

AD-A064 382

KENTUCKY UNIV LEXINGTON DEPT OF CHEMICAL ENGINEERING

F/G 7/4

ULTRAFILTRATION CHARACTERISTICS OF OIL-DETERGENT WATER SYSTEMS:--ETC(U)

AUG 78 D BHATTACHARYYA, A B JUMAWAN

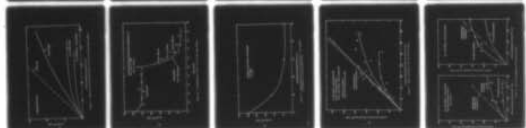
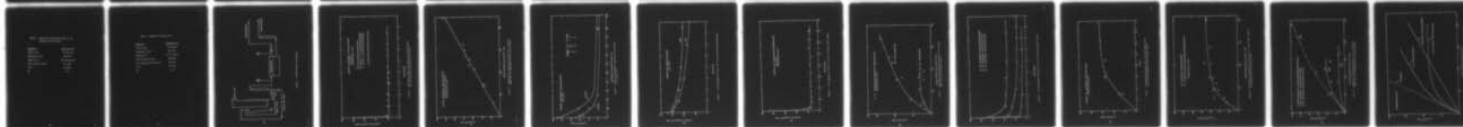
N00167-76-M-8520

UNCLASSIFIED

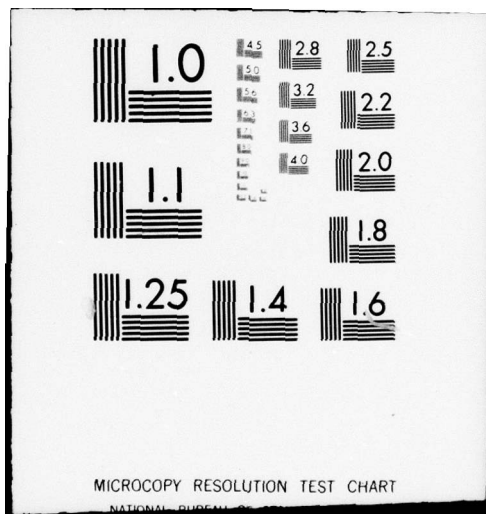
DTNSRDC/SME-78-76

NL

| OF |
AD
A064382



END
DATE
FILMED
4-79
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

② LEVEL II

ADA064382

ULTRAFILTRATION CHARACTERISTICS OF OIL-DETERGENT WATER SYSTEMS:
MEMBRANE FOULING MECHANISMS

DTNSRDC REPORT 78-76 ✓

August 1978

Prepared under Contract
N00167-76-M-8520

by

D. Bhattacharyya and A. B. Jumawan ✓
Department of Chemical Engineering
University of Kentucky
Lexington, Kentucky 40506

411 064

DDC FILE COPY

for
David W. Taylor Naval Ship Research and Development Center
Annapolis, Maryland 21402

DDC
RECEIVED
FEB 9 1979
RECEIVED

Handwritten initials and the letter 'B' below the stamp.

Approved for public release; distribution is unlimited.

Unclassified

18 DTNSRDC/SME

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SME-78-76 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 Ultrafiltration Characteristics of Oil-Detergent Water Systems: Membrane Fouling Mechanisms.		7. TYPE OF REPORT & PERIOD COVERED 9 Final Report.
7. AUTHOR(s) 10 D. Bhattacharyya and A. B. Jumawan		8. CONTRACT OR GRANT NUMBER(s) 15 N00167-76-M-8520
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Kentucky Lexington, Kentucky 40506		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62765N, ZF-57-572-003 2860-101-60
11. CONTROLLING OFFICE NAME AND ADDRESS David W. Taylor Naval Ship R&D Center Code 286, Annapolis, MD 21402		12. REPORT DATE 11 Aug 78
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 44p		13. NUMBER OF PAGES 38
		15. SECURITY CLASS. (of this report) Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited 16 F57572 / 17 ZF57572 DD3		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Ultrafiltration Synthetic oil Tubular membrane Bilge water Fouling Detergent Oily water Mathematic model		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The ultrafiltration characteristics of processing oily bilge water, synthetic lubricating oil, and nonionic detergents with distilled river and seawater are evaluated with noncellulosic tubular membranes. Water flux behavior (membrane fouling) is dictated by membrane resistance increase due to detergent-membrane interaction and due to surface fouling in the presence (Over)		

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract (Contd)

ENT

→ of oil-detergent emulsion and suspended solids. Membrane fouling, as well as membrane cleaning requirements, are dependent on the type of oil/detergent/water system. Flux decline could be minimized by operating at temperatures above 35°C and/or with short-term membrane depressurization. In all cases the steady state water flux is a function of initial membrane water flux. Depending on the water/detergent system, water flux of 15-103 gal/ft²/day at 25°C and pressures less than 25 psi can be obtained.

(Authors)

39 ft

Unclassified

ACKNOWLEDGEMENTS

This work was supported by the David W. Taylor Naval Ship Research and Development Center under N00167-76-M-8520. The valuable technical contributions of Mr. L. R. Harris (project monitor) is gratefully acknowledged.

ACCE	
NTIS	<input checked="" type="checkbox"/>
DDC	<input type="checkbox"/>
	<input type="checkbox"/>
	<input type="checkbox"/>
	<input type="checkbox"/>
	<input type="checkbox"/>
A	

LIST OF ABBREVIATIONS

A°	- angstrom unit
°C	- degrees centigrade
gal/ft ² -day	- gallons per square foot per day
gal/min	- gallons per minute
≈	- approximately equal to
≤	- is less than or equal to
%	- percentage
>	- is greater than
≥	- is greater than or equal to
ft	- feet
ft ²	- square feet
ft/sec	- feet per second
mg/l	- milligram per litre
pH	- negative logarithm of the hydrogen ion concentration
μmho/cm	- micro mho per centimetre

79 01 12 041

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	i
LIST OF ABBREVIATIONS	ii
INTRODUCTION	1
EXPERIMENTAL	4
WATER FLUX BEHAVIOR: FOULING MODEL	6
RESULTS AND DISCUSSION	9
Nonionic Detergent - Distilled Water System	9
Oil-Water Systems	11
Oil-Detergent-Water Systems	12
Bilge Water System	13
Membrane Water Flux Recovery (cleaning)	14
CONCLUSIONS	15
REFERENCES	17

LIST OF FIGURES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Ultrafiltration Test System	22
2	Variation of Water Flux Behavior with Operational Time for Detergent-Distilled Water System	23
3	Dependence of Steady-State Water Flux on Initial Water Flux for Detergent-Distilled Water System	24
4	Effects of Detergent Concentration on Steady-State Water Flux	25
5	Time Dependence of Water Flux for Oil- Distilled Water System	26
6	Time Dependence of Water Flux for Oil- River Water System.	27
7	Dependence of Steady-State Water Flux on Initial Water Flux for Oil-Water System	28
8	Time Dependence of Water Flux for Oil- Detergent-Water Systems	29
9	Transmembrane Pressure Effect on Steady- State Water Flux for Oil-Detergent- Distilled Water System	30
10	Dependence of Steady-State Water Flux on Initial Water Flux for Oil-Detergent- Distilled Water System	31
11	Dependence of Steady-State Water Flux on Initial Water Flux for Oil-Detergent- River Water System	32

LIST OF FIGURES

(continued)

<u>Number</u>	<u>Title</u>	<u>Page</u>
12	Comparison of Steady-State Water Flux for Various Distilled Water Systems	33
13	Comparison of Steady-State Water Flux for Various River Water Systems	34
14	Time Dependence of Water Flux for Bilge Water Systems	35
15	Steady-State Water Flux of Bilge Water in the Presence of Detergent at Various Concentrations	36
16	Water Flux Recovery with Tap Water Flushing . . .	37
17	Water Flux Recovery with Chlorine Cleaning . . .	38

LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Tubular Membrane Characteristics	19
2	Analysis of River Water Used in the Ultrafiltration Studies	20
3	Analysis of Bilge Water	21

INTRODUCTION

Membrane ultrafiltration with non-cellulosic membranes is a promising technique for the simultaneous removal of various organic compounds, chemical or mechanical emulsions, and particulates present in wastewaters. Ultrafiltration is generally carried out at low pressures (10 to 100 psi) and offers an attractive alternative in many processing areas. This process produces a dilute ultrafiltrate (permeate) stream and a concentrate stream (only 5 to 10% of raw feed stream). Depending on the type of feed waste (size of organic molecules) stream and the nature of membrane (polymer type and pore size) utilized, the ultrafiltrate stream can meet water quality guidelines for direct discharge^{1,2} and/or water reuse.^{3,4} However, performance limitations (flux drop) may be encountered during ultrafiltration due to the high-flux characteristics of the membranes, which results in the rapid convection of retained solutes to the membrane surface leading to the well-documented phenomenon of concentration polarization or gel formation (membrane fouling). Thus, for the successful operation of a membrane ultrafiltration unit, water flux loss must be minimized by establishing proper operating conditions.

The treatment of oily waste (free oil and emulsified oil and detergents) by ultrafiltration for the purpose of meeting proposed 1980 marine discharge (oil less than 15 mg/l) standards is a promising application. This study is directed towards the processing of shipboard "bilge water" containing fuel oils, lubricating oils, hydraulic oils, detergents, etc. Bilge oil characteristics and

generation rates depend on ship types and ship operating modes.

Smookler and Harden⁵ have investigated bilge wastes aboard various classes of Navy ships.

Oil separation techniques have included gravity separation for free oil removal, and combination gravity separators with coalescing plates for free and dispersed oil droplets.^{6,7} The presence of detergents (such as bilge cleaners) and/or high suspended solids causes chemical emulsification of oil and inadequate oil removal⁷ would be expected with gravity or coalescer systems. Effluent oil concentration from these separators are dependent on the specific gravity of oil, emulsification, oil droplet size, and inlet oil concentration. In the absence of detergents, bilge water treatment with tight coalescers elements has provided effluents less than 20 mg/l oil.⁷

The use of ultrafiltration for the treatment of various types of oily wastewaters has been reported in the literature.^{1,8,9,10,11,12} Harris, et al,¹ in their studies with turbine lubricating (synthetic) oil, and bilge oil, showed that ultrafiltrate containing less than 10 mg/l oil could be consistently obtained even in the presence of detergents. The ultrafiltrate concentration was found to be independent of feed oil (100 to 5000 mg/l oil) concentration and of the oil specific gravity. In their studies with tubular non-cellulosic membranes, extensive flux decline was reported with oil-water systems containing detergent. The cumulative flux decline behaviour was also found to be dependent on the type of water (tap, river or sea water). The objectives of this study are to investigate (experimentally) the water flux and fouling mechanisms of tubular non-cellulosic membranes with specific

oily waters (with and without detergents), and to identify membrane operating conditions necessary to minimize flux decline and membrane cleaning requirements. The water flux characteristics and fouling behaviour are explained in terms of mathematical models.

