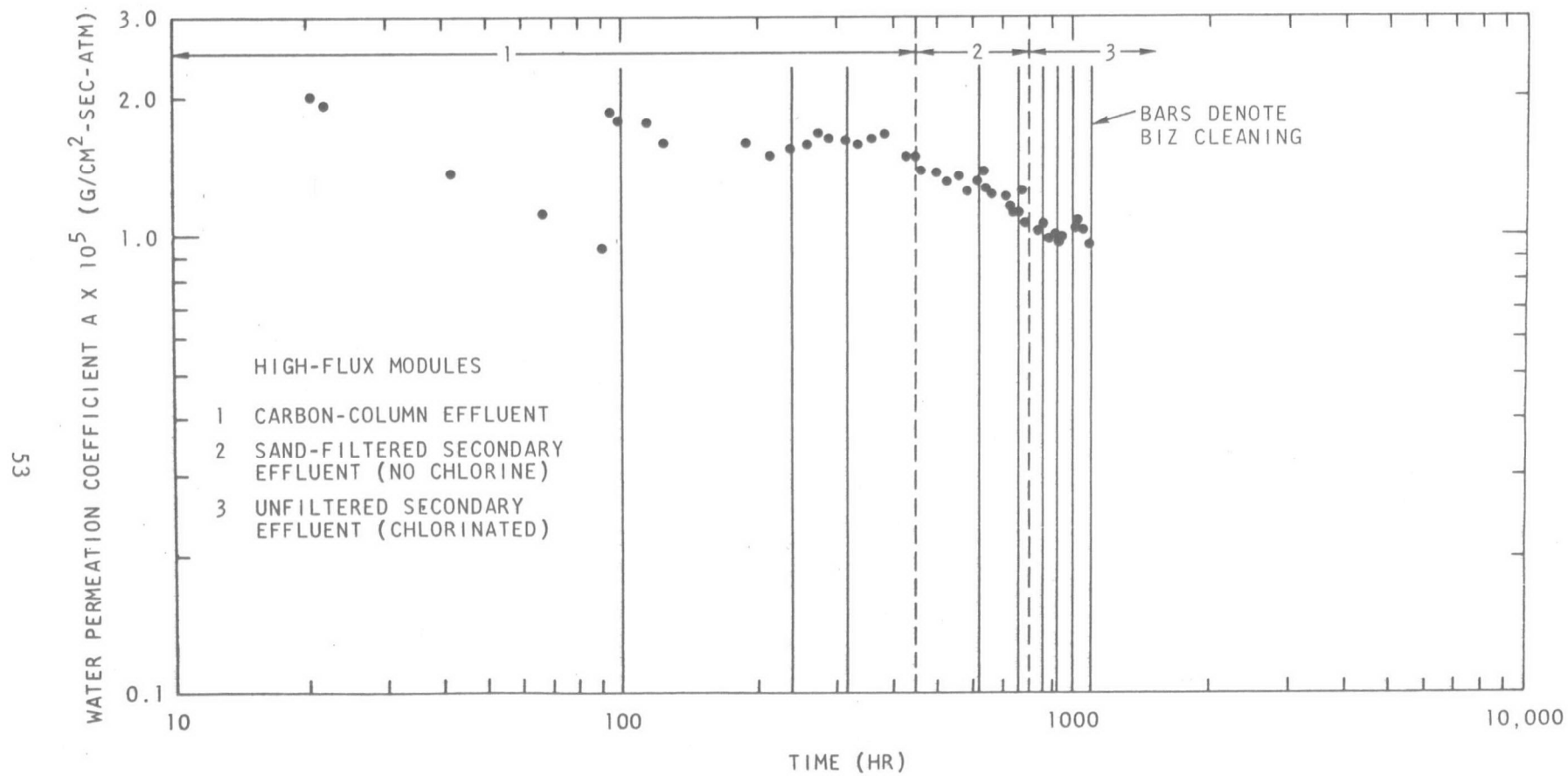Fig. 24. Percent TDS rejection versus time; Pomona Unit II, Phase V

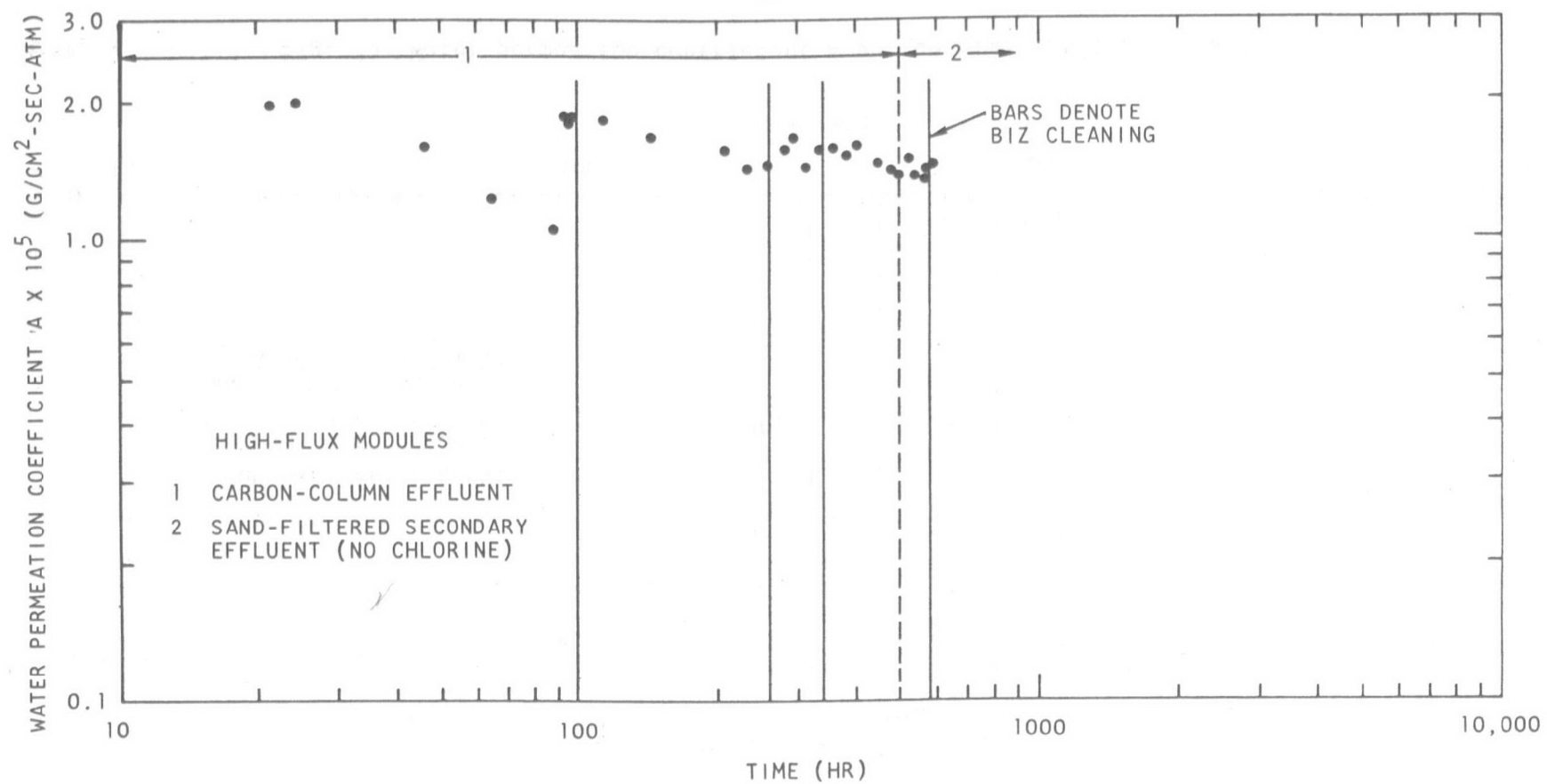Fig. 25. Water permeation coefficient A versus time; Unit I, Phase V

53

Fig. 26. Water permeation coefficient A versus time; Unit II, Phase V

54

MEMBRANE/MODULE CLEANING TESTS

Almost immediately after the initiation of operation of the two new 10,000 gpd reverse osmosis pilot plants at the Pomona facility, it became apparent that the available techniques for controlling membrane fouling were not adequate.

Preliminary procedures for screening various compounds and techniques in the laboratory were established. Earlier consideration had been given to three basic approaches. The first involves the removal from the feed of substances to which fouling could be attributed; the second involves addition to the feed of additives that would inhibit fouling; and the third is the use of cleaning techniques and additives to remove from the membrane rejection surface and brine channels the materials that seriously affect plant performance and efficiency. This discussion is primarily concerned with the third approach, although there is included within this report some information on the first and second approaches obtained during the field operations.

The criteria for any approach to cleaning required that the technique or materials should be economical, generally available, easily controlled, and not detrimental to the reverse osmosis modules or system. One classification of materials which came to the attention of the project was the new, commercial, enzyme-containing laundry presoaks, and enzyme-containing laundry detergents. The use of enzymes as an aid to cleaning reverse osmosis modules was under review since gross analyses performed on scrapings from modules used at Pomona and at Santee in earlier studies had shown that these scraped materials were principally organic. Dean et al. (Ref. 1) and Busch and Stumm (Ref. 2) have described the colloidal and suspended material in secondary effluents as mostly biological debris

consisting of proteins, lipids, and polysaccharides. It thus appeared
possible that an enzyme product might be found that would loosen the
bond of the deposited material on the membrane and hasten its removal.

The first tests were made with BIZ (Proctor and Gamble), an enzyme
laundrey presoak. A sample of membrane from a "dirty" Pomona module was
immersed in a solution containing 10,000 mg/l of BIZ at 35°C for 30 min.
The solution had a pH of 9.9. The membrane cleaned up rapidly, compared
with no change in a control sample in water.

A fouled Pomona module (3009A, No. 423) was placed in a laboratory
test loop at 600 psi and checked on a sodium chloride solution. The
following performance was recorded:

$$\text{Rejection.} \ldots \ldots \ldots \ldots \ldots \ldots .92.42\%$$
$$\text{A (water permeability coefficient)} \ . \ .0.92 \times 10^{-5} \text{ g/sq cm-sec-atm}$$
$$\text{B (salt permeability coefficient).} \ . \ .2.95 \times 10^{-5} \text{ cm/sec}$$

The module was then given a static soak in a BIZ solution (pH 9.9,
2000 mg/l) for 30 min at 40°C. The module was retested at 600 psi,
with the following results:

$$\text{Rejection.} \ldots \ldots \ldots \ldots \ldots \ldots .92.16\%$$
$$\text{A.} \ldots \ldots \ldots \ldots \ldots \ldots \ldots .1.016 \times 10^{-5} \text{ g/sq cm-sec-atm}$$
$$\text{B.} \ldots \ldots \ldots \ldots \ldots \ldots \ldots .3.4 \times 10^{-5} \text{ cm/sec}$$

There was an approximately 10% increase in water flux. A postmortem
showed that the module was cleaner than a similar uncleaned module from
the same pressure vessel. To determine the effect of the BIZ solution
on salt rejection, samples of cellulose acetate membrane were immersed
in 10,000 mg/l BIZ solutions. One solution had a pH of 9.9, and one was
adjusted to pH 7.5 with HCl. The membrane was tested several times over
a 48-hr period. The sample at pH 7.5 was unaffected; the sample at

pH 9.9 showed a more than tenfold increase in B. As expected, the membrane could be seriously damaged by hydrolysis on exposure to a pH of about 10 in relatively short periods. However, the potential of being able to clean the membrane with the laundry presoak was important enough to extend the tests to the field operation and to expand the laboratory investigation to determination of the parameters that might be controlled to improve cleaning while limiting membrane damage. The field units were flushed in a recycle mode (closed loop) with a BIZ solution of 10,000 mg/l for 50 min at ambient temperatures. Each pilot plant showed a 20% increase in product water flow following the cleaning, with no significant change in TDS rejection.

A survey was made of the available compounds on the market which might be of value in module cleaning. These were tested on "dirty" membrane samples from a used module from Phase I of the field study. A proteolytic enzyme, Rhozyme PF, and non-ionic detergent were included. The results, based on visual observation as noted, are shown in Table 8. Any attempt to test these samples in a high-pressure reverse osmosis cell would have caused scouring of the rejection surface and affected the results.

Since BIZ appeared to be clearly superior to the other products tested at that time, additional tests were run on BIZ in an effort to optimize the cleaning conditions for reverse osmosis modules. The results are detailed below:

(a) pH 10.2 (normal BIZ solution pH). Samples of membrane from fouled Pomona modules were subjected to concentrations of 10,000, 20,000, and 40,000 mg/l at 23° (ambient) and 40°C for 10, 20, and 40 min. At 23°C, the best visual cleaning results were obtained at 20,000 mg/l in 40 min. The results at 40,000 mg/l showed no improvement over 20,000 mg/l. At 40°C, excellent cleaning was found at 10,000 mg/l in 10 min.

(b) pH 7 (BIZ solution adjusted with HCl). Tests listed in (a), above, were repeated at pH 7. The increase in temperature did not have as great

TABLE 8

INITIAL ENZYME DETERGENT SURVEY[a]

The concentration level for all tests was 10,000 mg/l.
The soak time was 30 min.

Product Sample[b]	pH at 23°C	Soak Test		
		At 23°C	At 55°C	At 23°C with pH 7.5, HCl
Axion (1) (Colgate Palmolive)	10.4	Fair	Good	Poor
BIZ (1) (Proctor and Gamble)	10.20	Good	Excellent	Fair
Family Tree (2) (Calusa Chemical Co.)	10.15	Poor	Good	Poor
Gain (2) (Proctor and Gamble)	10.25	Fair	Good	Very poor
Tide XK (2) (Proctor and Gamble)	9.92	Poor	Good	Very poor
Drive (2) (Lever Bros.)	10.0	Fair	Good	Poor
Rhozyme PF (Rohm and Haas Enzyme with 0.1% Triton X-100)	7.5	Poor	Good	Poor

[a]Definition of visual appraisal terms: Excellent = definite slime removal
Good = definite loosening of slime
Fair = small amount of slime is loosened
Poor = very little slime loosening
Very poor = very little to no slime loosening

[b]Samples are categorized as follows: (1) = laundry presoak, and (2) = enzyme detergent. Use of trade name does not constitute an endorsement or recommendation by the Federal Government of the item or product mentioned.

an effect on cleaning as in (a). At pH 7, higher BIZ concentrations were required. The best cleaning results at pH 7 were not as good as could be obtained at pH 10 and required a 50,000 mg/l concentration. Satisfactory cleaning can be reached with the 50,000 mg/l at pH 7 and 40°C in 40 min. Solutions containing 60,000 mg/l were difficult to prepare.

(c) pH 5 (BIZ solution adjusted with HCl). Very poor cleaning resulted at pH 5 with all concentrations, time, and temperatures. An unknown precipitate is formed in the low pH solution.

Membrane was then subjected to 20,000 mg/l BIZ solutions at pH values of 7, 8, 9, and 10.3. Hydrochloric acid was used to adjust the pH. The initial membrane parameters were sodium chloride rejection 97.3% with an A of 1.9×10^{-5} g/sq cm-sec-atm.

At pH 7 no significant changes were observed after two days and after four days. Slight changes were observed at pH 8. After two days at pH 9, rejection had dropped to 92.4% and an A of 1.9×10^{-5}. Membrane exposed at pH 10.3 gave 60% salt rejection and A of 1.8×10^{-5}. These data are consistent with previous information obtained on the effect of pH on cellulose acetate membranes. The rapid membrane deterioration observed in the static tests, however, has not been observed when the enzyme preparation was used at its normal solution pH in the weekly field cleaning procedures. Figure 27 shows the results of the 28-day static exposure but is somewhat misleading since during the period of the experiment the pH changed, probably due to acetic acid from membrane hydrolysis and atmospheric carbon dioxide absorption.