EXPERIMENTAL

All continuous-flow ultrafiltration experiments were conducted in a commercially available non-cellulosic tubular unit of 1 inch diameter and 1.1 ft² membrane area. The membrane characteristics are shown in Table 1. Experiments were conducted for 6-8 hours (approximate steady state), and in a few experiments the ultrafiltration time was extended to 15 to 90 hours. A schematic diagram of the experimental unit is shown in Figure 1. Most experiments were conducted at negligible water recovery, and the feed concentration was maintained constant by the recycle of both the concentrate and the ultrafiltrate stream to the feed tank. The experiments conducted at the David W. Taylor Naval Ship Research and Development Center are designated in this paper as DTNSRDC data.

The average transmembrane pressure, Δp was varied between 7 and 38 psi. The flow regime was always in the turbulent region, and most experiments were conducted at a linear velocity (tube) of 14 ft/sec (27 gal/min). The feed solution temperature was maintained constant during the course of an experiment.

The feed solutions (to the ultrafiltration unit) investigated in this study were: detergent-distilled water, oil-distilled water, oil-detergent-distilled water, river water, oil-river water, and oil-detergent-river water. Bilge oil (oil layer from shipboard bilge) was used in most experiments. The bilge oil used was a mixture of fuel oil, lubricating oils, and hydraulic oils. Some experiments (DTNSRDC data) were conducted with synthetic base,

turbine engine lubricating oil (Military Specification MIL-L-23699B). The detergent used in this study was nonionic in nature (Military Specification MIL-D-16791E) and contained 99% iso-octyl aryl polymer alcohol. Several studies were also conducted with commercial nonionic surfactant (Triton X-100 and Neodol 25-9).

Experiments with river water were conducted with water obtained from the Severn River, Annapolis, Maryland (Table 2). A series of ultrafiltration experiments was also conducted with shipboard bilge water.

The membrane rejection behavior was primarily monitored by total organic carbon analysis. At the DTNSRDC laboratory the oil content in the ultrafiltrate was determined by a solvent extraction-infrared spectrophotometry technique.¹

WATER FLUX BEHAVIOR: FOULING MODEL

Water transport through ultrafiltration membranes is by viscous flow, and in the absence of any concentration polarization, surface fouling, and membrane-solute interaction, the ultrafiltrate flux, J_w , is dependent only on transmembrane pressure (Δp) and intrinsic membrane resistance (R_m),

$$J_w = \frac{\Delta p}{R_m} \quad (1)$$

R_m is a function of temperature only and since water viscosity (μ) decreases with temperature, J_w is inversely proportional to μ .

The observed water flux with wastewaters containing particulates, emulsions, and organic molecules, may be considerably lower due to membrane-solute interaction (adsorption in membrane pores) and/or surface fouling,

$$J_w = \frac{\Delta p}{R_m + R_i + R_f} \quad (2)$$

The additional resistance R_i due to membrane-solute interaction (particularly by long chain polar nonionic surfactants) may be due to physical adsorption in the membrane pores and/or surfactant micelle formation inside the pores. The adsorption behavior is dependent on the hydrophilic nature of the membrane. Membrane-surfactant interaction is possible even with zero rejection.

R_i is expected to be a function of solute concentration and temperature only. Thus $(R_m + R_i)$ is an effective membrane resistance in the presence of an interacting solute.

The fouling layer resistance, R_f , is a function of concentration and type of macromolecules, and/or suspended solids, transmembrane pressure, gel-layer compressibility characteristics, channel velocity, and operating time. With oil-detergent-water systems, surface fouling is due to suspended solids, free oil, and emulsified oil droplets. In all cases, R_f reaches an asymptotic value (thus J_w). The asymptotic surface fouling layer (gel layer) formed by macromolecular solutes will have resistance considerably higher than gel layers formed by relatively large particle size dispersions.

Membrane fouling is a very complex phenomena and the rate of fouling is dependent on both the type of feed wastewater and operating (pressure, velocity, and temperature) conditions. The fouling (scaling) mechanism can be compared to scaling problems¹³ in heat exchangers (heat flux versus water flux). The transient resistance is related to the asymptotic (steady-state) resistance (R_f^*) by,

$$R_f = R_f^* (1 - e^{-K_f t}) \quad (3)$$

R_f is related to the rate of build-up of fouling layer. The rate of change of fouling layer thickness (y_f) or mass of foulant per unit area (m) can be related by,

$$\begin{aligned} \frac{dy_f}{dt} = \frac{dm}{dt} &= \text{rate of deposition to} \\ &\quad \text{membrane surface} \\ &\quad - \text{rate of removal from} \\ &\quad \text{membrane surface} \\ &= K_2 C_b J_w - K_3 \tau y_f \end{aligned} \quad (4)$$

in which C_b is the concentration of fouling component at bulk liquid conditions and τ is the shear rate at the surface of deposited gel layer. τ is related to the mass transfer coefficient, K_S , where $K_S \propto U^{0.8}$ in the turbulent flow region. Kimura and Nakao¹⁴ have used a similar equation for surface fouling (no membrane-solute interaction) under unsteady-state condition with tubular reverse osmosis modules by replacing the removal term in Equation 4 by $K_S C_b \ln \frac{C_g}{C_b}$.

Gutman¹⁵ described membrane fouling by relating the rate of removal of deposited material on the membrane surface to the occurrence of random turbulent bursts and showed that J_w (thus R_f) always approached a limiting (asymptotic) value. The limiting flux is related by,

$$\frac{J_w \text{ at steady-state}}{J_w \text{ of initial unfouled membrane}} = \frac{1}{1 + \frac{K_f C_b}{A_b U R_m}} \quad (5)$$

in which A_b is the area of fouling layer removed by each turbulent burst and K_f is the resistance of fouling layer per unit thickness. From Equation 5, the percent flux loss is much worse with membranes of high initial water flux (low R_m) and the experimental results^{2, 14, 15} agrees with the trend.

RESULTS AND DISCUSSION

Various oil, detergent, water systems were utilized for the ultrafiltration experiments. Preliminary results showed that ultrafiltration of feed suspensions prepared in distilled water were similar to that obtained with sea water. Suspensions prepared in river water showed enhanced membrane fouling. In order to investigate different types of simulated bilge waters, feed solutions prepared in distilled water and in river water were both studied. The analysis of the river water used in this study is shown in Table 2. Most experiments were conducted at a linear velocity of 14 to 15 ft/sec and at pressure less than 25 psi.

Nonionic Detergent - Distilled Water System The membrane-detergent interaction was initially studied with three different nonionic detergents and Figure 2 shows that significant flux drop (76% drop) occurs with the three detergents during a very short period and reaches a steady-state value at less than one hour operating time. The effect of pressure (7 to 25 psi) and new membrane water (solute-free) flux variability at a constant pressure could be taken into account by membrane initial water flux. Figure 3 shows that steady-state water flux (at 200 mg/l detergent concentration) increases linearly with initial water flux indicating constant flux drop and that the flux drop is not due to surface fouling. The effect of detergent concentration on the steady-state water flux at a constant Δp (that is, constant initial water flux) is shown in Figure 4 for

two operating temperatures. The water flux approached a constant value above a 100 mg/l detergent concentration, for both temperatures. The concentration at which J_w reaches a constant value is related to the critical micelle concentration of the surfactant (critical micelle concentration of MIL-D nonionic detergent is approximately 150 mg/l). At 40°C, flux enhancement was due to lower viscosity of solution and due to the reduction of surfactant adsorption in pores.

The linear increase of J_w with initial water flux (Figure 3) and the decrease of J_w with detergent concentration (Figure 4), can be taken into account by an effective membrane resistance in Equation 2,

$$J_w = \frac{\Delta p}{R_m + R_i} \frac{\Delta p}{R_m (e^{KC_b/C_m})} \quad (6)$$

or in terms of initial water flux

$$J_w = \left(\frac{\text{initial water flux}}{e^{KC_b/C_m}} \right) R_m \quad (7)$$

in which the constant K is ≤ 0 and C_m is the detergent concentration at which J_w becomes constant. In Equation 7 the value of C_b/C_m is ≤ 1.0 . The assumption of R_f in Equation 2 to be zero is validated in Figure 4 where J_w is found to be independent of tube velocity, U .

The membrane-detergent interaction was due to physical adsorption and/or

due to micelle formation in the membrane pores and this was validated by the fact that complete flux recovery was obtained with short (less than 1 minute) distilled water flushing.

The rejection of detergents by the membrane was quite small, which again indicates that the flux drop was not due to surface fouling. The rejections with three nonionic detergents are shown below,

<u>Detergent</u>	<u>Rejection</u>
MIL-D	35%
Triton X-100	<10%
Neodol 25-9	25%

Oil-Water Systems. Oil-water mixtures were studied with both distilled and river water. Most experiments were conducted with 500 mg/l (total organic carbon 320 mg/l) bilge oil. This concentration is 5 to 10 fold higher than that observed in bilge waters. All DTNSRDC data were with synthetic based oil. Figures 5 and 6 show that the flux drop with river water was considerably faster than that obtained with distilled water. With river water gel-polarization occurred in a short time period because of the cumulative effect of surface fouling due to both oil and fine suspended solids. Flux enhancement (42% increase) was obtained at higher operating temperatures (Figure 5). Figure 7 shows that steady-state J_w with river water reached an asymptotic value for membranes of initial water flux greater than 100 gal/ft²-day. With distilled water, system J_w always increased with initial water flux

indicating complete gel-polarization was not achieved. The flux behavior trend shown in Figure 7 is consistent with Equation 5. With membranes operating at an initial water flux of 100 gal/ft²-day, the flux loss was approximately 72% with river water and only 23% with distilled water. The oil rejection was found to be independent of operating temperature, water type, and membrane initial water flux. The rejections were consistently between 98% and 99%, indicating ultrafiltrate oil concentration to be less than 10 mg/l.

Oil-Detergent-Water Systems. All experiments were conducted with a mixture of 500 mg/l oil and 100 mg/l MIL-D detergent. The total organic carbon of the feed wastes was 384 mg/l. Figure 8 shows that the presence of detergent causes considerable flux decline with both distilled and river water due to the presence of oil-detergent emulsion, and free detergent molecules. Figures 9 and 10 shows that gel-polarization (maximum R_f) with distilled water system will occur for membrane operation at > 20 psi or for membranes of initial water flux ≥ 200 gal/ft²-day. With river water (Figure 11) the flux drop was quite severe at 25°C. At 25°C no flux improvement was observed with membranes of initial water flux greater than 50 gal/ft²-day. At 40°C, a maximum water flux of 41 gal/ft²-day (corresponds to flux drop of 59% at 100 gal/ft²-day initial flux) could be achieved with the river water system.

The dependence of steady-state water flux, J_w , on the initial water flux for the oil-detergent-water system is compared with other systems and the results are summarized in Figures 12 and 13. It is

interesting to observe from Figure 12 that with membrane initial water flux less than 200 gal/ft²-day, membrane-detergent interaction (R_i in Equation 2) rather than surface fouling (R_f in Equation 2) determines the value of the steady-state water flux. In the lower initial water flux range since the free detergent concentration is lower in the presence of oil (because of emulsification), the water flux is higher than the detergent-distilled water system. With river water the steady-state water flux (Figure 13) is dictated by both membrane-detergent interaction and surface fouling; the surface fouling can be reduced by operating at higher temperatures. The increase in percent flux loss (with both oil-water and oil-detergent-water systems) with initial water flux is consistent with the surface fouling theory (Equation 5).

The overall organic carbon rejection was 96% to 98% with the oil-detergent-water system. Surfactant rejection (because of emulsification) was enhanced in the presence of oil. The oil concentration in the ultrafiltrate was always less than 10 mg/l.

Bilge Water System. A series of ultrafiltration experiments was also conducted with actual bilge water. Table 3 shows the analysis of the bilge water used in the ultrafiltration studies. Figure 14 shows long-term flux behavior (without any membrane cleaning) with the bilge water and bilge water plus added MIL-D detergent. The membrane tube was allowed to depressurize at the end of each 8 hour run for at least 1 hour. In the absence of detergent, excellent flux behavior was obtained; the flux stayed constant after 10 hours and the flux drop was only 13%. An abrupt flux drop occurred (Figure 14) after detergent

addition. Figure 15 shows the effect of detergent concentration on the steady-state water flux. It is interesting to observe that the water flux, J_w , becomes constant above a critical concentration. This behavior is similar to that observed in Figure 4. The higher critical detergent concentration (compared to detergent-distilled water system) was due to partial oil-detergent emulsification. The ultrafiltrate oil concentration was always less than 8.5 mg/l.

Membrane Water Flux Recovery (cleaning). Figure 16 shows the water flux recovery obtained after flushing with tap water at the end of each run. With the detergent system flux recovery was 100% even with membranes of high initial water flux (> 100 gal/ft²-day), could not be removed by simple water flushing. For example, with oil-detergent-distilled water system the steady-state water flux (Figure 12) for membranes of initial flux 200 gal/ft²-day was 64 gal/ft²-day and tap water flushing recovered the flux to 95 gal/ft²-day (Figure 16). Chlorine cleaning (Figure 17 right) provided complete flux recovery for oil-detergent-distilled water system. Since oil-detergent-river water system causes extensive surface fouling problems (Figure 11), particularly with membranes of high initial water flux, the flux recovery even with chlorine cleaning was incomplete (Figure 17 left). With membranes of high initial water flux (200 gal/ft²-day), chlorine cleaning restored the water flux from 15 gal/ft²-day to 88 gal/ft²-day. It was also observed that flux recovery (by cleaning) to values greater than 100 gal/ft²-day was unnecessary for maintaining adequate steady-state flux with waste systems.

CONCLUSIONS

Ultrafiltration studies with oil, detergent, water, systems indicate that nonionic surfactant causes substantial water flux drop due to adsorption and/or micelle formation of detergent molecules in the membrane pores. The water flux approaches a constant value above a critical detergent concentration. For all systems, steady-state water flux was a function of initial membrane water flux. Membrane surface fouling due to stable oil-detergent emulsions and fine suspended solids could be minimized by membrane operation at low pressure or with membrane of initial water flux less than 100 gal/ft²-day. Oil-detergent-river water system causes maximum surface fouling at an operating temperature of 25°C. Flux drop can be minimized by operating at higher temperature (40°C) and/or with membrane depressurization at intervals of 8 to 10 hours for at least 1 hour. Depending on the oil, detergent, water system, partial to complete flux recovery could be obtained with chlorine cleaning. Frequent membrane cleaning, however, is found to have an adverse effect on the final water flux.

At 25°C, the steady-state water flux values (in gal/ft²-day) with membrane operated at an initial water flux of 200 gal/ft²-day, and with distilled water systems (oil 500 mg/l, detergent 100 mg/l), are: 54 with detergent only, 103 with oil only, and 63 with oil plus detergent. With river water systems the steady-state water flux (in gal/ft²-day) values are: 30 with oil only and 15 for oil plus detergent with membrane of initial flux > 100 gal/ft²-day. The water flux with oil-detergent-river water system could be increased to 41 gal/ft²-day by operating at 40°C.

The water flux behavior is explained in terms of membrane resistance increase due to detergent interaction, and due to surface fouling in the presence of emulsions and suspended solids. Excellent oil rejections are obtained in all cases; even with oil-detergent systems, an ultrafiltrate oil concentration of less than 10 mg/l can be achieved.

Membrane area requirements are dependent on the type of oil-water mixture to be processed, i.e., whether the mixture contains distilled, river or sea water. Processing oil-river water mixtures requires approximately three-fold more membrane area than oil-distilled or oil-sea water mixtures.

REFERENCES

1. Harris, L.R., Jackson, D.F., and Schatzberg, P., "Oily Bilge Water Treatment with a Tubular Ultrafiltration System," *Journal of Engineering for Industry*, vol. 98, No. 4, November 1976.
2. Harris, L.R., Schatzberg, P., Bhattacharyya, D., and Jackson, D.F., "Ultrafiltration of Black and Grey Wastewater," ASME Publication 77-ENAS-57 (1977).
3. Bhattacharyya, D., Garrison, K.A., and Grieves, R.B., "Membrane Ultrafiltration for Treatment and Water Reuse of TNT-Manufacturing Wastes," *J. Water Poll. Control Fed.*, 49, 800 (1977).
4. Bhattacharyya, D., Jumawan, A.B., Grieves, R.B., and Witherup, S.O., "Ultrafiltration of Complex Wastewaters: Recycling for Nonpotable Use," *J Water Poll. Control Fed.*, 50, 846 (1978).
5. Smookler, A.L., and Harden, J.W., "Navy Shipboard Investigations of Oily Waste," *Proc. Joint Conf. on Prevention and Control of Oil Poll.*, Washington, D.C. (1975).
6. Finger, S.M., and Tabakin, R.B., "Development of Shipboard Oil/Water Separation Systems," ASME Publication 73-ENAS-38 (1973).
7. Smookler, A.L., Harden, J.W., and Conroy, P.D., "Navy Development of Suitable Shipboard Bilge Oil/Water Separators," *Proc. of 1977 Oil Spill Conference*, 423 (1977).
8. Schatzberg, P., Harris, L.R., Adema, C.M., Jackson, D.F., and Kelly, C.M., "Oil/Water Separation with Non-Cellulosic Ultrafiltration Systems," NSRDC Report 4530, AD-A008315/4WP (1975).
9. Bansal, I.K., "Concentration of Oily and Latex Wastewaters," *Proc. 3rd Natl. Conf. on Complete Water Reuse*, Cincinnati, Ohio (1976).
10. Goldsmith, R.L., Roberts, D.A., and Burre, D.L., "Ultrafiltration of Soluble Oil Wastes," *J. Water Poll. Control Fed.*, 46, 2183 (1974).
11. Gollan, A., "Treatment of Chemical and Mechanical Diesel Oil-Water Emulsions by Ultrafiltration Membranes," ASME Publication 75-ENAS-57 (1975).
12. Matz, R., and Meitlis, Y., "Design and Operating Parameters for Tubular Ultrafiltration Membrane Modules," *Desalination*, 24, 281 (1978).

13. Sutor, J.W., Marner, W.J., and Ritter, R.B., "The History and Status of Research in Fouling of Heat Exchangers in Cooling Water Service," *Canad. J. Chem. Eng.*, 55, 374 (1977).
14. Kimura, S., and Nakao, S., "Fouling of Cellulose Acetate Tubular Reverse Osmosis Modules," *Desalination*, 17, 267 (1975).
15. Gutman, R.G., "The Design of Membrane Separation Plant," *The Chemical Engineer*, 510 (July, 1977).