The pH values of the solutions at 4 and at 28 days are shown below:

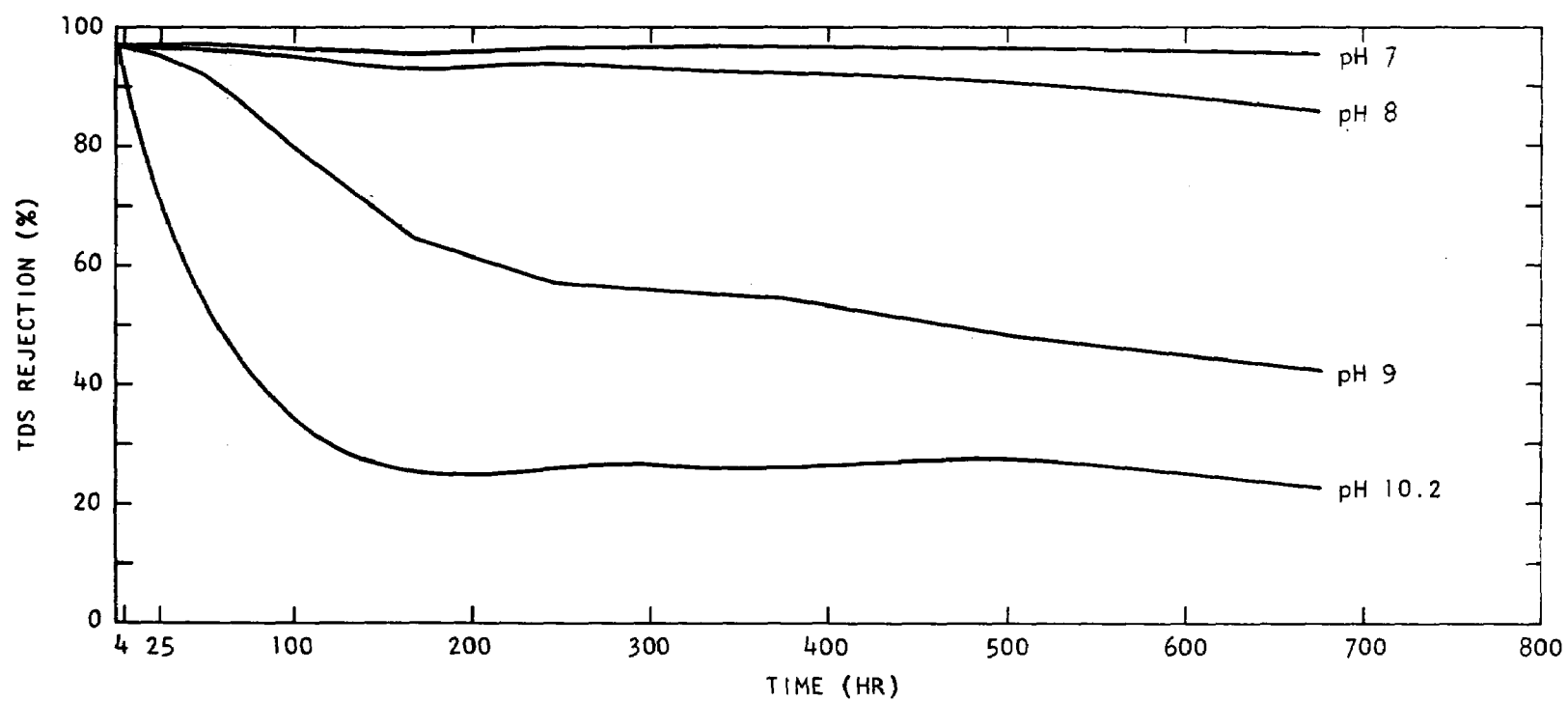| Original pH	4 days	28 days
7	7	6.4
8	7.7	7.3
9	8.9	8.0
10.3	9.2	8.3

59

Fig. 27. Percent TDS rejection versus time; membrane life test in BIZ solutions at various pH levels

MODULE CLEANING

A portable individual module cleaning system (Fig. 28) was built at the laboratory and taken to Pomona. Modules were removed from the 10,000 gpd reverse osmosis loops and each was cleaned in a 10,000 mg/l solution of BIZ. Modules from Unit II operating on secondary effluent were cleaned by recirculating the BIZ solution for 30 min at 29°C and were then flushed with tap water for 10 min. Modules from Unit I operating on carbon-column-treated secondary effluent were cleaned for 20 min at a temperature of 19°C and then flushed with tap water for 10 min. The cleaning took place during Phase III of the field operations.

Unit II modules had an average pressure drop of 6.2 psi before cleaning and 3.9 psi after cleaning under the cleaning-loop flow conditions of about 3 gpm and low pressure. After cleaning, the flow rate through the brine channels was observed to increase. Before the modules were cleaned, Unit II (secondary effluent) was producing only 0.75 gpm of product water. After cleaning, the product flow had increased to 3.3 gpm. After 100 hr of operation, the product water flow rate had dropped to 2.3 gpm. One of the modules, the first one in tube 1, Unit II (secondary effluent), Phase III, was removed from Unit II at about 100 hr after the individual module cleaning and was postmortemed to find out why a flux level approaching the original value had not been restored and why the pressure drop was higher than that for Unit I. Solid inorganic deposits were present in substantial amounts. Samples were collected and submitted for analysis with the results shown below. The composition of the solid material was based on X-ray diffraction data.

% Ash (600°C) 80.9

% Calcium in ash 29.8

% Magnesium in ash. 0.026

% Sulfate in ash 48.4

% Phosphate in ash. 15.4

Crystalline material. . . . . . $Ca(SO_4)_x (HPO_4)_y \cdot 2H_2O$, where $y/x = 4$.

SYSTEM PRESSURE

PRODUCT WATER

PVC
VESSEL
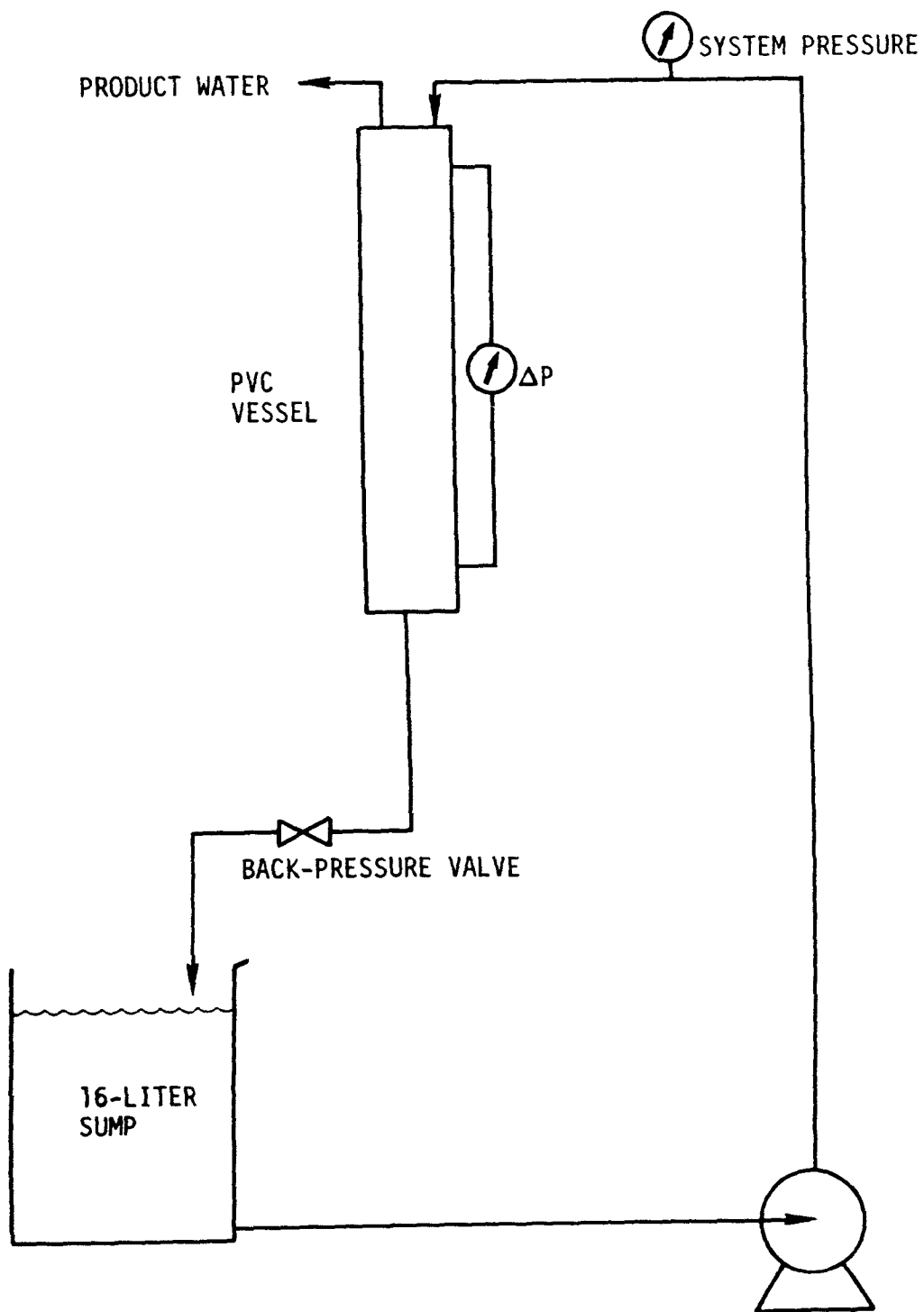
ΔP

BACK-PRESSURE VALVE

16-LITER
SUMP

Fig. 28. Schematic diagram of portable cleaning loop

Deposition of this material could have been caused in several ways basically associated with poor flow conditions within the brine channels, such as can be caused by seal failure that permits water to bypass the modules or loss of pH control.

The modules from Unit I which treated carbon-column effluent had experienced much less fouling and had an average initial pressure drop of 1.26 psi before cleaning, which decreased to 0.9 psi per module after cleaning. The product water flow from Unit I increased from 4.4 gpm to 4.8 gpm after the modules were cleaned. The module cleaning procedure had not been entirely effective, inasmuch as the initial performance, on January 16, 1969, had been 8 gpm. This decline could not be attributed solely to compaction but obviously included fouling.

Several modules from Phase III of the field study which had operated on carbon-column effluent were returned to the laboratory for cleaning. Individual modules were placed in the portable cleaning loop noted above, and a number of different solutions were tried at room temperature. The following results are based on visual observations of the disassembled modules.

(a) A solution containing 10,000 mg/l of BIZ was recirculated for 30 min at 22°C; the pH of the solution was 10.2. The flushing solution turned dark. Much of the membrane remained covered with a loose coating of slime.

(b) A commercially available heavy duty detergent ("409") solution* prepared by diluting 200 ml in 12 liters of water was circulated for 30 min at 22°C. The water remained clear. Postmortem showed loosening of the slime, but no removal.

(c) A solution of hydrogen peroxide was prepared by diluting 500 ml of 30% H_2O_2 in 12 liters of water and flushing for 30 min at 22°C. The

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*Mention of commercial products does not imply endorsement by the Federal Water Pollution Control Administration.

water became dark in color, and effervescence due to oxygen appeared in the sump. There did not appear to be any slime removal from the membrane.

(d) An attempt was made to use osmosis to clean the membranes by filling the brine channels with a 3% sodium chloride solution. The product water side of the modules was filled with distilled water by connecting the product water tube to a carboy of distilled water. In effect then, a flow of clean water was created back through the membrane since there was an osmotic pressure difference of about 300 psi. The brine remained clear, and 10,000 mg/l of BIZ was added after 15 min. The test ran for 30 min at 22°C. On examination, compared with previous subjective examination, the cleaning was considered to be fair to good except near the product water tube, where limited recirculation occurs.

(e) A 10,000 mg/l solution of Rohm and Haas Bate 1130D (pancreatic enzyme) was tried for 30 min at 22°C. The slime was loosened but not removed.

Two modules from Phase III that had operated on an activated-carbon-processed feed were cleaned with a BIZ solution in the laboratory to determine the effects of elevated temperatures and BIZ concentrations. Both modules had shown a significant reduction in water flux over the initial quality control performance. The modules were cleaned with a 20,000 mg/l BIZ solution at 45°C for 60 min. The solution was adjusted to pH 5 with HCl to minimize any possible change in membrane characteristics. There was little change in the module performance after cleaning. The modules were opened, and the membrane examined. The membrane appeared very clean; in fact, it was characterized visually as the best that had been observed. However, after samples of the membrane were cleaned ultra-sonically, there was a 50% increase in water flux and the A values increased from 1.24×10^{-5} to 1.74×10^{-5}.

A module made with a thinner brine-side spacer (Chicopee woven fabric) from Phase IV of the field study was tested and examined after

650 hr of operation on carbon-column effluent. The module had been subjected to a regular cleaning program while in operation and visually was in very good condition and clean. Ultrasonic cleaning of the membrane samples gave about a 10% increase in the membrane water flux. The ultrasonic cleaning procedure for cleaning membrane samples restores the surface to a "new" condition and is valuable for preparing controls. There is no damage to the rejection surface by ultrasonic cleaning. It has also been demonstrated that the cleaning procedures are not entirely adequate. It appears that the slimes or membrane coatings can be loosened by treatment with various cleaning solutions, but that some sort of turbulent action within the brine channels is necessary for wholesale removal of fouling. Increasing the flow of the cleaning solution may be of significant help in attaining clean membrane.

A series of preliminary tests were run with enzyme samples obtained from several manufacturers. Slime-coated membrane from used modules were exposed to enzyme solutions with and without a non-ionic detergent, Triton X-100.* The results were poor. None of these materials produced results as good as the best compound found thus far, BIZ. Data sheets obtained from the manufacturer, Proctor and Gamble, indicate that BIZ contains, in addition to the enzyme, a detergent, a builder (probably a polyphosphate), and sodium perborate. Evidently, this is a synergistic combination as far as membrane cleaning is concerned.

Only a relatively small amount of effort has been expended as yet, however, in developing satisfactory cleaning techniques, compounds, and systems for reverse osmosis loops, particularly in waste water treatment and renovation. The work performed in this contract has been useful in demonstrating that a certain group of materials may have value. Additional screening of enzymes and combinations of enzymes and other compounds is necessary to develop a "cleaning" compound that will produce the maximum cleaning in the minimum time and with minimum damage to the modules.

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*Mention of commercial products does not imply endorsement by the Federal Water Pollution Control Administration.

Additional work is required on the "direct" osmosis approach, including combining this approach with cleaning compounds. More data are required on the effect of increasing brine-channel flow and turbulence as an aid in cleaning. Pressure differential measurements across the modules or pressure tubes have had only limited usefulness as an indicator of fouling since a module with coated membrane may have suffered a major flux decline with virtually no change in pressure drop.

CHLORINATION

Disinfection of reverse osmosis systems and of the feed and product water appears to be desirable for a number of reasons. The presence of biological forms such as bacteria, algae, and molds in the raw water feed may cause fouling of the membrane and brine channels. Some evidence has been published (Ref. 3) that demonstrates membrane degradation by bacteria or other microbiological organisms on membranes that were contaminated before or during service.

The disinfectant, if possible, should be low in cost, generally available, effective in low concentrations, easily handled and fed, and the solution concentration readily determinable at low concentrations. Chlorine in its various active forms fits this picture of a suitable disinfectant for reverse osmosis systems. It is the most commonly and widely used chemical for biological control of potable, waste, and industrial waters, so much so that chlorine may be almost impossible to avoid in feed waters and from potable or waste water sources.

An important consideration is that the disinfectant must not damage or degrade either the cellulose acetate membrane currently in use for reverse osmosis or other module or system components. Periodic references to free chlorine in feed waters have been ambivalent about the effect of chlorine on cellulose acetate membranes. Previous experiments (Ref. 4) have shown that continuous exposure of the membrane to relatively high concentrations of free chlorine (10 to 50 mg/l) in San Diego tap water had measurable effects on cellulose acetate membranes in comparatively short times of 12 to 15 days. Definite deterioration had been initiated in the membranes with 50 mg/l chlorine exposure. Salt rejection had decreased and the water flux had increased. At the 10 mg/l continuous

exposure level in 15 days, the salt rejection measurements showed no change, however, and the membrane coefficient had shown a slight increase which did not appear significant.

Little or nothing has been known about the effect of prolonged exposure to concentrations of about 2 mg/l or less of free chlorine. Prior experience at the Pomona facility was obtained on the 5000 gpd spiral-wound system operating on activated-carbon-treated secondary effluent at approximately 2 mg/l combined chlorine residual, and on secondary effluent at the same residual processed through single modules at low pressures. At Pomona, 2 mg/l combined chlorine residual appeared to exercise satisfactory biological control and to have little effect on the membrane in exposures exceeding six months.

The laboratory experiment on the effects of chlorination on the membrane was an effort to obtain quantitative long-term exposure data since the field experiments were limited to 30 days.

The laboratory experiment was conducted using City of San Diego tap water as a basic supply. A set of controls was established by using membrane samples that were immersed in flowing tap water that was de-chlorinated in an activated-carbon column. Two complete sets of membrane samples, including controls, were run. One set consisted of high-selectivity, standard-rejection membrane, and the other set consisted of high-flux membrane. The selectivity and flux of the semipermeable cellulose acetate membrane are controlled by the heat treatment to which the membrane is subjected; the higher the temperature, the greater the rejection and the lower the water flux. Enough membrane was used in the experiment to permit at least four samples each of the chlorinated and control membranes to be taken for testing every week. The membrane samples of each type were taken from the same roll or production lot. Since the pH of San Diego tap water may be as high as 8.0 or higher, which could easily affect the membrane by hydrolysis of the cellulose acetate, the pH of the water was adjusted to below 7 using sulfuric acid, and was between pH 5.5 and 7

during the test. An Advance Chlorinator operating on gaseous chlorine was used to control the concentration at 2 mg/l in the test stream to which the chlorinated samples were exposed. Chlorine concentrations were tested frequently and at least daily to ensure that the concentration was maintained. The ortho-tolidine test was used for control and was checked against the starch-iodide titration at the start. The laboratory tests were based on free chlorine exposures. Samples of the chlorinated membrane and the controls were removed weekly and tested at 800 psi with a 10,000 mg/l sodium chloride solution.