TABLE 1. TUBULAR MEMBRANE CHARACTERISTICS

<u>Parameter</u>	<u>Membrane</u>
Composition	Non-cellulosic
Diameter, inches	1.0
Length, ft	5.0
Membrane area, ft ²	1.1
Apparent pore size, A°	50
Maximum operating temperature, °C	60
pH range	2-13
Initial water flux (at 20 psi), gal/ft ² -day	150-300

TABLE 2. ANALYSIS OF RIVER WATER USED IN THE
ULTRAFILTRATION STUDIES

<u>Parameter</u>	<u>Concentration</u>
Total solids	11,156 mg/l
Suspended solids	594 mg/l
Conductivity	10, 800 μ mho/cm
Total Organic Carbon	3.1 mg/l
Iron	5.6 mg/l
pH	7.8

TABLE 3. ANALYSIS OF BILGE WATER

<u>Parameter</u>	<u>Concentration</u>
Total solids	11,135 mg/l
Suspended solids	575 mg/l
Conductivity	6,171 μ mho/cm
Total Organic Carbon	214 mg/l
Oil concentration (approx.)	280 mg/l
Iron	9.4 mg/l
pH	8.9

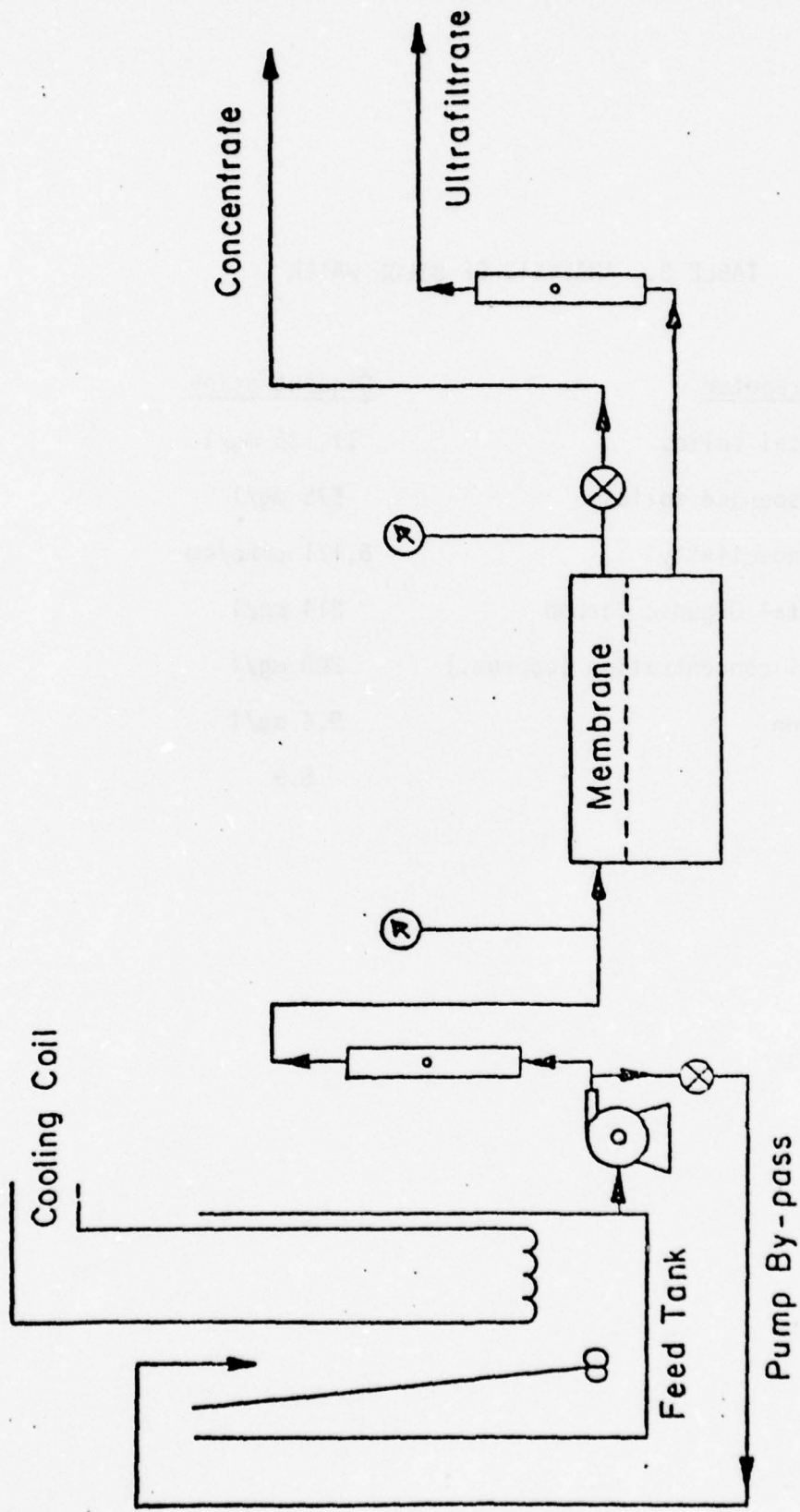


Figure 1. Ultrafiltration Test System.

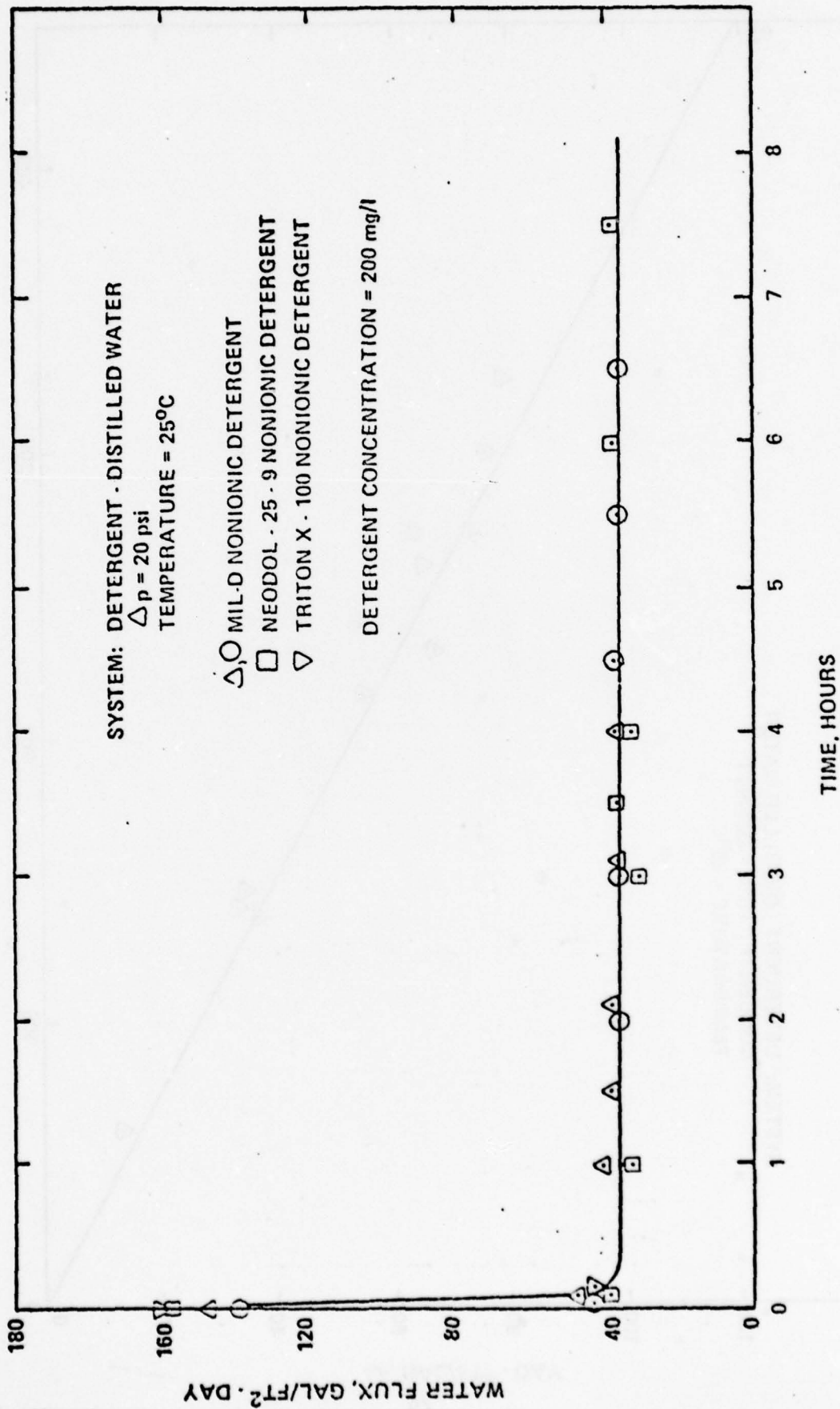


Figure 2. Variation of Water Flux Behavior With Operational Time for Detergent-Distilled Water System.

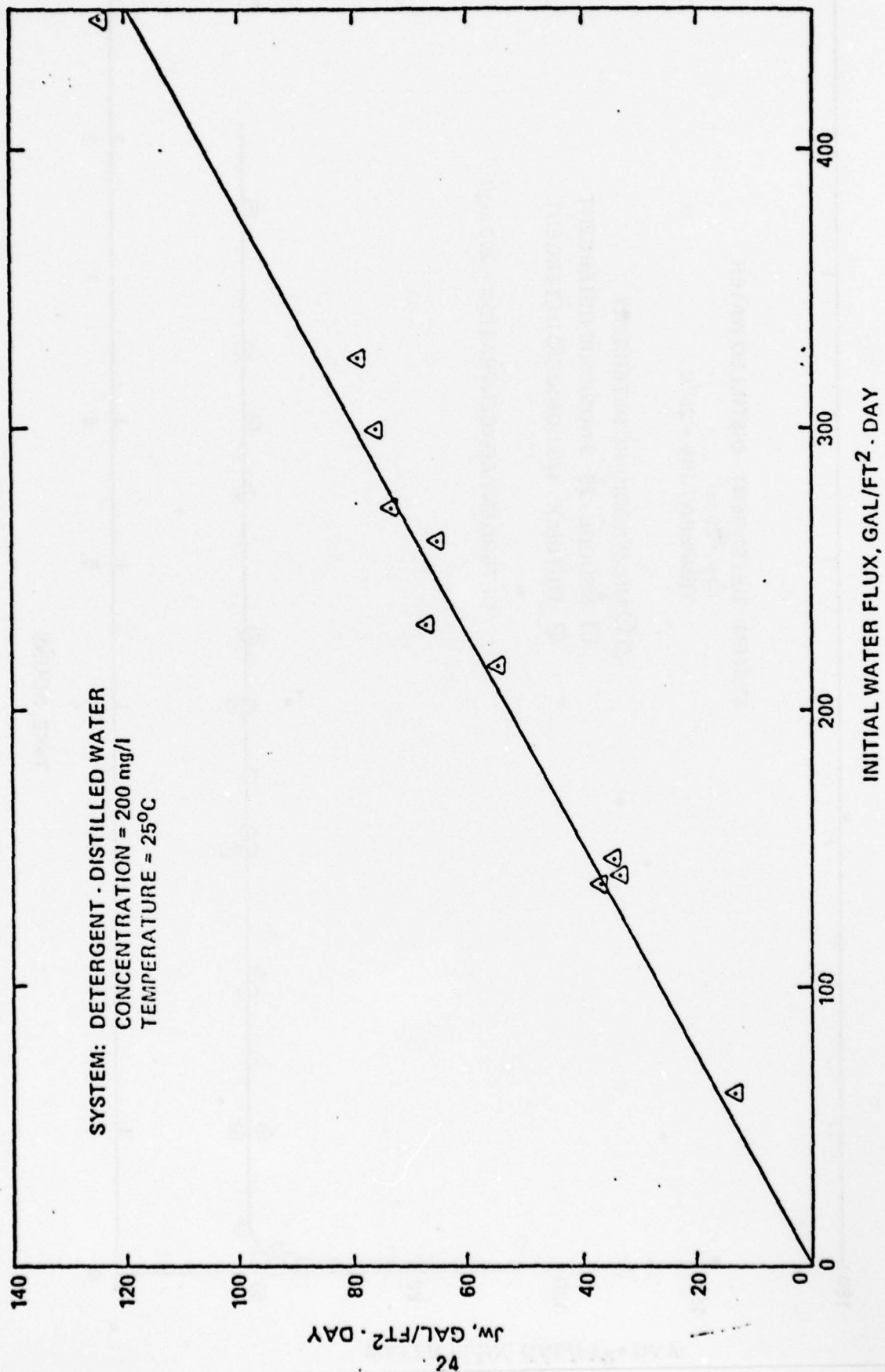


Figure 3. Dependence of Steady-State Water Flux on Initial Water Flux for Detergent-Distilled Water System