Figures 29 and 30 show the solute (NaCl) rejection versus time for high-flux and high-selectivity membranes, respectively, exposed to approximately 2 mg/l chlorine over a 29-week period. Figures 31 and 32 are plots of B, the salt permeability coefficient, for the same membranes during the same period. It is apparent that there have been some detrimental changes in the chlorinated membranes. There has been a small but significant change in the water permeation coefficient A and a large change in the salt permeation coefficient B of the exposed membranes. This is reflected in a decrease in salt rejection for the chlorine-exposed samples. A substantial decline in salt rejection occurred after the eighth week of exposure. The laboratory facility suffered a power and water failure during the eighth week, and a remote possibility exists that the samples could have been exposed to elevated chlorine levels for many hours. However, the Advance Chlorinator is a vacuum-feed unit, and in the event of a water failure should shut off completely. The high-selectivity membrane did not change between the eighth and twenty-ninth week following the initial loss in performance. The high-flux membrane did show some continuing change, but at a much slower rate than the change that occurred between the eighth and tenth weeks. This tends to lend credence to the possibility that excessive exposure occurred. Nothing that happened affected the control samples. The total chlorine exposure at 2 to 2.5 mg/l for the eight-week period was of the same order as the earlier 10 mg/l exposure for 15 days. During the 10 and 50 mg/l chlorination tests reported earlier (Ref. 4) the membrane changes were gradual, as expected, and not abrupt. Addtional chlorine exposures will have to be made under controlled laboratory
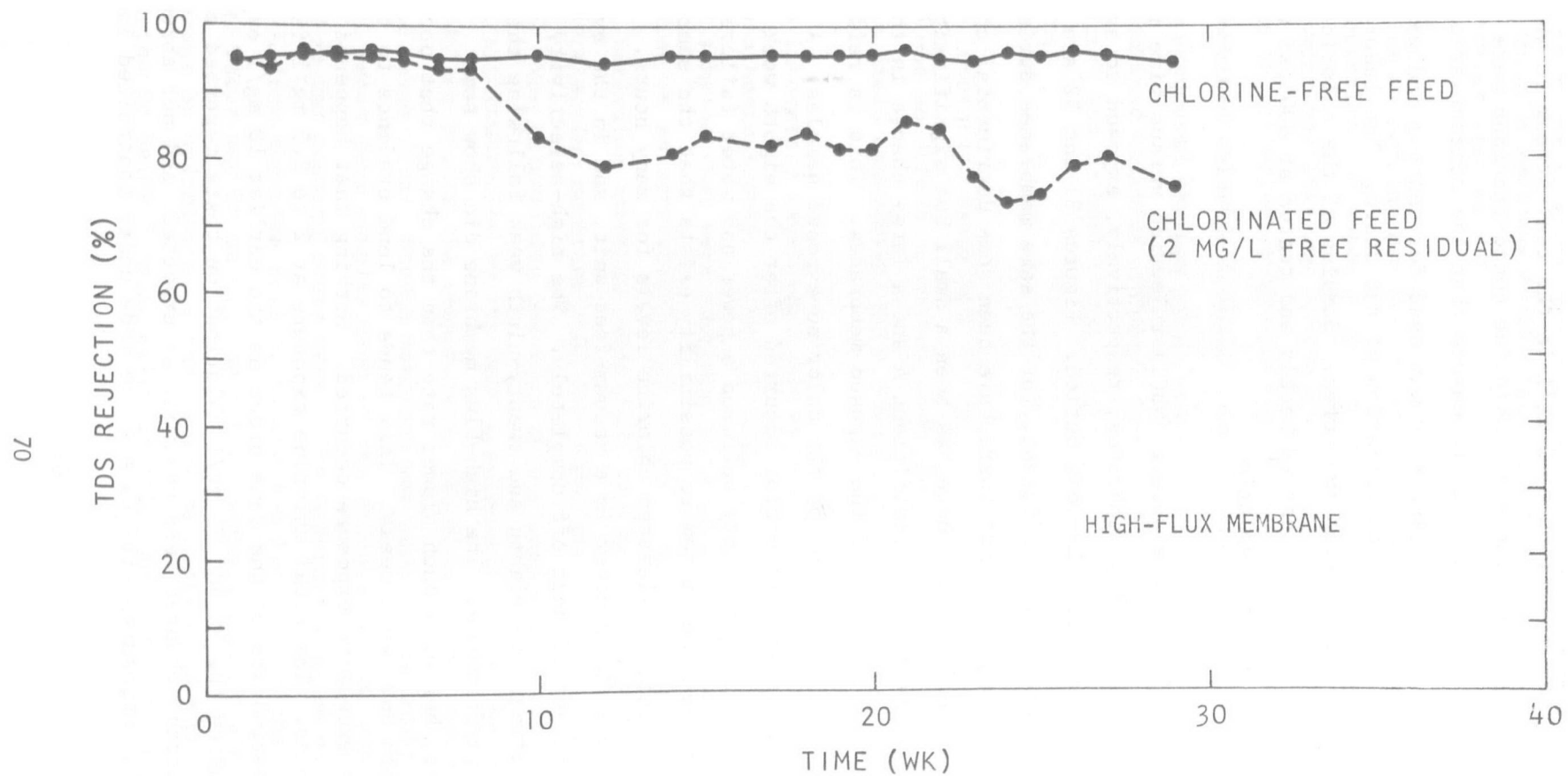
69

Fig. 29. Percent TDS rejection versus time; high-flux membrane operating on chlorinated feed (2 mg/1 free chlorine residual) and on chlorine-free feed
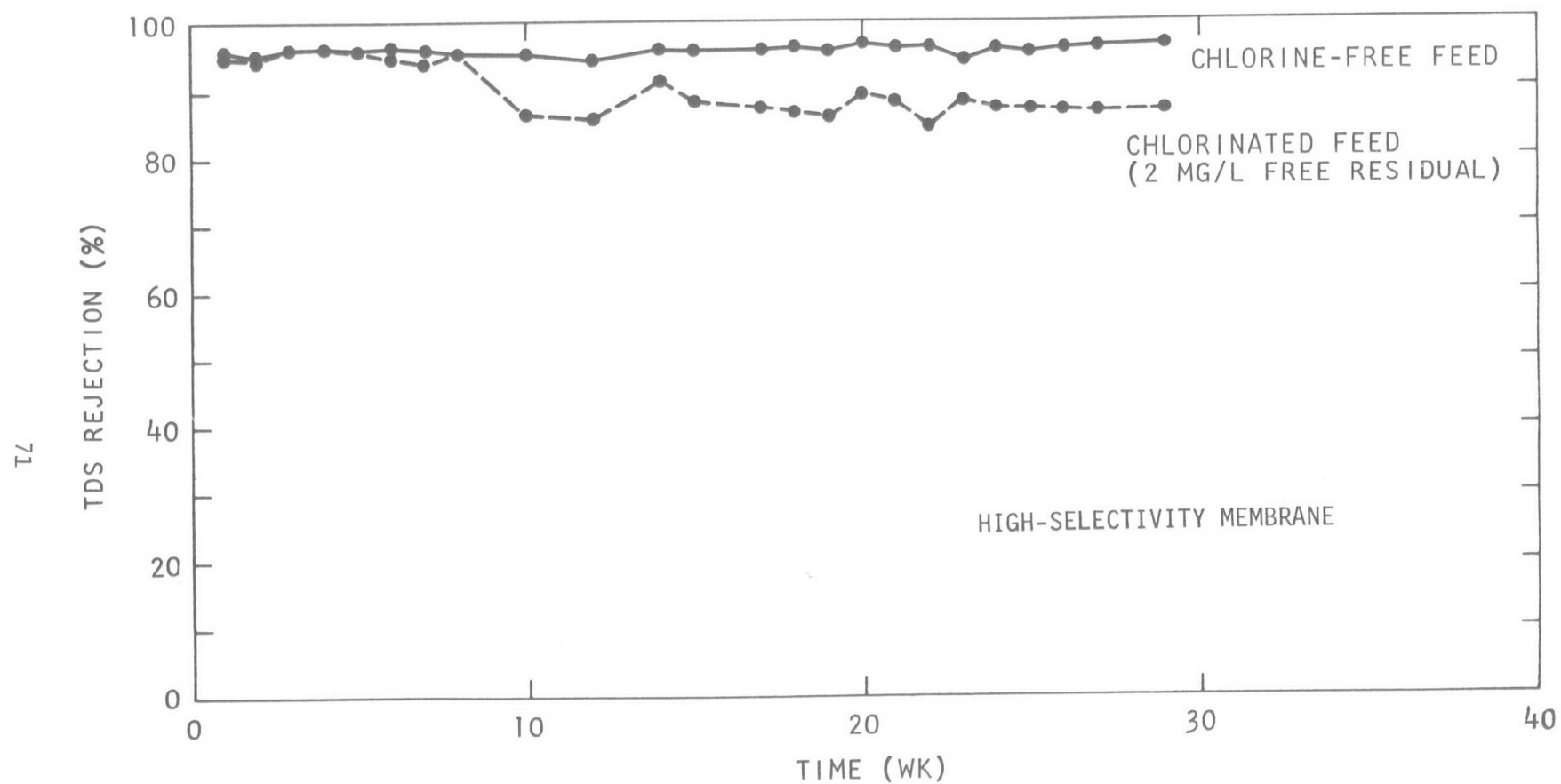
70

Fig. 30. Percent TDS rejection versus time; high-selectivity membrane operating on chlorinated feed (2 mg/1 free chlorine residual) and on chlorine-free feed
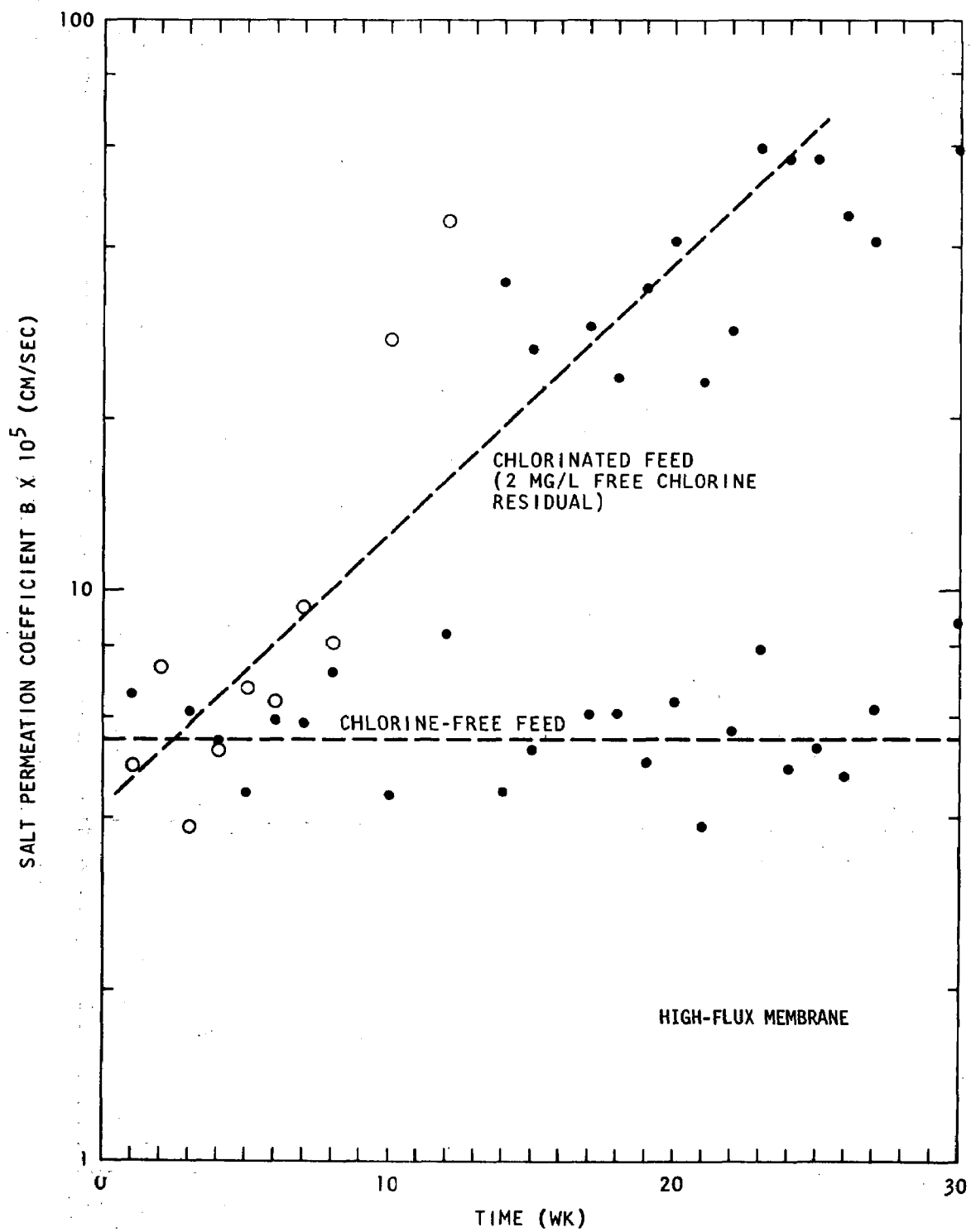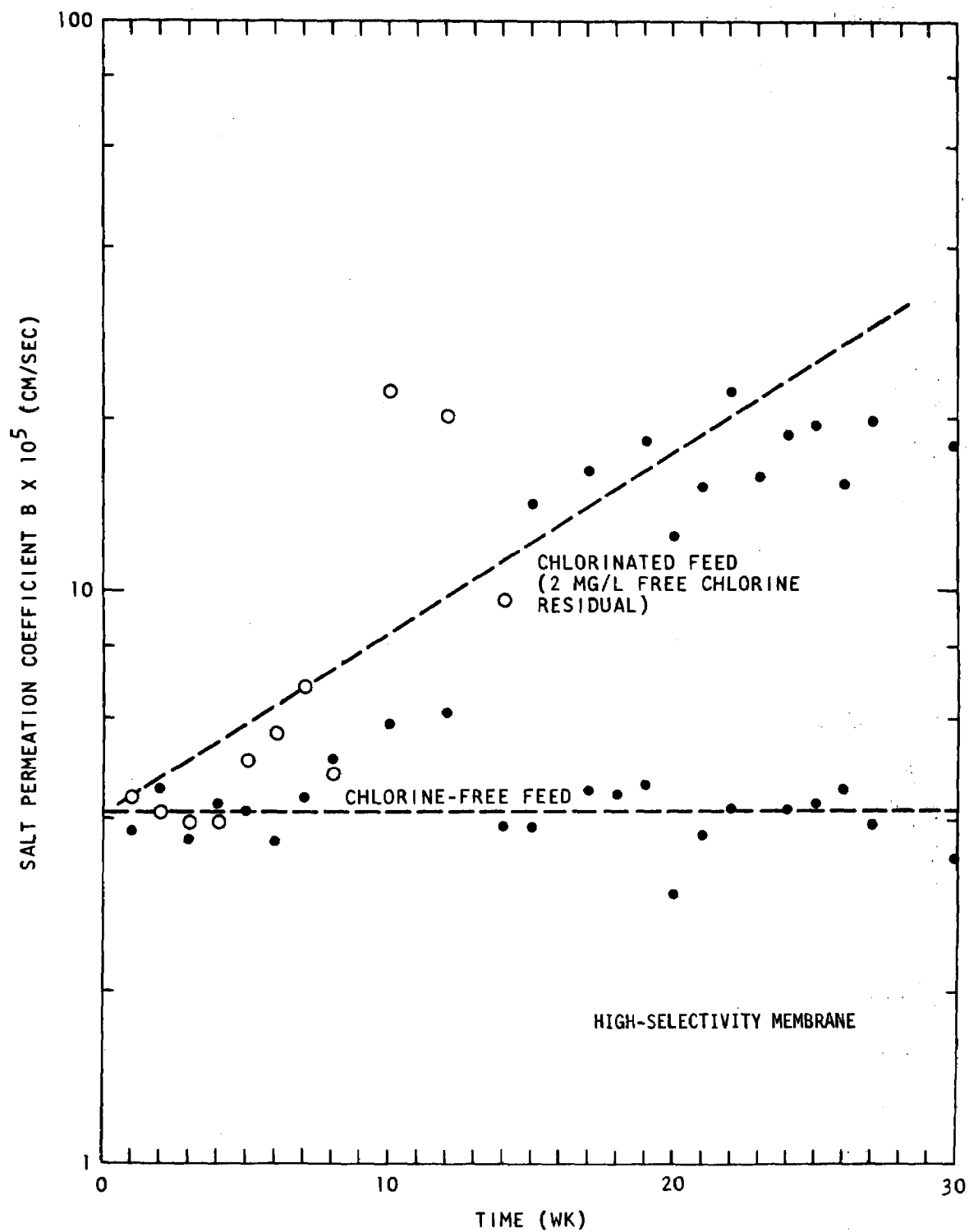
Fig. 31. Salt permeation coefficient versus time; high-flux membrane operating on chlorinated feed (2 mg/l free chlorine residual) and on chlorine-free feed

Fig. 32. Salt permeation coefficient versus time; high-selectivity membrane operating on chlorinated feed (2 mg/l free chlorine residual) and on chlorine-free feed

conditions, and tests using chloramines as well as free chlorine should be included since the ammonia concentration in secondary effluents such as at Pomona are high enough to ensure that all available chlorine will be present as chloramines. Weekly tests of intermittent chlorination at the 10 mg/1 level were not made.

SUMMARY AND CONCLUSIONS

A principal objective of the program was to find and develop the parameters and conditions that would best permit operation of reverse osmosis systems on waste waters receiving secondary treatment. To a considerable extent, the relatively short-duration tests made under this contract have accomplished the goals outlined in the proposal. The short-term tests that were conducted cannot substitute for prolonged runs of one to three years, which are necessary to show that reverse osmosis systems can produce a high-quality product water economically. The techniques that have been developed within the scope of this contract for maintaining membrane water flux have shown great promise but certainly are at an early stage of development. For example, the enzyme-based cleaning compound that made it possible to get sustained runs with feedwaters which can cause serious module fouling should be improved, if possible, to produce more complete and rapid cleaning with little or no effect on the membrane properties.

The first phase of the project was designed to compare and to attempt to achieve continuous operation of the two reverse osmosis pilot plants utilizing 50 sq ft modules made with high-selectivity membrane. One loop was fed with sand-filtered secondary effluent and the other with secondary effluent treated with granular activated carbon. (Prior to this study, sustained operation at 600 psi had been attained only with the carbon-column effluent. The air-water flushing method had been moderately successful in keeping the unit running.) Phase I demonstrated that the plants could not be operated continuously either on secondary effluent or carbon-column effluent without a great improvement in pretreatment or cleaning techniques to maintain water flux.