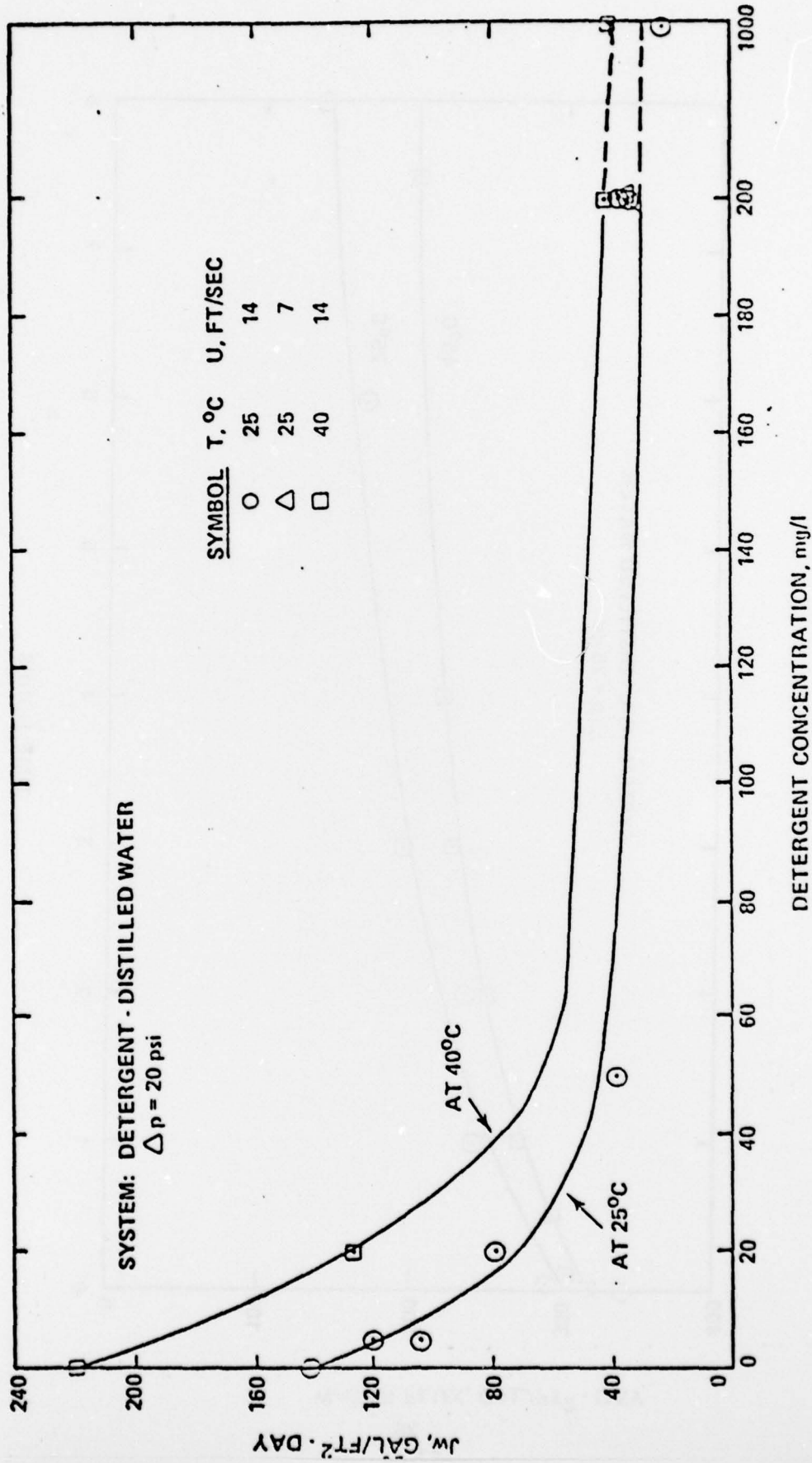


Figure 4. Effects of Detergent Concentration on Steady-State Water Flux.

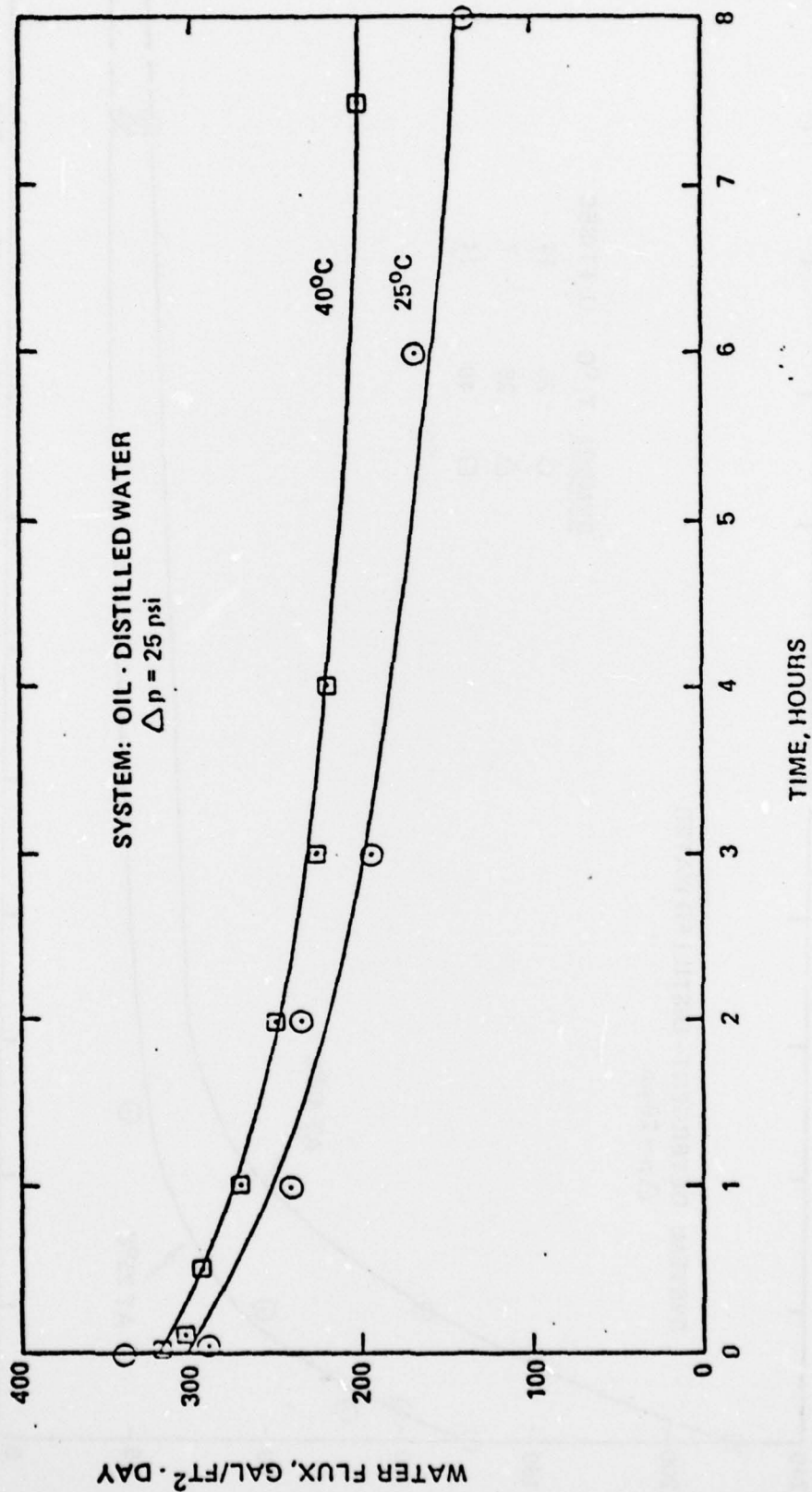


Figure 5. Time Dependence of Water Flux for Oil-Distilled Water System.

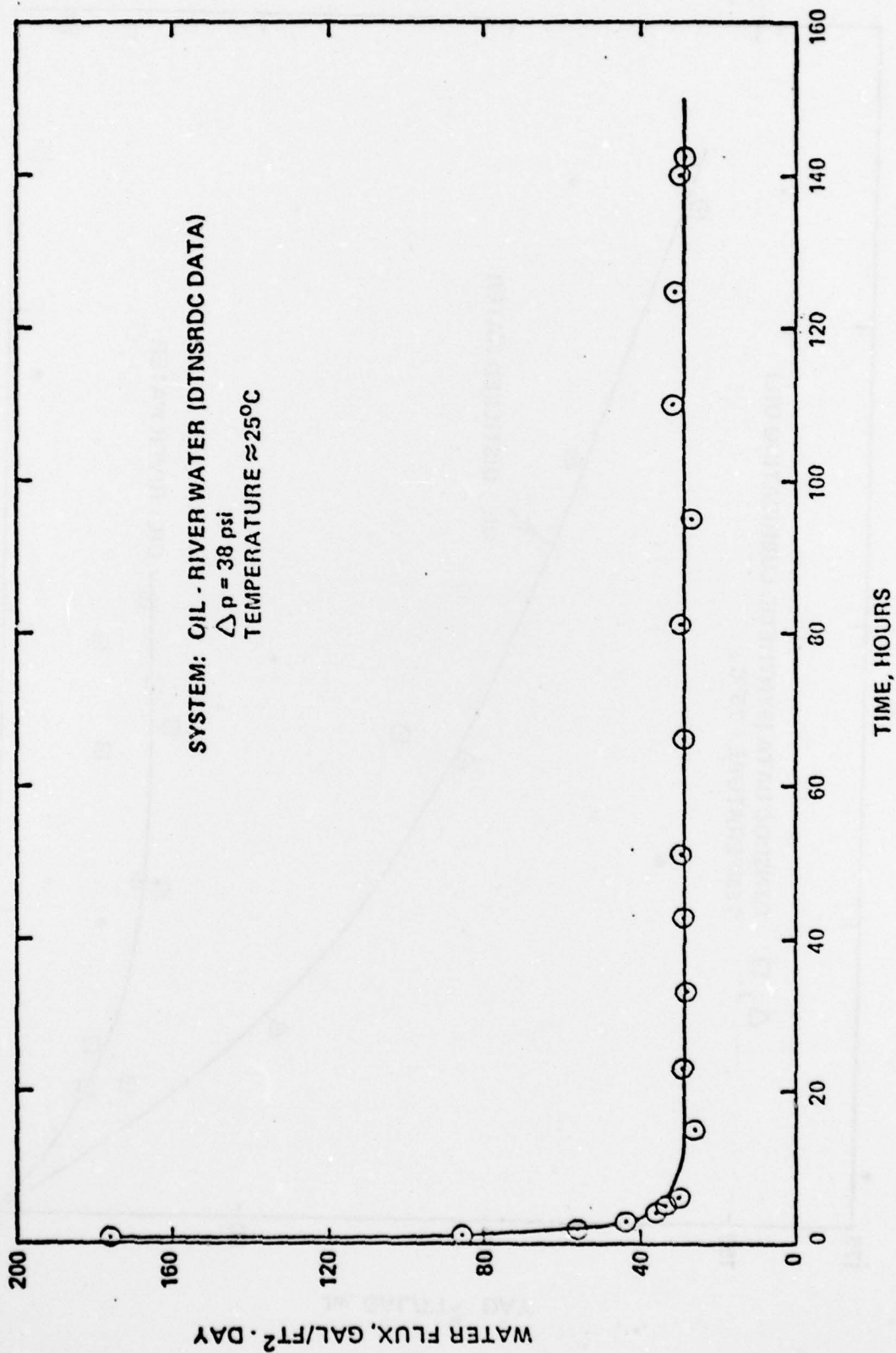


Figure 6. Time Dependence of Water Flux for Oil-River Water System.

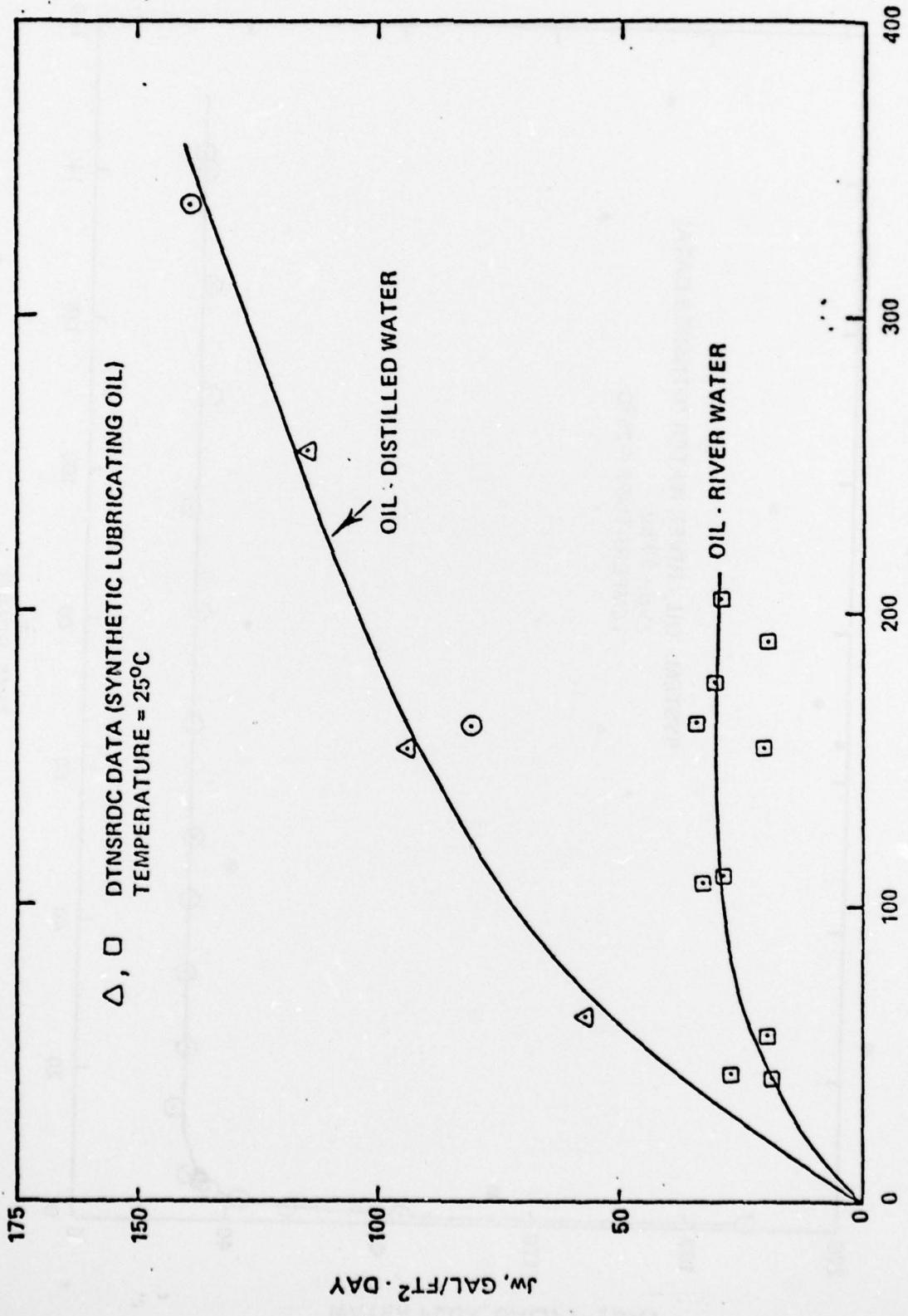


Figure 7. Dependence of Steady-State Water Flux on Initial Water Flux for Oil-Water Systems.

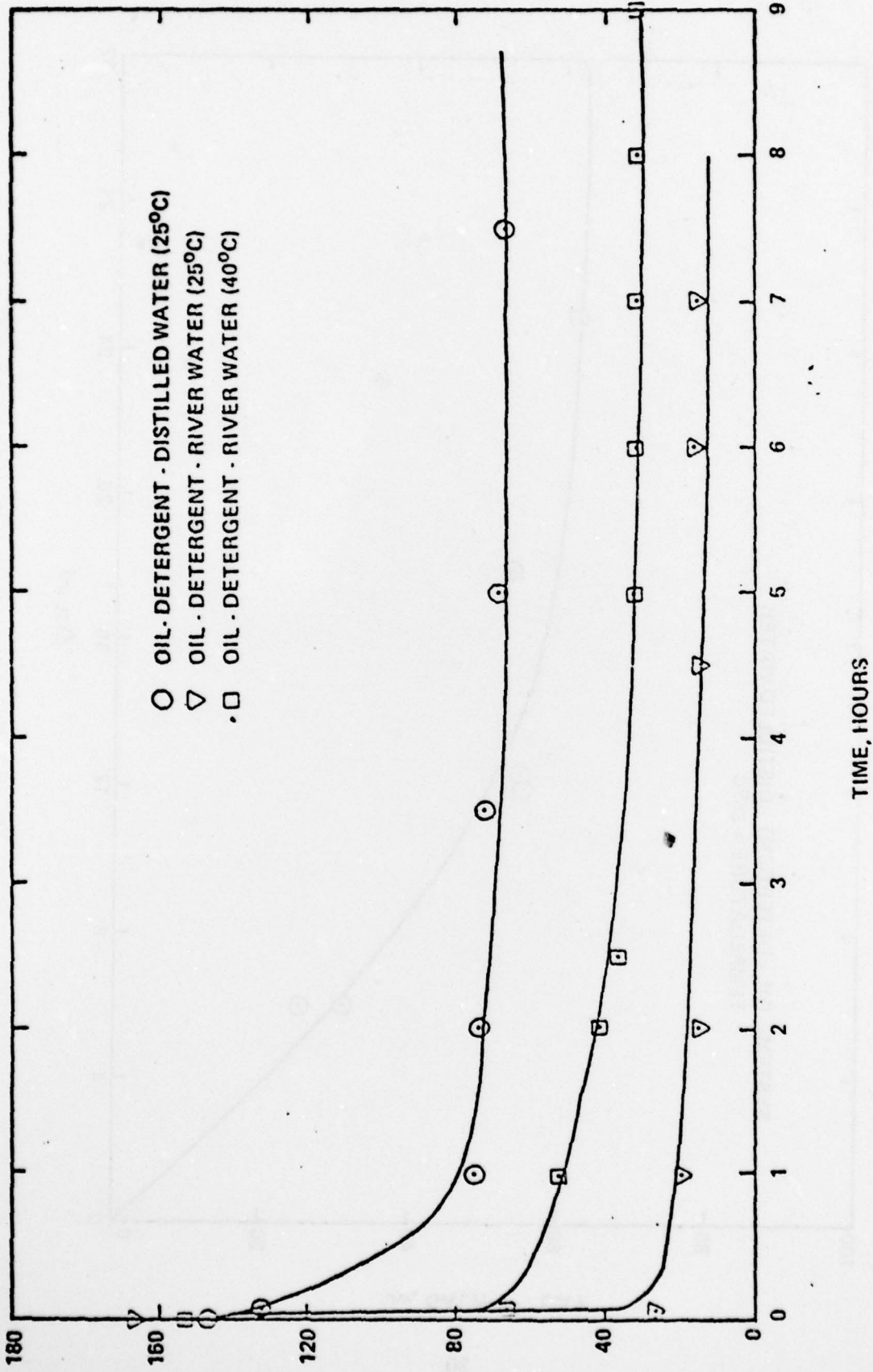


Figure 8. Time Dependence of Water Flux for Oil-Detergent-Water Systems.