Phase II of the project was originally established to compare the performance of high- and standard-water-flux membranes in the 50 sq ft modules operating under the best possible feedwater conditions. Operational data indicated this was the effluent from the carbon columns. At this point, the enzyme-based cleaning compound that had demonstrated definite cleaning potential in the laboratory was introduced into the field study. The flux decline slope of both the high- and standard-flux modules was maintained close to that which might be expected from compaction without fouling by use of the enzyme compound. Phase II demonstrated that it would be economical to operate with high-flux membranes in the modules since it was possible to maintain a water flux approaching reference values and that the product water from the high-flux membranes was of high quality.

The standard-flux system operating on carbon-column effluent reduced the total chemical oxygen demand (COD) from 6.3 to 0.25 mg/l (average values), the phosphate as PO_4 from 25.3 to <0.1 mg/l, and the total dissolved solids (TDS) from 651 to 40 mg/l (93.8% removal). The high-flux system operating on carbon-column effluent reduced the total COD of the feed from 7 to 0.8 mg/l (average values), the phosphate as PO_4 from 24.8 to <0.1 mg/l (>99% removal), and the TDS from 555 to 35 mg/l (93.7% rejection). The rejections noted are not based on a feed-brine average concentration but are based on the ratio of feedwater concentration to product-water concentration. Normally, the feed-brine concentration or a weighted mean is used in calculating membrane parameters and system operational effectiveness. To illustrate actual results obtained or desired in water renovation, the product-water values are compared directly with the feed concentrations. Of particular interest in organic carbon rejection is that the level of organic carbon (as shown by the COD) is very much lower in the product water from a reverse osmosis loop (<2 mg/l COD) than the effluent from activated-carbon treatment alone (6 to 12 mg/l COD). The constituents of the COD which are not removed by activated carbon are not necessarily the same as those that are not

rejected by reverse osmosis. For example, phenols, in general, will be transported through a reverse osmosis membrane, whereas they may be readily adsorbed by carbon.

In Phase III, comparisons were made of the results of operating modules containing high-flux membranes on unfiltered secondary effluent and on activated-carbon-processed secondary effluent using enzyme-based cleaning compounds to keep the systems functioning. The average total COD in the carbon-column feed (12.1 mg/l) was reduced by 96%, to 0.5 mg/l; the reduction in COD using secondary effluent (41.6 mg/l) was 95.7%, to 1.8 mg/l. Phosphate reduction was greater than 99% and TDS reduction was greater than 90%. Ammonia rejection on carbon-column feed was 85% and on secondary effluent, 70%. Nitrate rejection on carbon-column feed was 66% and on secondary effluent, 58%. Product-water COD values are so low that their accuracy may be subject to some suspicion. The flux decline slopes for Phase III were -0.24 for secondary-effluent feed and -0.14 for the carbon-column-treated feed. These were higher than expected. It was found that the COD of the feed from the carbon columns in Phase II was between 3 and 9 mg/l since the carbon had just been regenerated, whereas during Phase III, the feed had a COD of between 9 and 15 mg/l. A review of the operating data indicates that there is a direct relationship between the rate of membrane fouling and the increases in COD of the feed.

The brine seals, which were made of Buna-N rubber, failed in the loop operating on secondary effluent, which created serious boundary-layer problems since much of the brine bypassed the brine channels within the modules. This also caused excessive fouling to occur. New brine seals made from ethylene-propylene copolymer, which has superior resistance to oxidation and solvents, were installed, and the module diameter tolerances were adjusted to make the seals operate more effectively. Brine recirculation was initiated, which permitted higher product water recoveries.

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Phase IV was concerned with the use of brine spacers thinner in section than the standard polypropylene Vexar, which is 0.045 in. thick. The advantages to a thinner brine spacer are that it permits higher membrane packing densities per unit pressure-vessel volume and offers the possibility of greater turbulent flow conditions in the channel. The disadvantages are increased pressure losses and possibly greater module fouling. The study showed no marked differences in performance between modules made with large and with small brine-side spacers, except for higher pressure differentials. The pressure drop across the loop with the standard brine spacer was 16 to 20 psi; the pressure drop across the thin spacer was 70 to 75 psi. The 3.75-in.-diameter module made with the thin spacer would contain 25% more membrane area.

Phase V of the field operations was modified to permit the modules in one loop to be reoriented vertically. In single-module studies, it had appeared that cleaning was improved and fouling more readily controlled in a vertical position versus horizontal; however, the short-duration test showed no major differences in the operation of vertical versus horizontal pressure vessels. The pressure loss for the vertical system was 90 psi, due principally to the piping arrangement, almost 5 times that of the horizontal unit. At the start of Phase V, pH control of the feed was temporarily lost. Water production dropped very rapidly but was restored when operation of the acid control was resumed. The flux decline was due to the precipitation of calcium carbonate and calcium phosphate within the modules.

The use of the enzyme-based cleaning compound (BIZ) on a regular cleaning schedule has made it possible for the first time to get extended operation of reverse osmosis systems running on secondary effluents and on activated-carbon-treated secondary effluents. The most successful cleaning compound has an optimum pH of approximately 10; at this pH, membrane degradation can occur rapidly. Additional work is required on formulating and testing a compound that will work at a less alkaline pH. However,

the limited field experience with the alkaline enzyme detergent using short contact periods of 30 min has not shown the severe membrane degradation found in the laboratory soak test. This may be due partly to the less severe exposure in use under dynamic conditions and to a protective effect of membrane coatings and slimes. More work is also required in optimizing methods of flushing to remove the fouling material from the membranes. The cleaning techniques developed on spiral-wound modules will be useful for all kinds of reverse osmosis configurations. One specific advantage to the spiral-wound module for this purpose is the ability to examine individual modules easily and to test membranes during extended runs with a minimum amount of disturbance to the test as a whole.

Some of the variations that were introduced require long-term tests to determine whether any advantages are to be gained or improvements made, as in vertical versus horizontal module orientation and large versus small brine spacers. Additional work is required in optimizing the frequency of cleaning during long-term operation.

The chlorination studies did not provide, at this time, a firm answer to the effect of low-level chlorination on membrane life and performance. Additional investigations are to be undertaken on specifically evaluating the effect on cellulose acetate membranes of low-level continuous chlorination versus intermittent application of chlorine. A comparison should also be made of the effect of chloramines as compared with free chlorine since the prevalent forms of active chlorine in waste-water chlorination are the chloramines.

APPENDIX

NOMENCLATURE

There are several relationships and expressions that have been used
in this report which may require some amplification or clarification.
Since no standard terminology is yet in use for reverse osmosis technology,
the expressions shown are those used at Gulf General Atomic. A comprehensive
review of reverse osmosis is available in Ref. 5, and there is a great
deal of information in the current literature.

The basic behavior of semipermeable cellulose acetate reverse osmosis
membranes can be described by two basic equations.

The product water flow through a semipermeable membrane may be
expressed as:

$$F_w = A(\Delta P - \Delta \pi) \, , \tag{1}$$

where

F_w = water flux (g/sq cm-sec),

A = water permeability coefficient (g/sq cm-sec-atm),

ΔP = pressure differential applied across the membrane (atm), and

$\Delta \pi$ = osmotic pressure differential across the membrane (atm).

The water permeability coefficient A has the following components:

$$A = \frac{D_1 C_1 \bar{V}_1}{RT \, \Delta x} \, , \tag{2}$$

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where

D_1 = diffusion coefficient for water in the membrane (sq cm/sec),

C_1 = dissolved water concentration in the membrane (g/cc),

$\overline{V}_1$ = partial molar volume of water in the external phase,

R = gas constant,

T = absolute temperature, and

Δx = membrane thickness (cm).

The salt flux through the membrane may be expressed as

$$F_s = B \ \Delta C , \qquad\qquad (3)$$

where

F_s = salt flux (g/sq cm-sec)

B = salt permeability coefficient (cm/sec), and

$\Delta C = C_1 - C_2$ = concentration gradient across the membrane (g/cc).

The salt permeability B has the following components:

$$B = \frac{D_2 K}{\Delta x} , \qquad\qquad (4)$$

where

D_2 = diffusion coefficient for salt in the membrane (sq cm/sec),

K = distribution coefficient ratio of the salt concentration in the membrane (g/cc) to the salt concentration in the solution (g/cc), and

Δx = membrane thickness (cm).

The water permeability and salt permeability coefficients are characteristic of the particular membrane which is used and the processing that it has received.

An examination of Eqs. (1) and (3) shows that the water flux is
dependent upon the applied pressure, whereas the salt flux is not. As
the pressure of the feedwater is increased, the flow of water through the
membrane should increase while the flow of salt remains essentially
constant. It follows that both the quantity and the quality of the purified
product should increase with increased driving pressure.

In Eq. (1), the water flux through the membrane, F_w, is directly
proportional to and increases with the net driving pressure $(\Delta P - \Delta \pi)$.
The osmotic pressure of a water solution is proportional to the concentra-
tion of the solute. Since the water flux F_w is proportional to the net
driving pressure, the amount of water from a given system operating at
a specific applied pressure will depend on the osmotic pressure of the
feedwater. As the feed passes through the reverse osmosis systems, and
water (and, to a very small extent, salt) passes through the membrane,
the concentration of dissolved substances in the feedwater (or brine)
increases. This causes a marked increase in the osmotic pressure differ-
ence $\Delta \pi$ and reduces the available driving pressure, which in turn results
in a lower water flux. The average osmotic pressure to which the membrane
is exposed is a function of the amount or percentage of the water recovered
as product. In a system operating at 50% water recovery, the osmotic
pressure of the brine will reach a value approximately twice that of the
feed. If a system is operated at 75% recovery, the osmotic pressure in
the brine will approach four times that of the feed. From this considera-
tion and from Eq. (3), it can be seen that the product quality will also
be affected by the amount of product water recovered.

These points are well illustrated by Figs. A-1 and A-2. Figure A-1 shows
the variation in water flux for a reverse osmosis system operating under
fixed pressure conditions as a function of water recovery, with feed
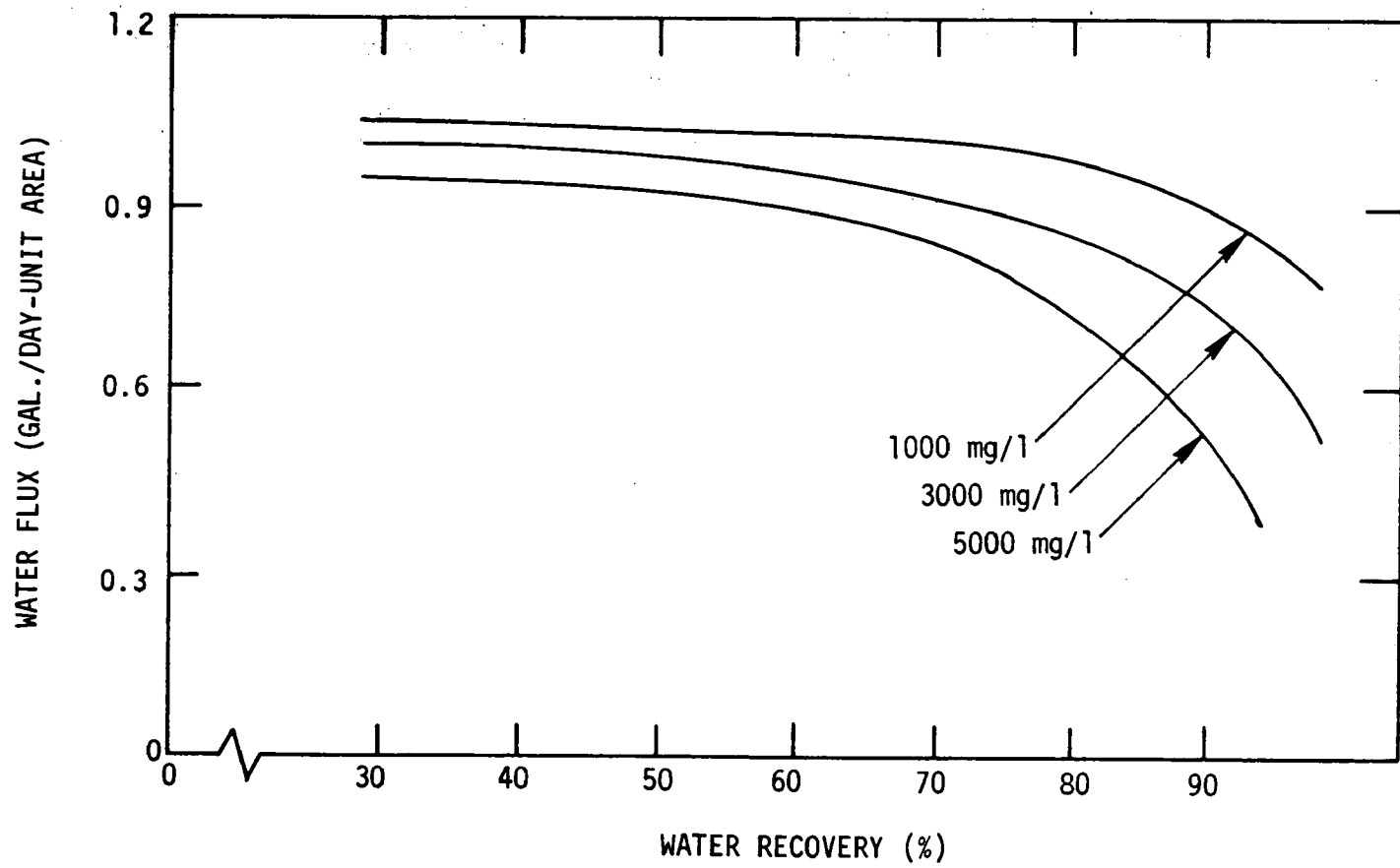salinity as a parameter. It is seen that the water flux per unit of area

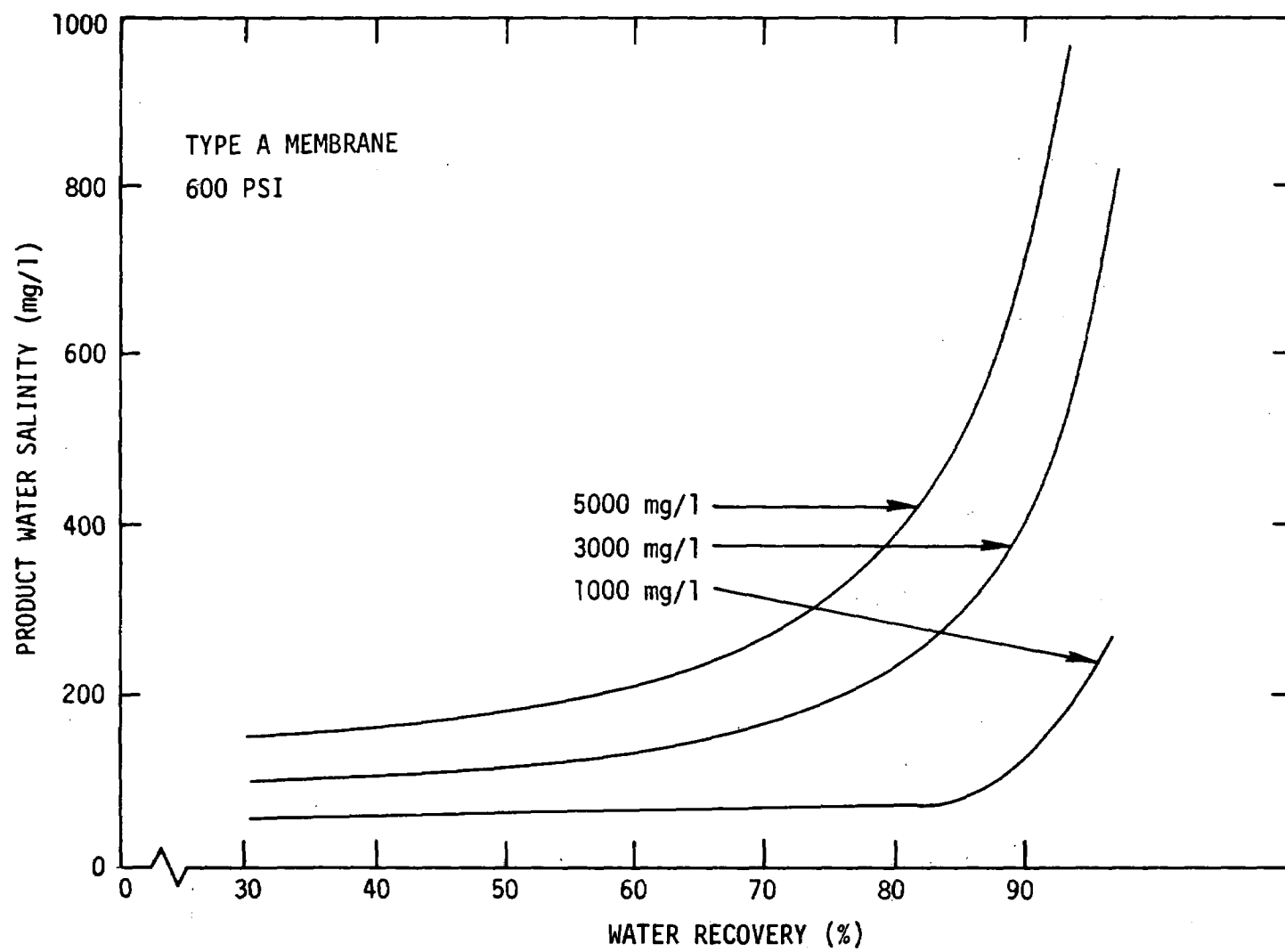Fig. A-1. Variation in performance with feedwater concentration

Fig. A-2. Effect of feedwater concentration on product-water quality

decreases with increasing feed salinity and with increasing recovery percentages. Figure A-2 is a similar plot, except that product-water quality (salinity) is plotted versus recovery. Again, we see that the quality of the product water decreases with increasing feed salinity and increasing recovery percentages. It is noteworthy that for recoveries below about 75%, the reduction in water flux and water quality is fairly low, particularly on feed of low salinity.