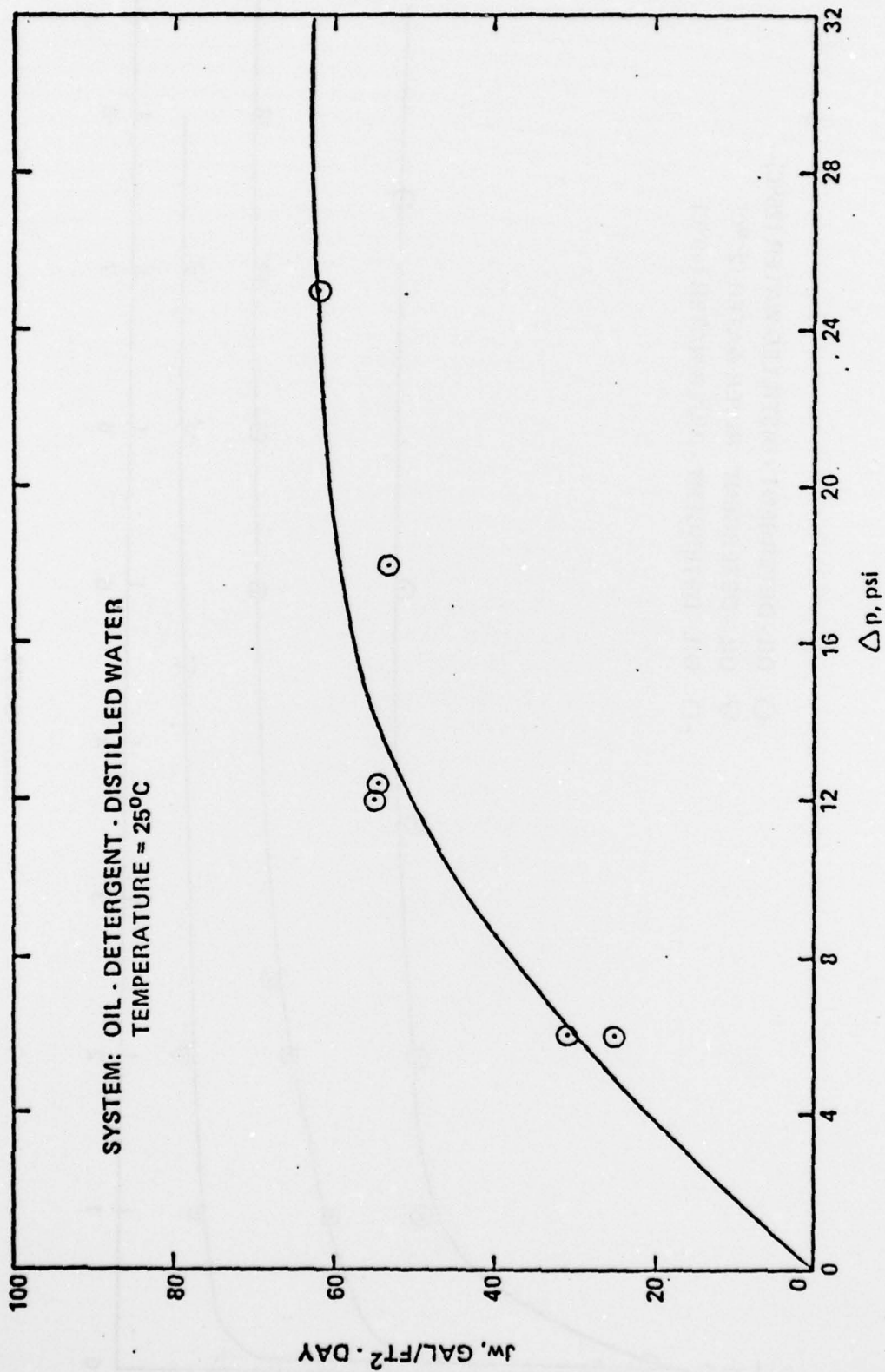


Figure 9. Transmembrane Pressure Effect on Steady-State Water Flux for Oil-Detergent-Distilled Water System.

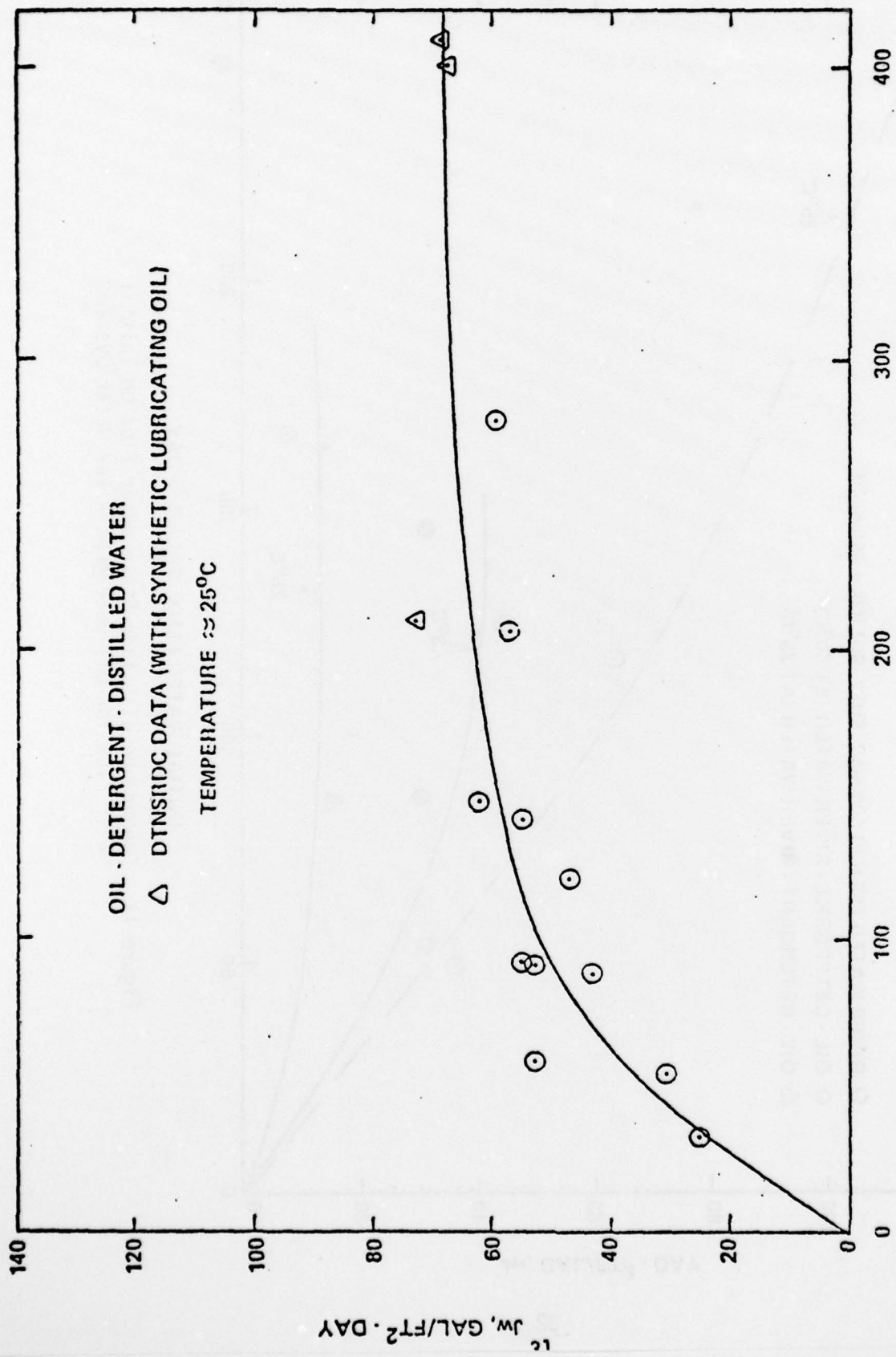
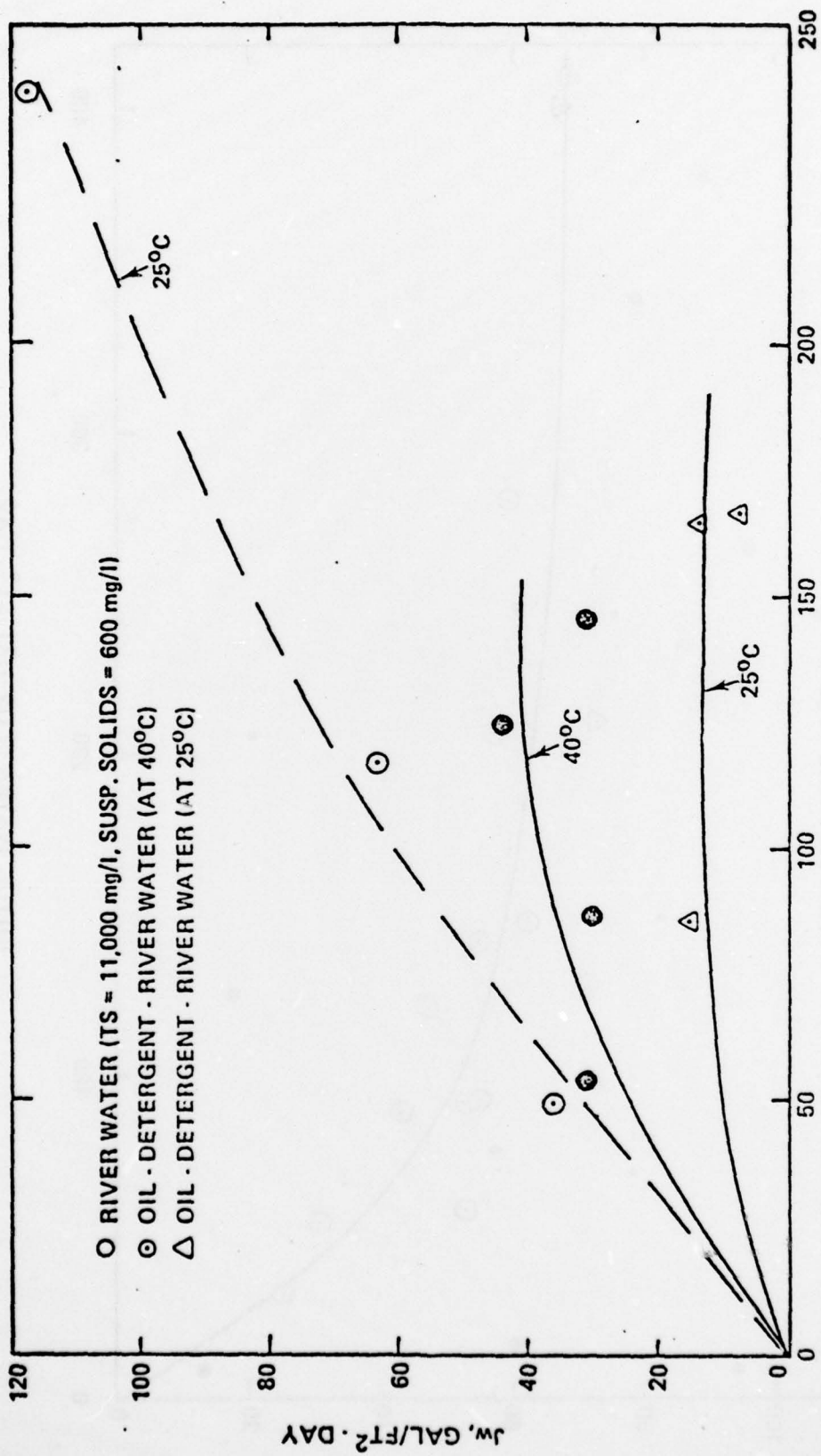