As noted above, the specific water and salt flows depend on the water and salt permeation coefficients (A and B) of the membrane in question. It is possible, as will be discussed later, to prepare membranes over a range of specific water and salt permeation constants. When $A = 1.5 \times 10^{-5}$ g/sq cm-sec-atm, the water flux rate corresponds to 13 gal./sq ft-day at 600 psi.

As noted earlier, B is given in units of cm/sec. An alternative method of expressing B, in more readily measurable terms, is

$$B = \frac{C_p \times F_p}{a\overline{C}} \, ,$$

where

C_p = salt concentration of product (g/cc),

F_p = flow of product (cc/sec),

$\overline{C}$ = average concentration of feed and concentrate (g/cc), and

a = area (sq cm).

The percent salt rejection (S.R.) is defined by the equation

$$\% \text{ S.R.} = \left(1 - \frac{C_p}{\overline{C}}\right) \times 100 \, ,$$

where

C_p = concentration (or conductivity) of the product, and

$\overline{C}$ = average concentration (or conductivity) of the feed and brine.

It then follows that a membrane exhibiting a water flux ratio of 13 gal./sq ft-day at 600 psi and 95% salt rejection will have a B value of 3 x 10^{-5} cm/sec.

RELATION BETWEEN MEMBRANE PROPERTIES AND ACETYL CONTENT OF CELLULOSE ACETATE

General-purpose reverse osmosis membrane is cast from solutions prepared with commercial grades of cellulose acetate, usually described as the 2.5 acetate, whose corresponding acetyl content is approximately 40%. Since each glucose unit in the original cellulose backbone contains two secondary and one primary hydroxyl group, the terminology, "2.5 acetate" means that an average of five out of every six hydroxyl groups are esterified by an acetyl group (see Fig. A-3).

The permselectivity and transport properties of a particular membrane result in part from what may be simply envisioned as a porosity at the molecular dimension level. This porosity is attained and controlled by several factors in combination:

1. The acetyl content of the cellulose acetate used to cast the film.
2. The additives to the casting solution, such as magnesium perchlorate, zinc chloride, etc.
3. The choice, and proportions, of casting solution solvents, generally among acetone, water, and formamide.
4. The casting conditions, including air-drying rate, temperature, etc.
5. The heat-treatment (annealing) conditions.

The most fundamental consideration is the acetyl content of the polymer. Once it is established, the other factors are employed to achieve the desired range of properties under reproducible conditions. Figure A-4 illustrates the changes in water and salt permeability values over a range of acetyl contents. The semilog plot shows a much greater slope for salt permeability than for water permeability. The values range from insignificant salt rejection at 33% acetyl content to very low water
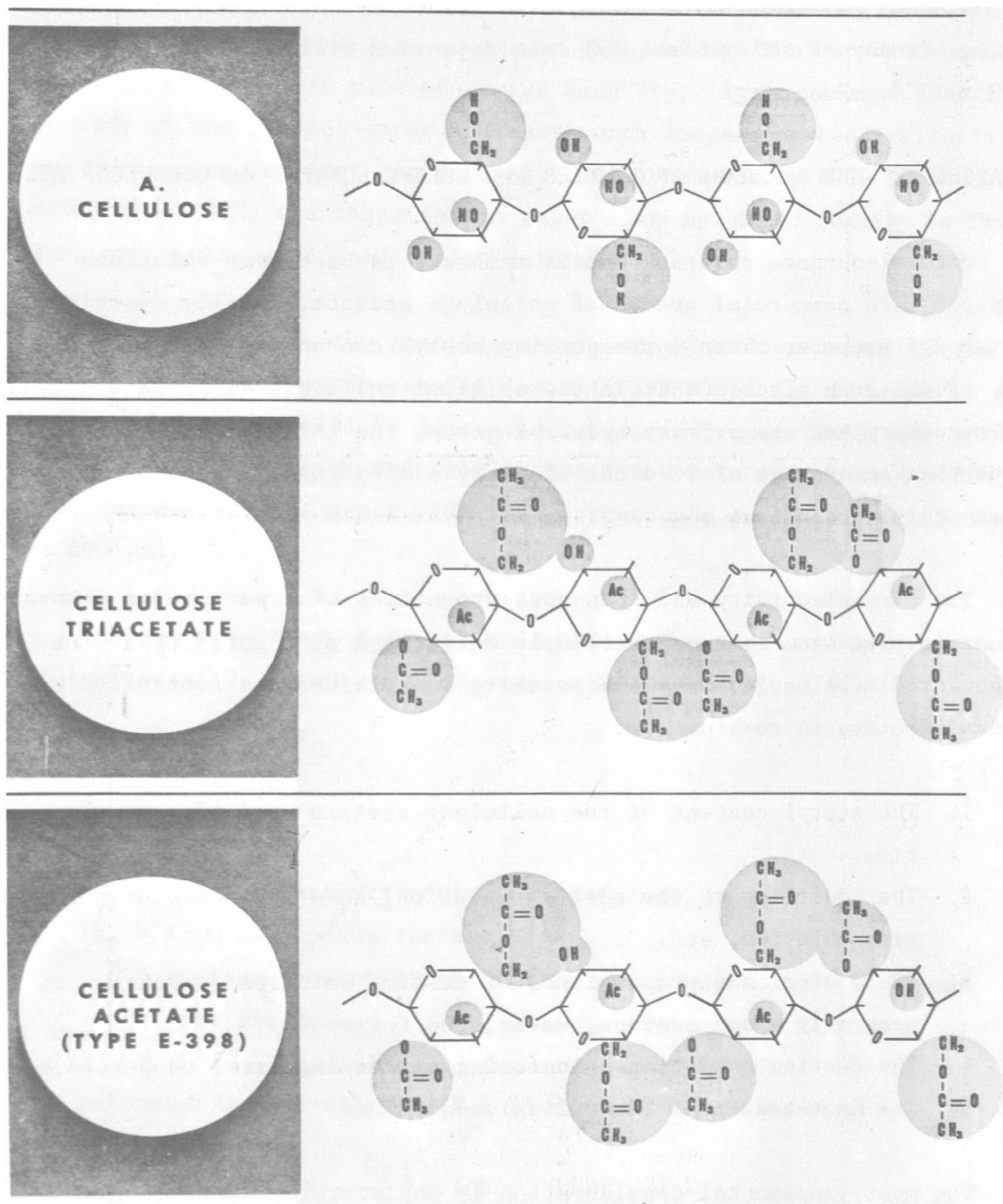
Fig. A-3. Molecular representations of cellulose, cellulose acetate, and cellulose triacetate; for clarity, the hydrogen atoms have been omitted in the ring structure of the anhydroglucose units (from Eastman Kodak Bulletin on Eastman Cellulose Acetate, 1959)
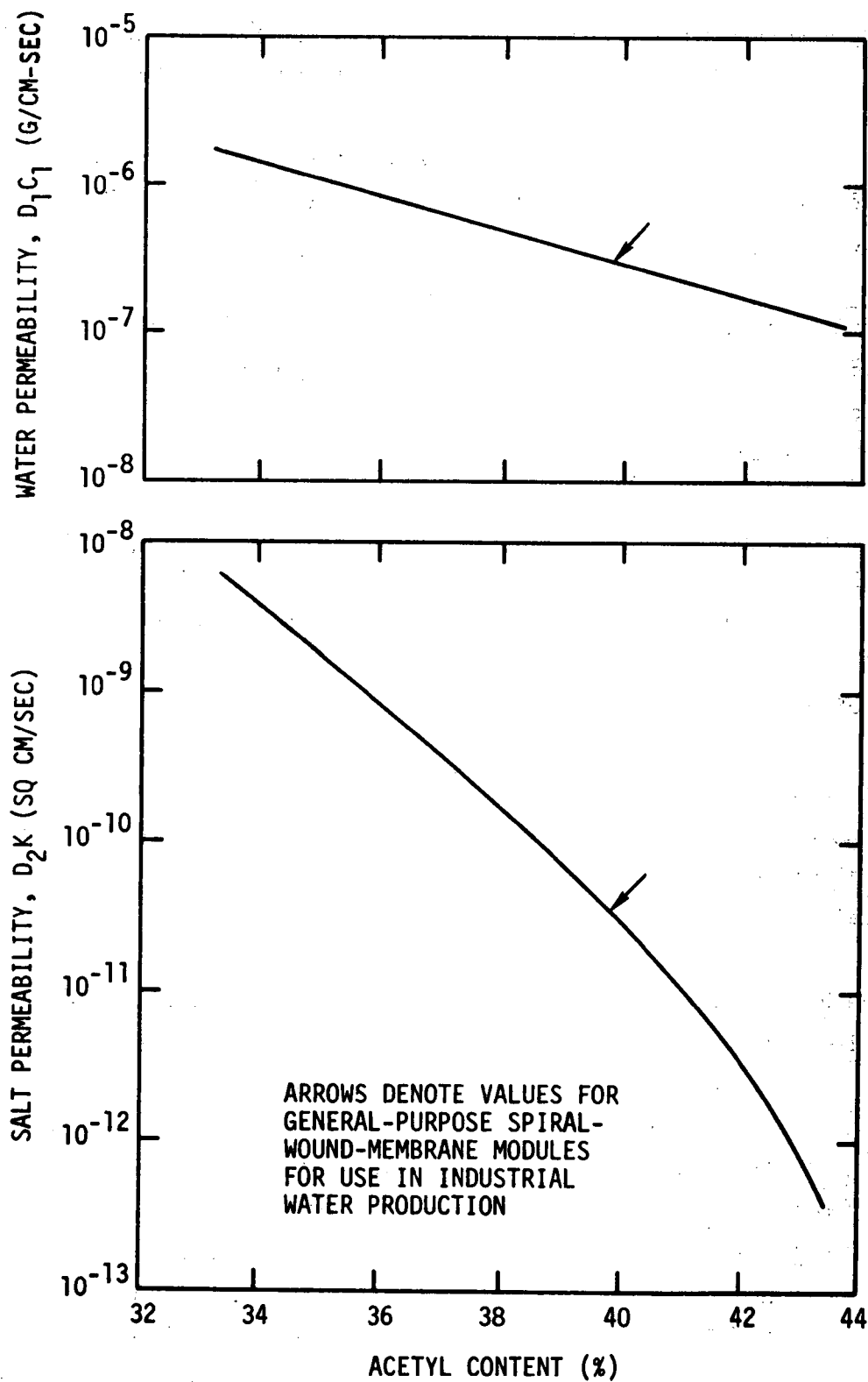
Fig. A-4. Permeability to water (D_1C_1) and NaCl (D_2K) of cellulose acetate membranes as functions of acetyl content

flux, with very high salt rejection, at 43.2% acetyl content. This
relationship is illustrated in more practical and common terminology and
units in Table A-1. A hypothetical system operating at 75% recovery on
a 700 mg/l feed at 600 psi will produce purified water over the listed
range of water flux and salt rejection values (and corresponding product
salinity).

As a comparison of the two examples for the 39.8% acetyl value with
the 37.6% acetyl value shows, increased flux at a modest rejection penalty
can be obtained more readily by heat treatment than by varying the acetyl
content. The data in Table A-1 illustrate the many combinations available
for a very wide range of operating requirements. The 39.8% acetyl content
membrane is a good general-purpose membrane that has been extensively studied
and utilized. Continued intensive developmental work will result in an
ever-expanding availability and performance range of proved membrane.

EFFECT OF HEAT TREATMENT ON MEMBRANE PROPERTIES

For practically all applications involving demineralization, heat
annealing of the cellulose acetate membrane is required. Heat treatment
involves immersion of the membrane in water for periods of up to 30 min
at closely controlled temperatures.

The heat-treatment temperature profoundly influences the water flux
capability, the salt rejection properties, and another property (compaction),
which is defined and discussed in more detail below. Simply stated, the
higher the heat-treatment temperature, the lower the water flux and the
better the salt rejection. This can be seen from the curves in Fig. A-5,
which show the influence of heat-treatment temperature on water flux rate
and salt rejection capability. Thus, modules containing general-purpose
membranes, heat-treated in the range of 85°C, exhibit (1) an initial water
flux capability of approximately 18 gal./sq ft-day at 800 psi net driving
pressure, and (2) a salt rejection capability (NaCl), at the same pressure,
in the range of 95%. These values are derived from standard-membrane
test cell conditions (1% NaCl feed, 25°C, 800 psi, "zero" water recovery).

TABLE A-1

SPIRAL MEMBRANE MODULE PERFORMANCE[a] VERSUS ACETYL CONTENT

	Acetyl Content (%)				
	33	37.6	39.8	39.8[b]	43.2
H_2O flux, gal./sq ft-day	49	17	10	15	3.7
Product salinity, mg/l	Comparable to feed	225	45	67	2
Rejection (based on avg. conc. = 1120 mg/l), %	Not significant	80	96	94	99.8

[a] Feed H_2O contains 700 mg/l TDS; brine contains 2500-2800 mg/l TDS; pressure = 600 psi; recovery = 75%. All membrane was heat-treated at 85°C except as noted.

[b] Heat-treated at 81°C.

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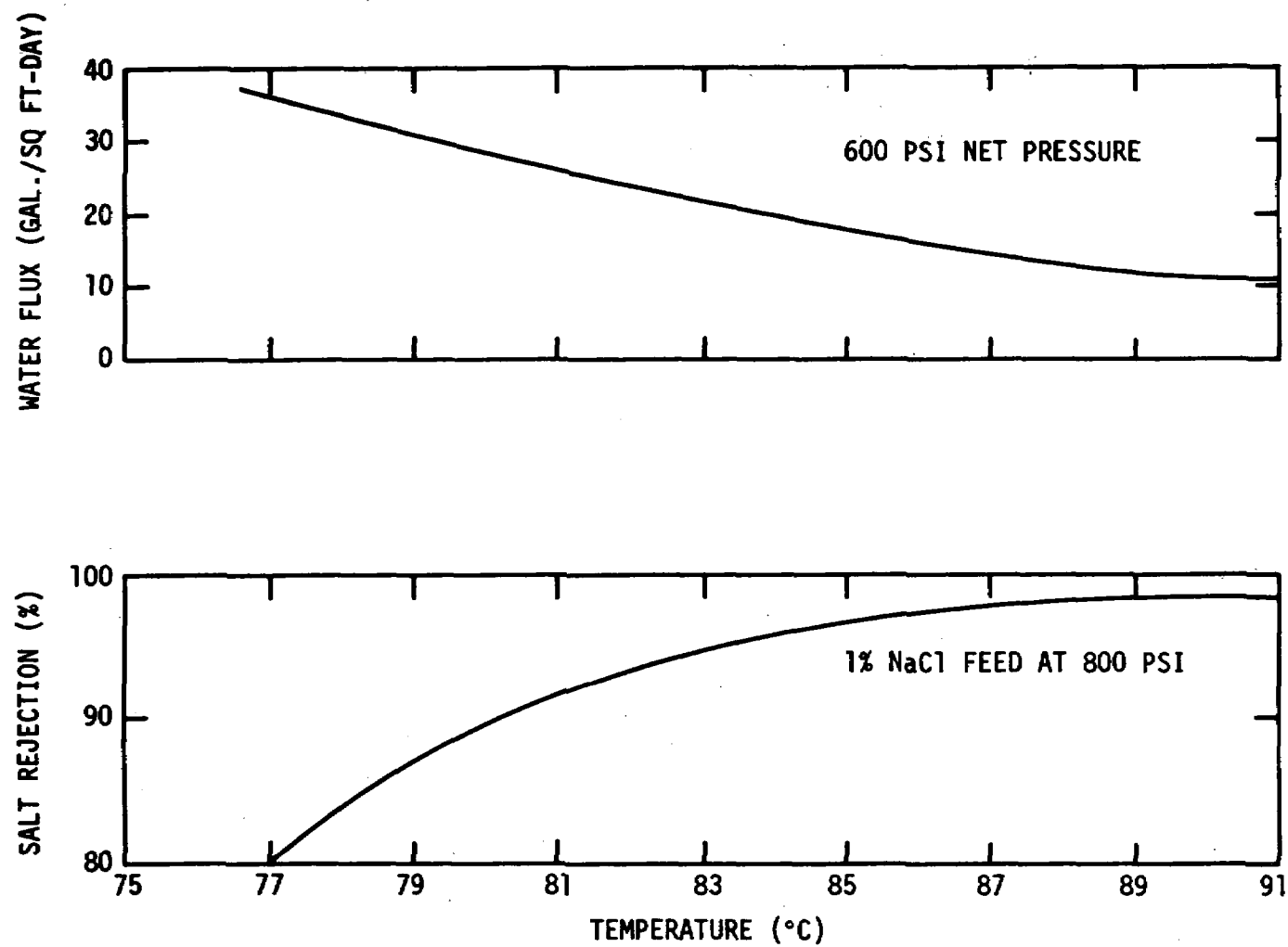
Fig. A-5. Dependence of water flux and salt rejection on membrane heat-treatment temperature

As mentioned above, the third important property of cellulose acetate membrane which is significantly determined by the heat-treatment temperature is compaction. Even under idealized conditions, i.e., a pure water feed and no fouling of the membrane surface due to other factors, there is a decline in water flux with operational time. Flux decline behavior is illustrated in Fig. A-6, which is a log-log plot of water flux versus time. A plot of the membrane permeation constant A versus time gives precisely the same curve. Membrane compaction is considered to be comparable to creep observed in plastics, metals, etc., under compression-stress conditions. The fact that compaction exhibits behavior that is amenable to a straight-line log-log plot means that if the negative slope is of an acceptable magnitude, a practical reverse osmosis system can be designed to ensure rated water output performance over the estimated membrane lifetime. As shown by the figure, the 1-hr water flux at 600 psi on a typical feed is 13 gal./sq ft-day. The flux decline rate, which is the slope of the straight line, is shown as -0.05. The term "flux decline" is used deliberately in preference to "compaction" because, in real-world systems, the observed flux decline is the sum of the fundamental compaction effect already defined plus a tolerable amount of membrane surface fouling. The flux decline slope can be obtained by plotting observed flux values as a function of time on suitable log-log paper. The best straight line is then drawn. By taking the values from the graph, the slope (m) may then be calculated from the equation

$$m = \frac{\log F_2 - \log F_1}{\log T_2 - \log T_1} .$$

If T_2 and T_1 are selected so that they differ by a factor of 10, then the denominator is equal to one, and the above equation can be simplified to
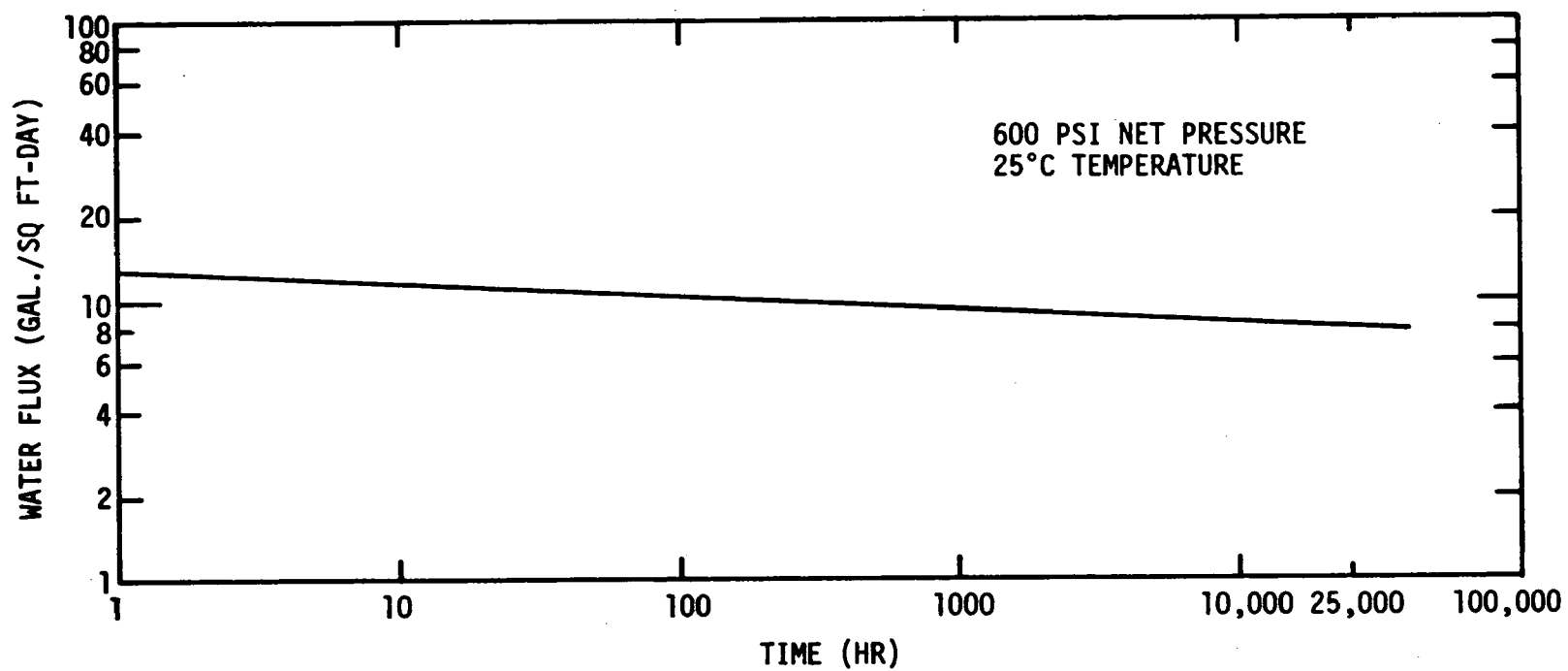
$$m = \log (F_2/F_1) .$$

Fig. A-6. Module water flux decline versus time

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Since F_2 will always be smaller than F_1, m equals the log of a fraction less than one; hence, m is a negative number, consistent with the observed flux decline behavior. Experience has indicated that a reasonable value of m for a properly controlled system is -0.05, as illustrated. This means that the water flow rates a 3-yr period will be as follows:

Time (hr)	Flow Rate (gal./sq ft-day)
10	13
100	11.7
1,000	10.2
10,000	8.3
25,000	8.0

The design point used by Gulf General Atomic is currently the 10,000-hr value: 8.3 gal./sq ft-day at 600 psi. It decreases very slightly over the next two years, and incremental increases of pressure will provide the rated capacity during that period. Initial output will be substantially in excess of rated capacity, and it is desirable at all times to run the system at the lowest pressure in the 400 to 600 psi range that will produce the rated output.

The inherent compaction properties of the membrane are initially set, in large measure, by the heat-treatment temperature. The lower the heat-treatment temperature, the less the compaction resistance of the membrane. For operation in the range of 600 psi, the inherent compaction properties of membrane do not vary widely over a heat-treatment range of 80° to 90°C, and it is in this heat-treatment range that maximum resistance to compaction is attained. For higher operating pressures, however, the differences in both initial flux value and compaction slope are substantial, as illustrated in Fig. A-7.
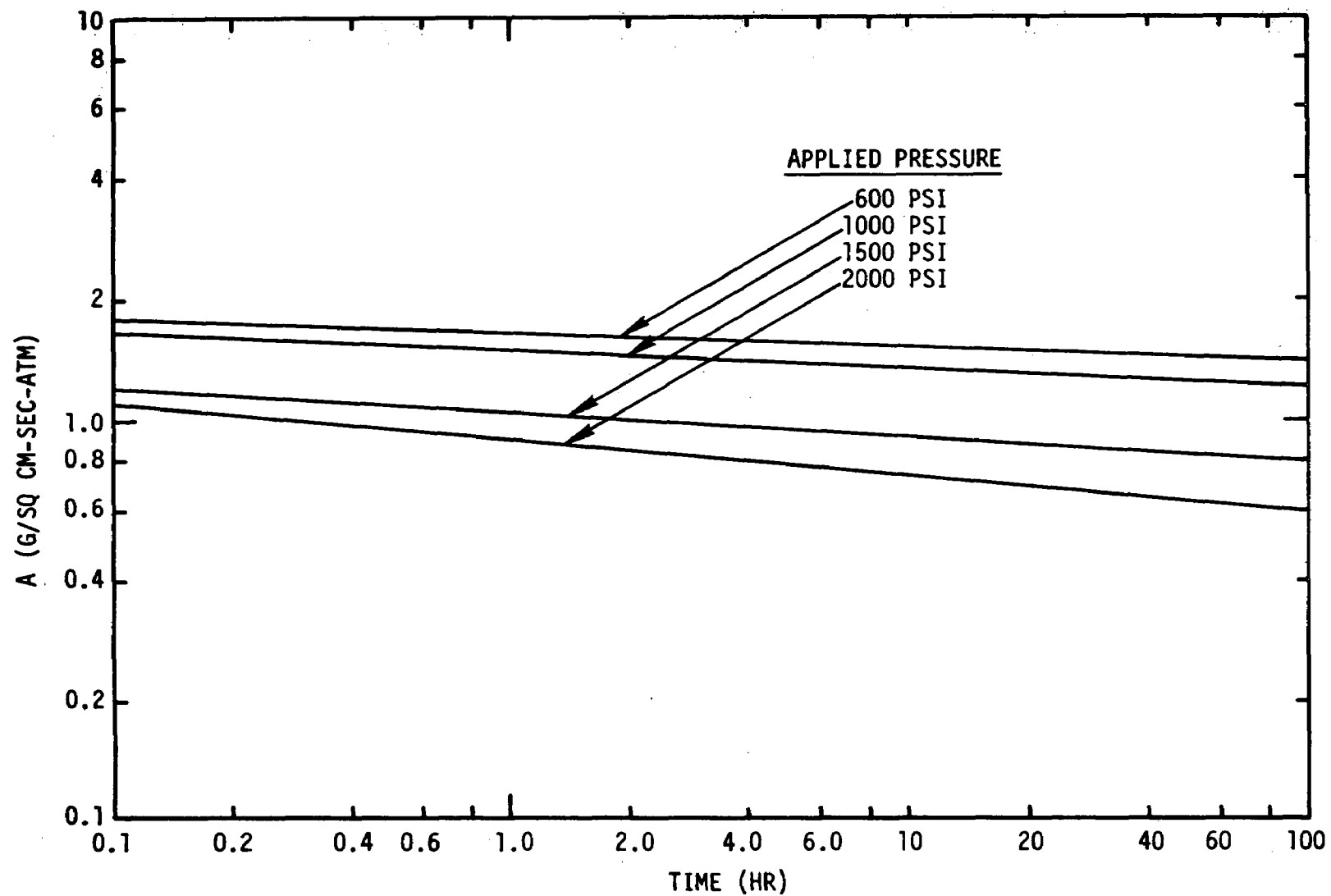
Fig. A-7. Change of membrane coefficient A with time at various pressures for modified cellulose acetate membrane annealed at 80°C

For any one combination of membrane heat-treatment temperature and operating pressure, compaction rate is affected by feedwater temperatures. At temperatures up to approximately 25°C, the effect is not very significant. Beyond that, it accelerates, as illustrated in Fig. A-8.

EFFECTS OF FEEDWATER TEMPERATURE AND pH ON MEMBRANE PERFORMANCE

In reverse osmosis operation, feedwater temperature has a significant effect on membrane performance and must therefore be taken into account in system design. Essentially, the value of the water permeation constant is only constant for a given temperature. The value of A will increase with increased temperature and vice-versa. Figure A-9 illustrates the effect of temperature on the water flux rate of the membrane. The flux rate at 25°C is taken as unity, and the appropriate multiplier shown on the ordinate is used to calculate the added or lessened membrane area that is required to produce the same quantity of water at any other temperature, assuming equal feed salinity, pressure, and other conditions.

At any given time, the observed salt rejection does not vary substantially with temperature, because the salt flux varies by approximately the same magnitude as the water flux in the normal operating temperature range. It must be recalled, however, that the membrane is an ester and therefore subject to long-term hydrolysis. Hydrolysis results in a lessening of salt rejection capability. The rate of hydrolysis is accelerated by increased temperature and is also a function of feed pH. Slightly acidic pH values (5 to 6) ensure the lowest hydrolysis rate, as do cooler temperatures. This relationship is illustrated in Figs. A-10 and A-11.

It is noted that the hydrolysis rate increases sharply above 40°C, below a pH of 3, and above a pH of 7. This phenomenon is taken into account in the system design, particularly with reference to the choice of initial salt rejection capability. The addition of mineral acids to the feed in small amounts (equal to approximately 50% of alkalinity) performs a double function by providing the optimum pH to minimize hydrolysis while controlling and preventing $CaCO_3$ scale formation in the system.
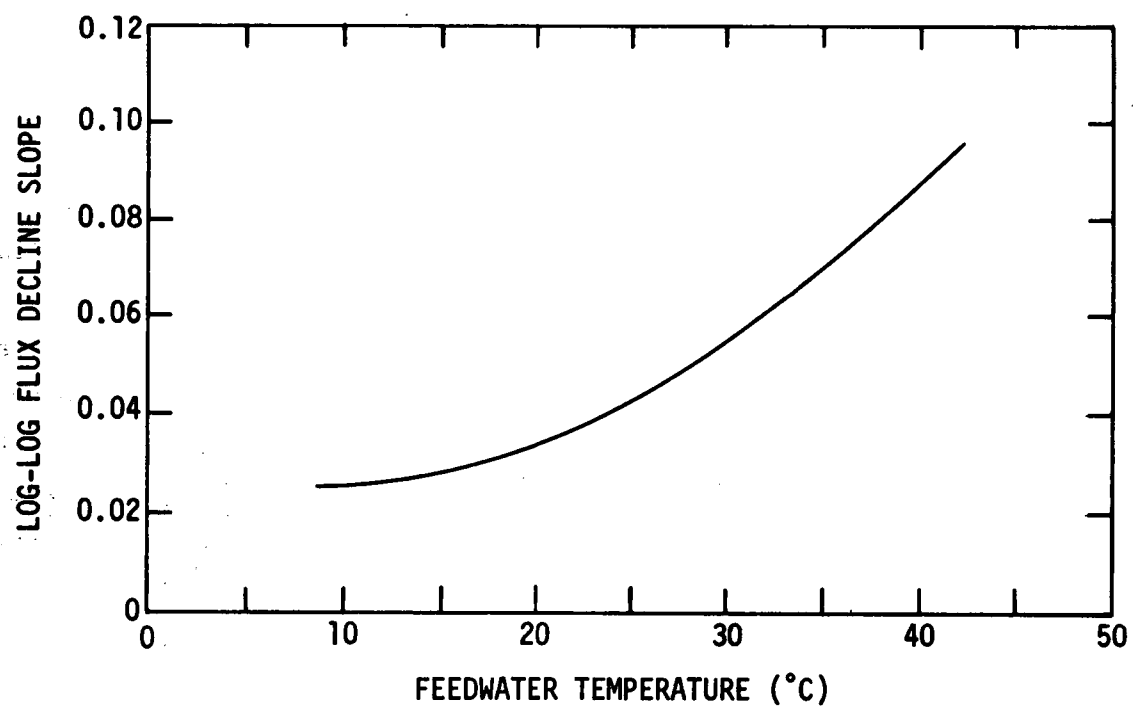
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Fig. A-8. Effect of feedwater temperature on log-log flux decline slope
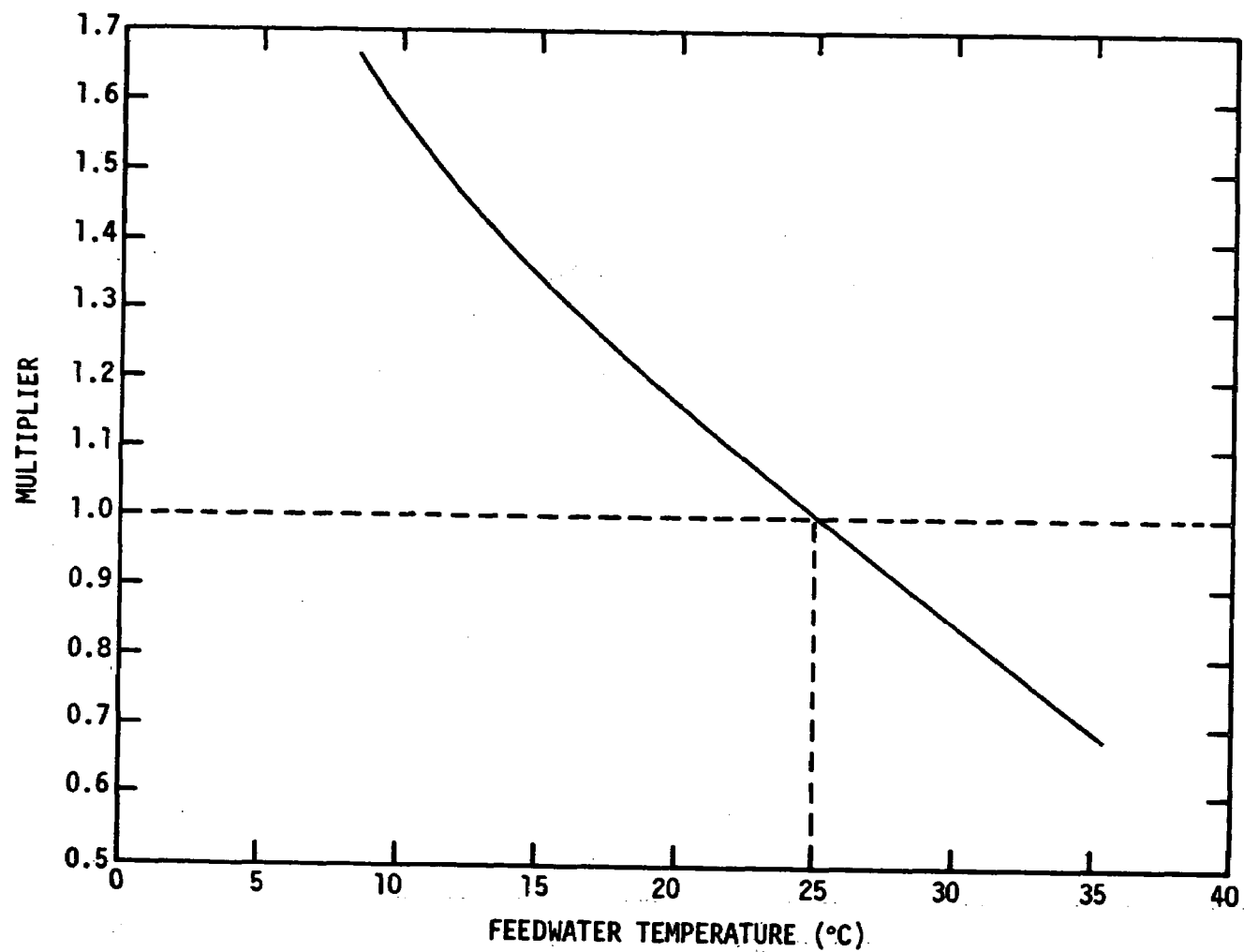
Fig. A-9. Dependence of water flux on temperature; for values other than 25°C, use indicated multiplier to determine the membrane area required for equal water flux
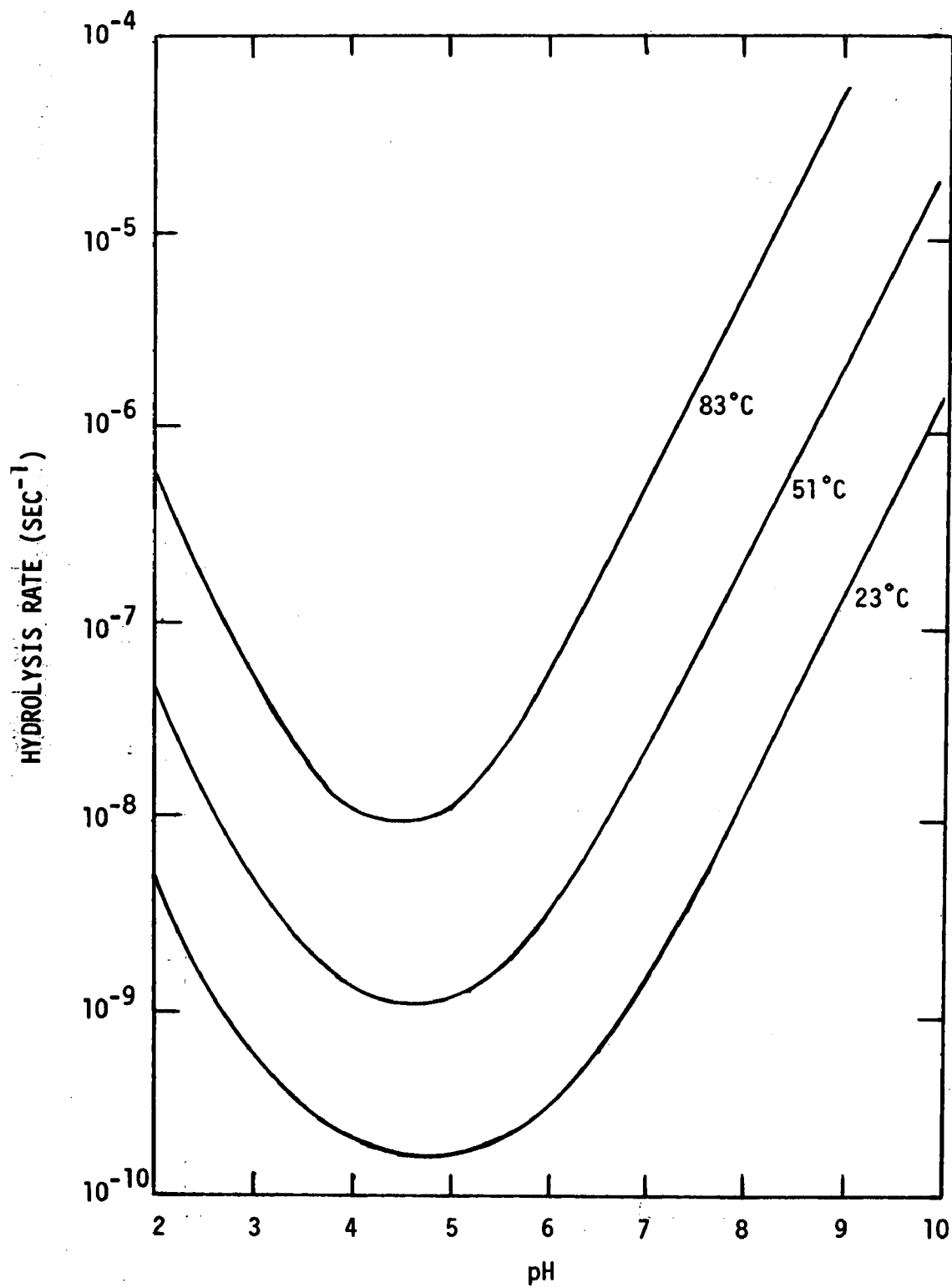
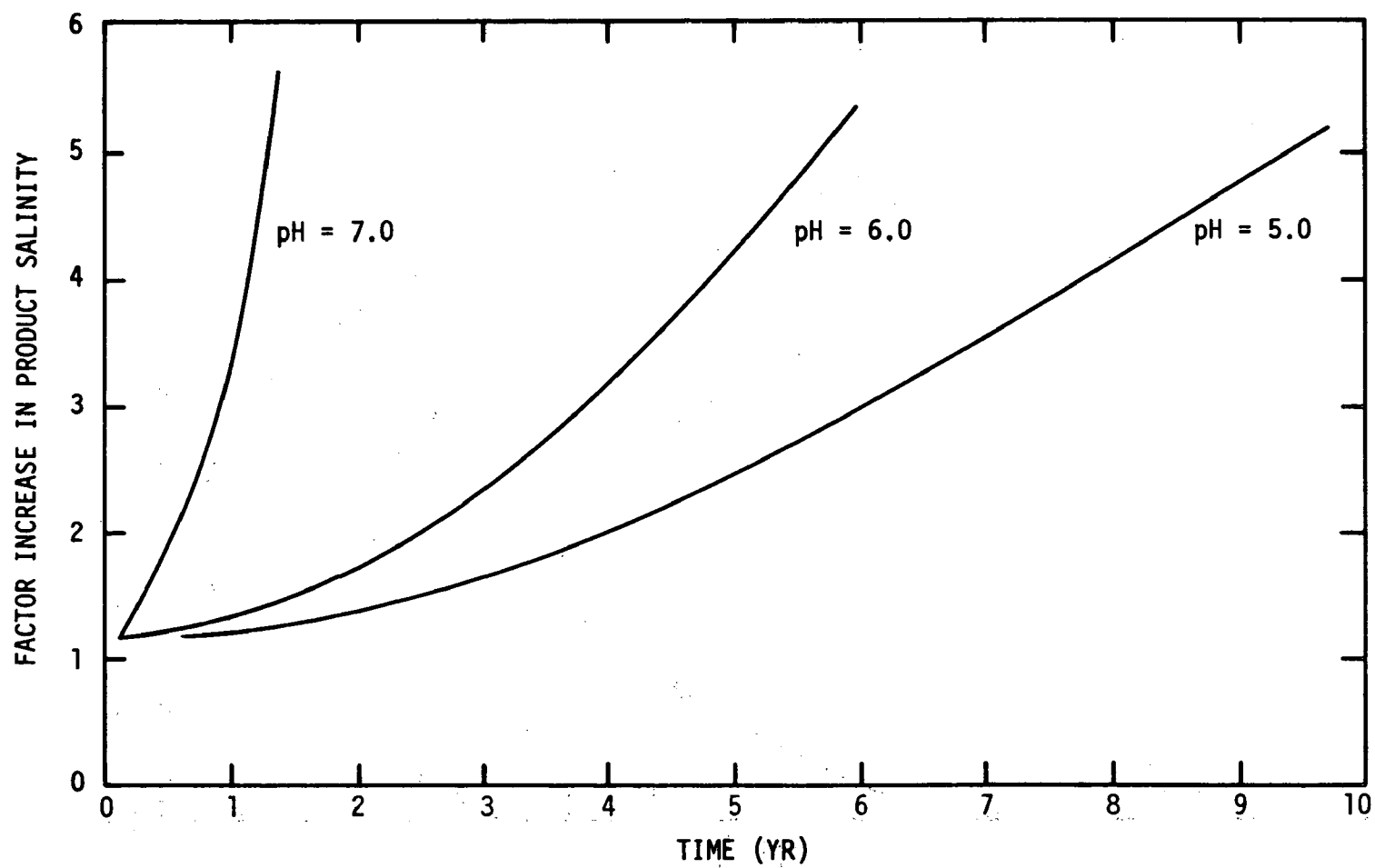Fig. A-10. Effect of pH on rate of hydrolysis

Fig. A-11. Performance based on hydrolysis of membrane

Based on this information and experience, design and predicted demineralization performance over the membrane lifetime is summarized in Table A-2. If other pH values prevail, salt concentration in the product water will increase more rapidly. This is illustrated in Fig. A-11, which is a plot of the time required for given factor increase in salt concentration of the product water at a temperature of 23°C, with pH as a parameter, based on the curves of Fig. A-10.

GENERAL PERFORMANCE

Figure A-12 shows the effect of pressure on the product water flow for a standard-flux module having a membrane coefficient of 1.5×10^{-5} g/sq cm-sec-atm. The three curves represent the predicated performance of a system operating on a solution containing 1000, 5000, and 10,000 mg/l of sodium chloride. These concentrations are the average in the system rather than the specific values in the feed or brine solution. The deviation from linearity at low pressure is due to the fact that at low pressures osmotic pressure is a significant fraction of the applied pressure. The deviation from linearity at high pressure reflects the compaction that can be expected after a period of operation.

Figure A-13 shows the effect of pressure on the sodium chloride rejection for a standard-flux module. The three curves again represent 1000, 5000, and 10,000 mg/l of sodium chloride, the average concentration in the module. The decrease in salt rejection with increasing salt concentration results from the increase in the osmotic pressure of the feed/brine. If the plot were made using net driving pressure, the three curves would be superimposed. The improvement in rejection with increasing pressure results from the fact that the salt flow is essentially independent of pressure, whereas the water flow increases with pressure.

Three grades of membrane are currently in use. These are usually designated "high-rejection", "standard", and "high-flux". The high-

TABLE A-2

REVERSE OSMOSIS EQUIPMENT PERFORMANCE

	Time After Startup (hr)		
	1	10,000[a]	25,000
Product Volume, gal./day (at 600 psi and 25°C)	13	8.3	8.0
Product Quality, mg/l TDS (assuming 500 mg/l TDS in feed of typical ion species and distribution at 75% recovery)	15-30	25-50	40-80

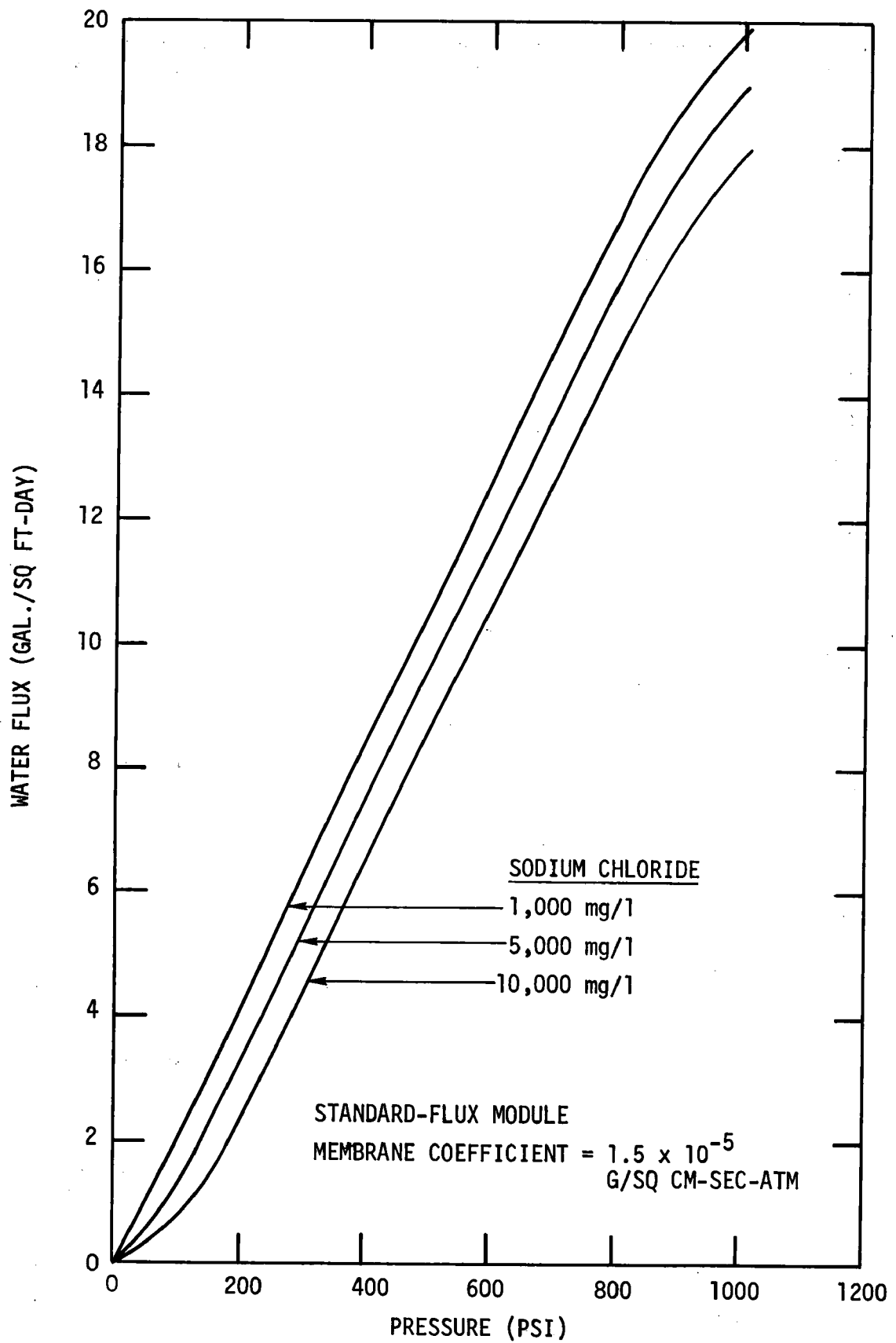[a] Design basis (Gulf General Atomic Incorporated): standard flux membrane.
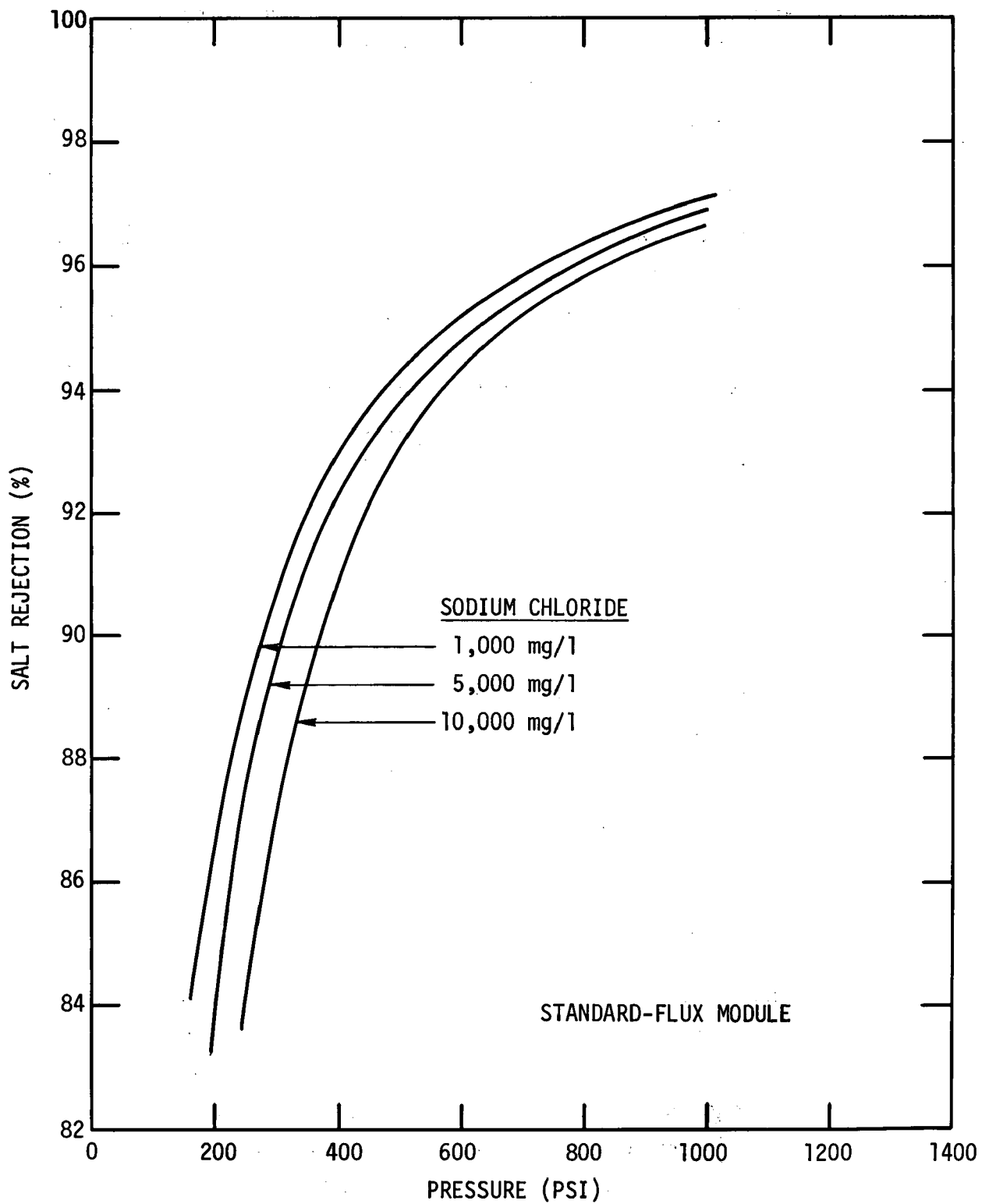
Fig. A-12. Product flow versus applied pressure

Fig. A-13. Sodium chloride rejection versus applied pressure

rejection membrane is normally used in the home drinking water units. The high-flux membrane is used in experimental applications. Typical performance characteristics of modules made with these membranes are given in Table A-3.

If the salinities indicated in Figs. A-12 and A-13 are taken as feed salinities, the values represent the condition of zero recovery. In a unit with a significant water recovery, the concentration of the brine is proportionally higher than the feed concentration because of the removal of purified product water. An accurate method for calculating the average salt concentration in the brine channels is to divide the average salt flow through the brine channel by the average brine flow; i.e.,

$$\overline{C} = \frac{(C_f)\ (F_f) + (C_b)\ (F_b)}{F_f + F_b} \quad ,$$

where $\overline{C}$ = average brine concentration, g/cc or mg/l,

$\quad C_f$ = feed concentration, g/cc or mg/l,

$\quad C_b$ = brine concentration, g/cc or mg/l,

$\quad F_f$ = feed flow, cc/sec or gpm,

$\quad F_b$ = brine flow, cc/sec or gpm.

The effect of increasing concentration due to recovery on the product water flow and quality is shown in Fig. A-14. This curve is appropriate for a feed of 1000 mg/l with new standard-flux membrane operated at 600 psi but does not reflect any boundary layer effect (see the next section). The relatively small change in product water flow is due to the fact that the osmotic pressure is relatively small in all cases. It should be noted that with a membrane giving 95% rejection, if the recovery is carried to 95%, the product from the final section of membrane is approximately the same as the feed concentration.

TABLE A-3

TYPICAL PERFORMANCE OF MODULES AT 600 psi
WITH A FEED OF 1000 mg/l OR LESS

	High Rejection	Standard	High Flux
Initial membrane coefficient, A (g/sq cm-sec-atm x 10^5)	1.2	1.4	2.25
Initial water flux (gal./sq ft-day)	10.6	12.7	19
Sodium chloride rejection (%)	97	95	92
Flux after 1 yr (gal./sq ft-day)	7.5	8.4	12[a]

[a]Estimated from short-term data.
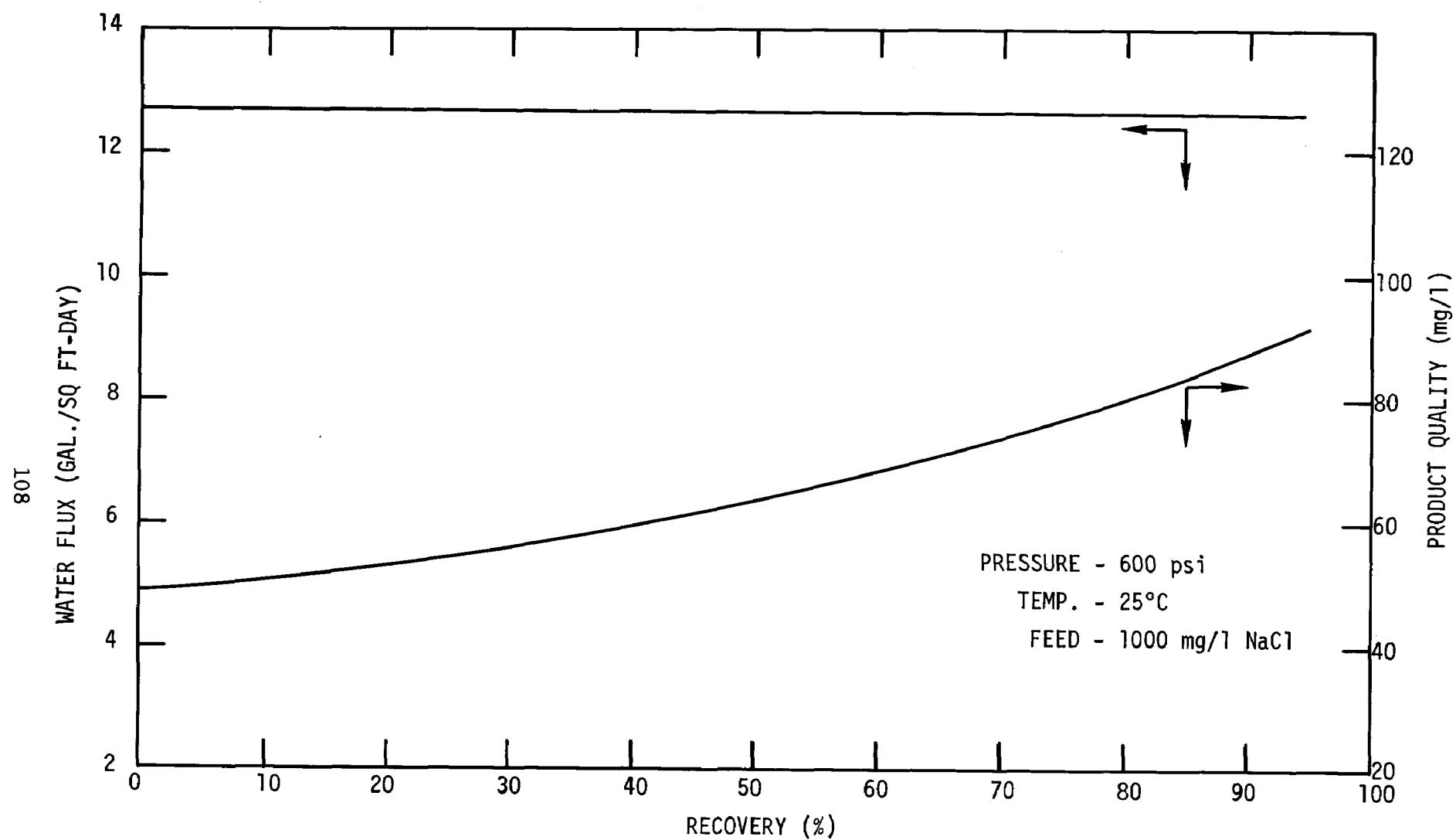
Fig. A-14. Typical performance of a new standard-flux module as a function of recovery

This section of membrane is thus not contributing useful product water, and could be considered the limit of recovery. Normally, however, system recovery is limited by the solubility of calcium sulfate or other sparingly soluble salts and very high recoveries will not be practical. Figures A-1 and A-2 show the gross effects of increasing salinity on the flux and product quality versus recovery.

BOUNDARY LAYER

The previous illustrations of typical performance are for systems where the flow in the brine channel is sufficient to keep the concentration polarization to a minimum. In many systems, this may not be the case. When water permeates through the membrane, nearly all of the salt is left behind in the brine channel. In any dynamic hydraulic system, the fluid adjacent to the wall of the vessel is moving relatively slowly. Even though the main body of the stream is turbulent, a thin film adjacent to the wall (membrane) is laminar. This thin film is called the boundary layer. The salt left behind by the product water must diffuse through this boundary layer.

The concentration polarization is defined as the ratio of the salt concentration at the membrane surface to the salt concentration in the bulk stream. The concentration polarization has been found to fit the equation

$$\frac{C_m}{\overline{C}} = \beta = \exp\ [K(F_p/F_b)] \qquad ,$$

where C_m = concentration at the membrane surface, g/cc or mg/l,

$\overline{C}$ = average bulk concentration, g/cc or mg/l,

β = concentration polarization,

K = a proportionality constant,

F_p = product flow, cc/sec or gpm,

F_b = average brine flow, cc/sec or gpm.

The proportionality constant K is inversely proportional to the diffusion coefficient of the salt and inversely proportional to the length of the brine channel. Typical values of the concentration polarization for a 3-ft module as a function of the product-to-brine ratio for a sodium chloride solution and for a magnesium sulfate solution are shown in Fig. A-15.

There have been numerous requests for a curve showing concentration polarization as a function of brine flow. Constructing such a curve is somewhat impractical in that there is a separate line for each pressure and each type of membrane. The ratio of the product flow to the average brine flow is approximately the same as the recovery ratio. Thus, a 10% recovery per module gives a concentration polarization factor for sodium chloride of approximately 1.1. For a standard 50-sq-ft module operating at 600 psi, this corresponds to a brine flow of about 4.5 gpm.

The effect of concentration polarization on the performance of a unit is shown by a comparison of Fig. A-14 with Fig. A-16. The plot in Fig. A-16 shows the initial performance of a 10K unit operating at 600 psi with a feed of 1000 ppm NaCl. The decrease in product flow with increasing recovery is still very small. The decrease in product quality, the result of an increase in salt concentration in the feed with increased recovery, is considerably larger when the boundary layer is considered.

At recoveries below 75%, the effect of concentration polarization on the product quality and quantity where the feed is a naturally occurring water with a total dissolved solids content of less than 5000 mg/l is of little importance when the ratio of the brine flow to the product flow $\geq$8:1.
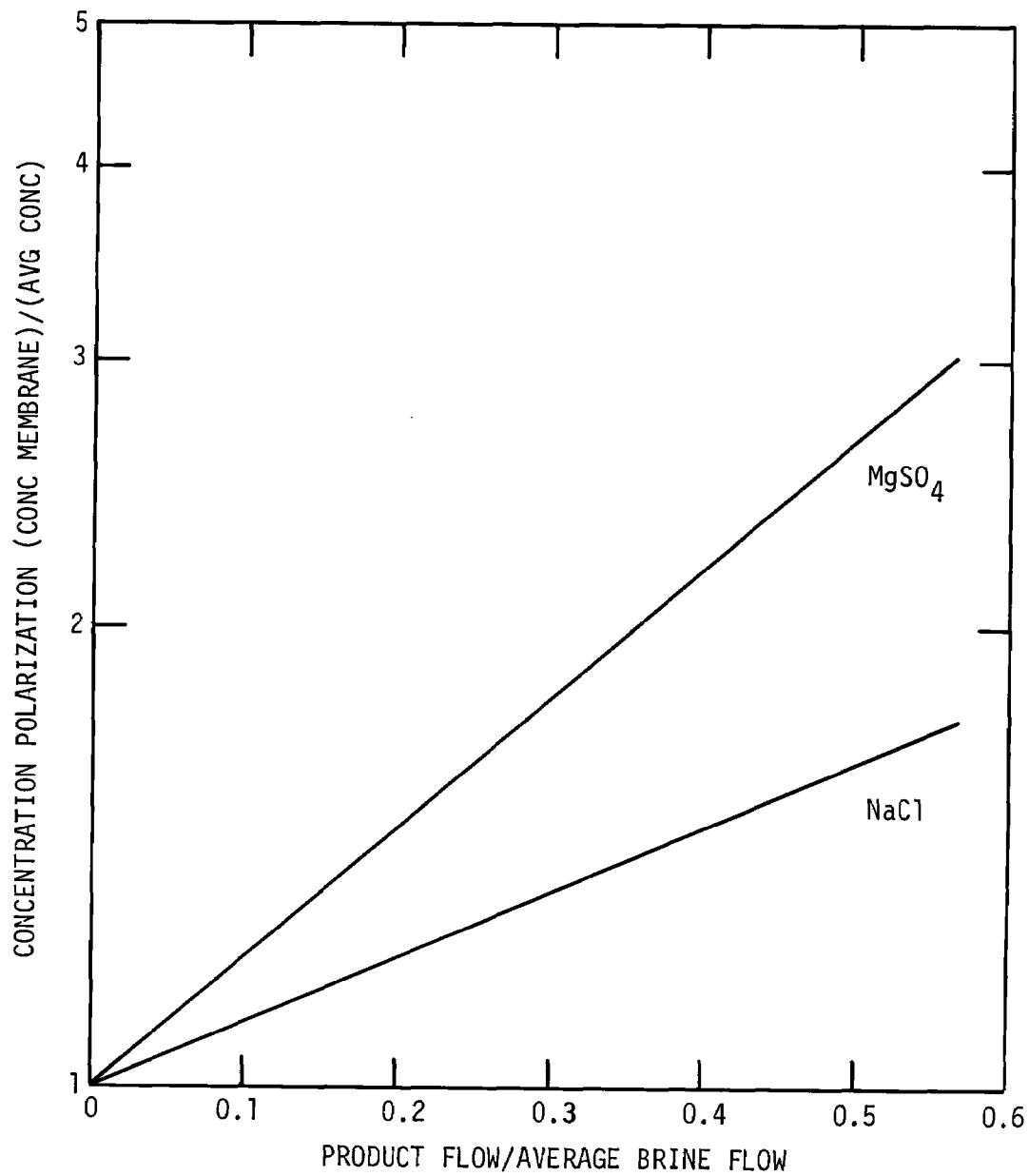
Fig. A-15. Concentration polarization versus product-flow-to-brine-flow
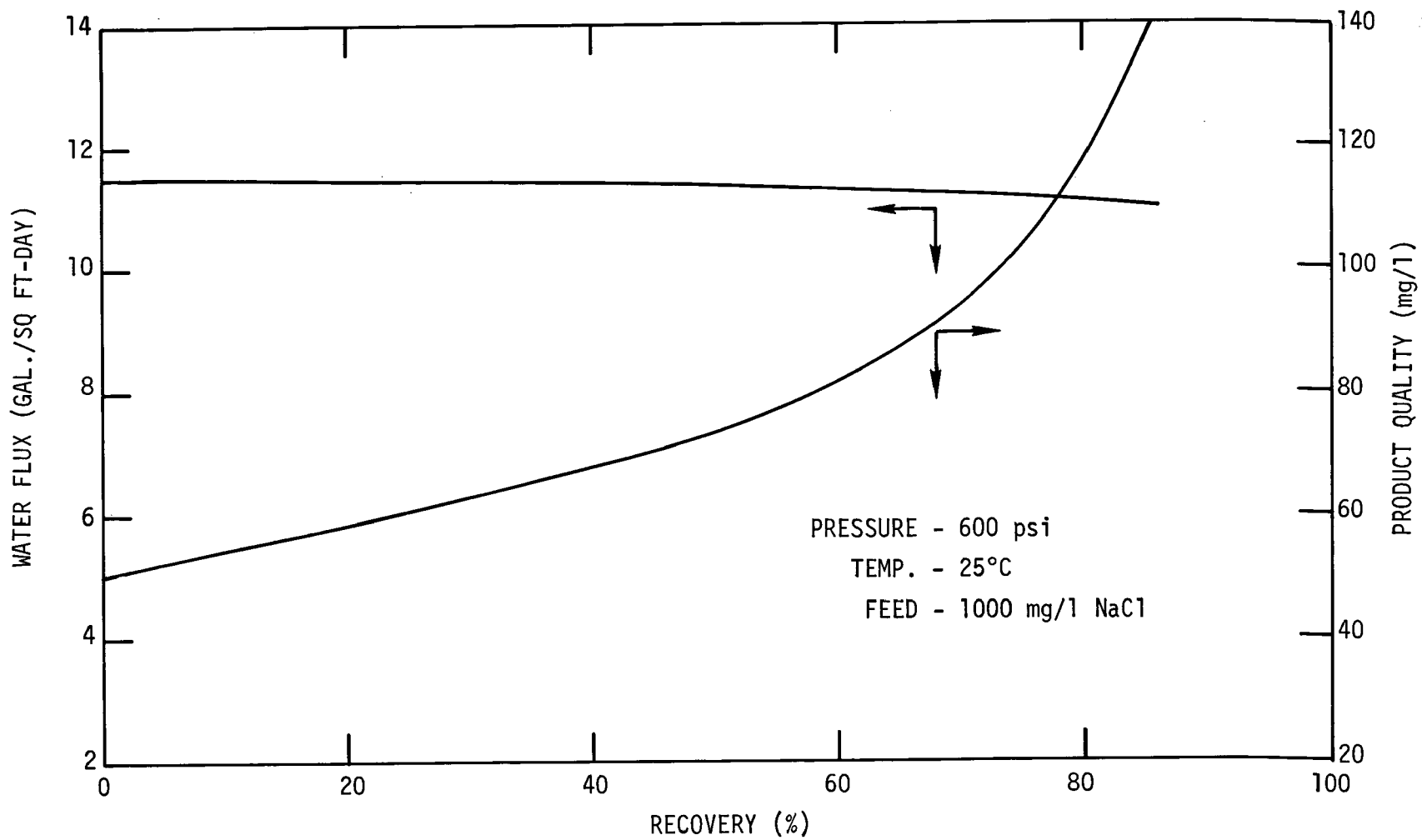ratio for magnesium sulfate and sodium chloride in a 3-ft module

Fig. A-16. Typical performance of a new 10,000 gpd unit as a function of recovery

The most common problem resulting from concentration polarization is the increasing tendency for precipitation of sparingly soluble salts and the deposition of particulate matter on the membrane surface. As a general rule, the sparingly soluble salts have a smaller diffusion coefficient than does sodium chloride. Although the diffusion coefficient of calcium sulfate is not readily available, it can be expected to be similar to that of magnesium sulfate. The concentration polarization effect for magnesium sulfate is somewhat more than twice that of sodium chloride at any given conditions of flow.

To illustrate the effect on precipitation, assume a system with 10% recovery in the final module. The concentration polarization for magnesium sulfate is approximately 1.25. Assuming that calcium sulfate behaves the same way, the brine at the membrane surface is approximately 25% more concentrated than the average brine in this module. This local concentration effect markedly lowers the system recovery which may be obtained without adding precipitation inhibitors.

ACKNOWLEDGMENTS

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