Figure 10. Dependence of Steady-State Water Flux on Initial Water Flux for Oil-Detergent-Distilled Water System.



INITIAL WATER FLUX, GAL/FT² · DAY

Figure 11. Dependence of Steady-State Water Flux on Initial Water Flux for Oil-Detergent-River Water System.

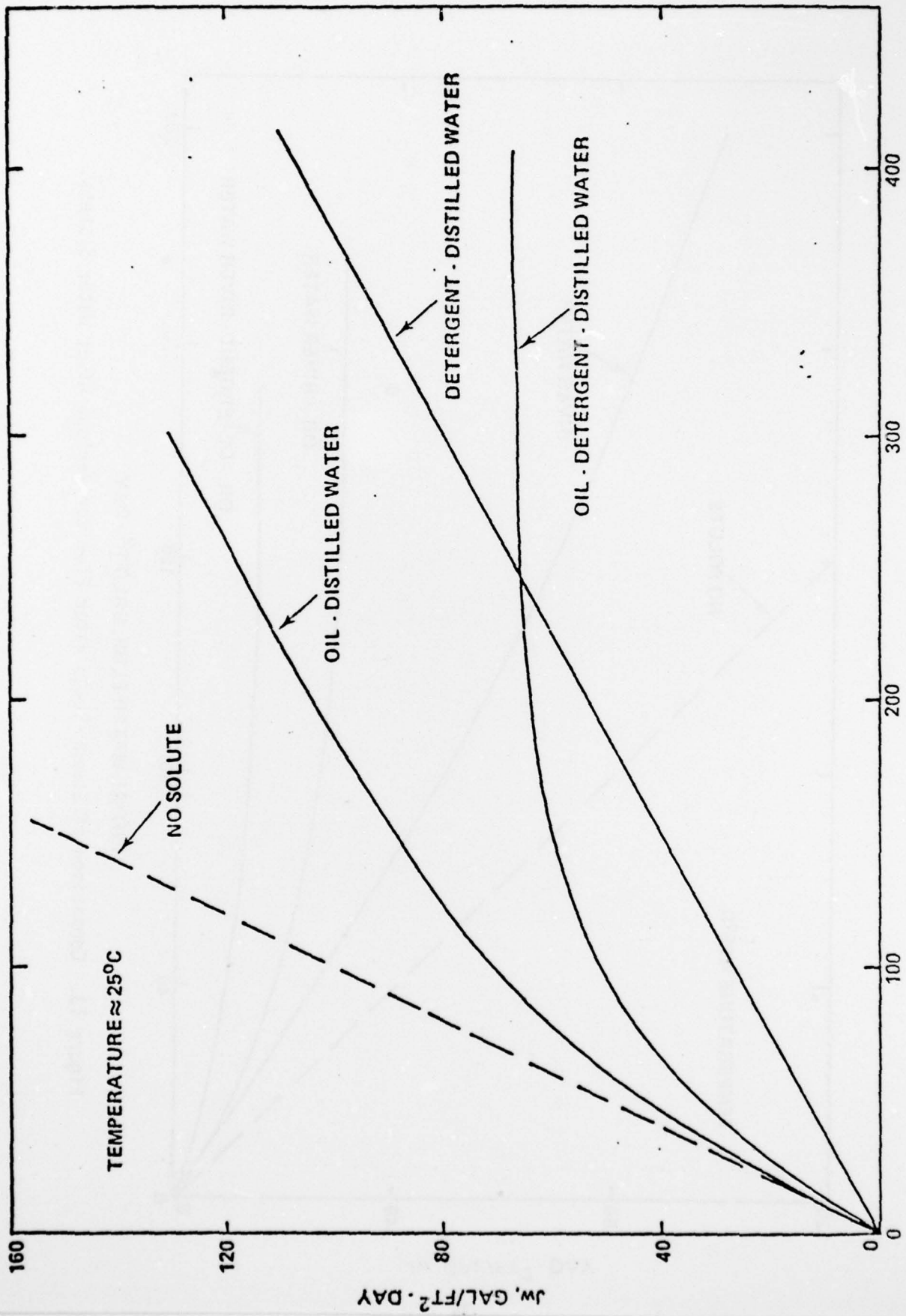
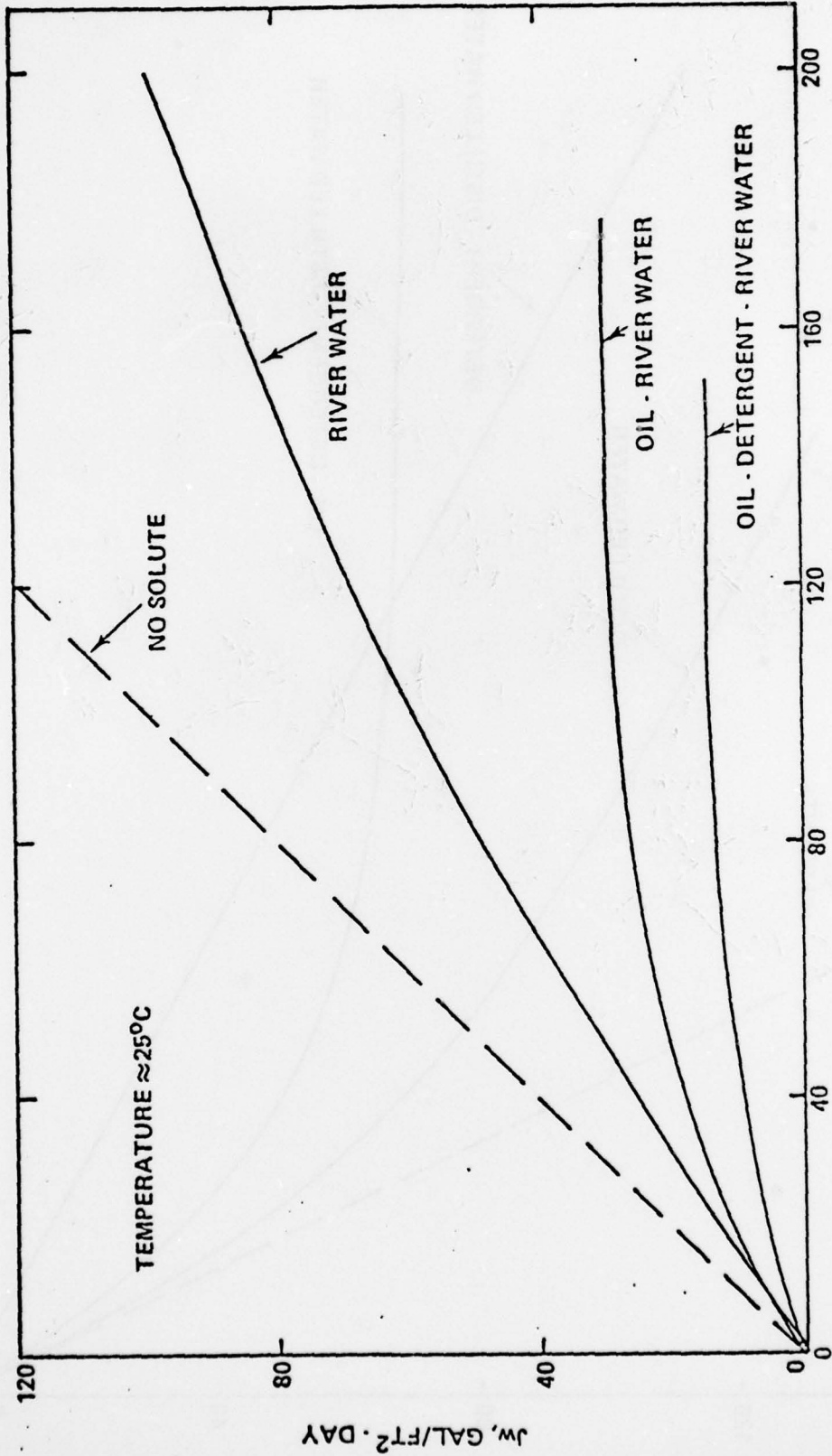


Figure 12. Comparison of Steady-State Water Flux for Various Distilled Water Systems.



INITIAL WATER FLUX, GAL/FT² · DAY

Figure 13. Comparison of Steady-State Water Flux for Various River Water Systems.

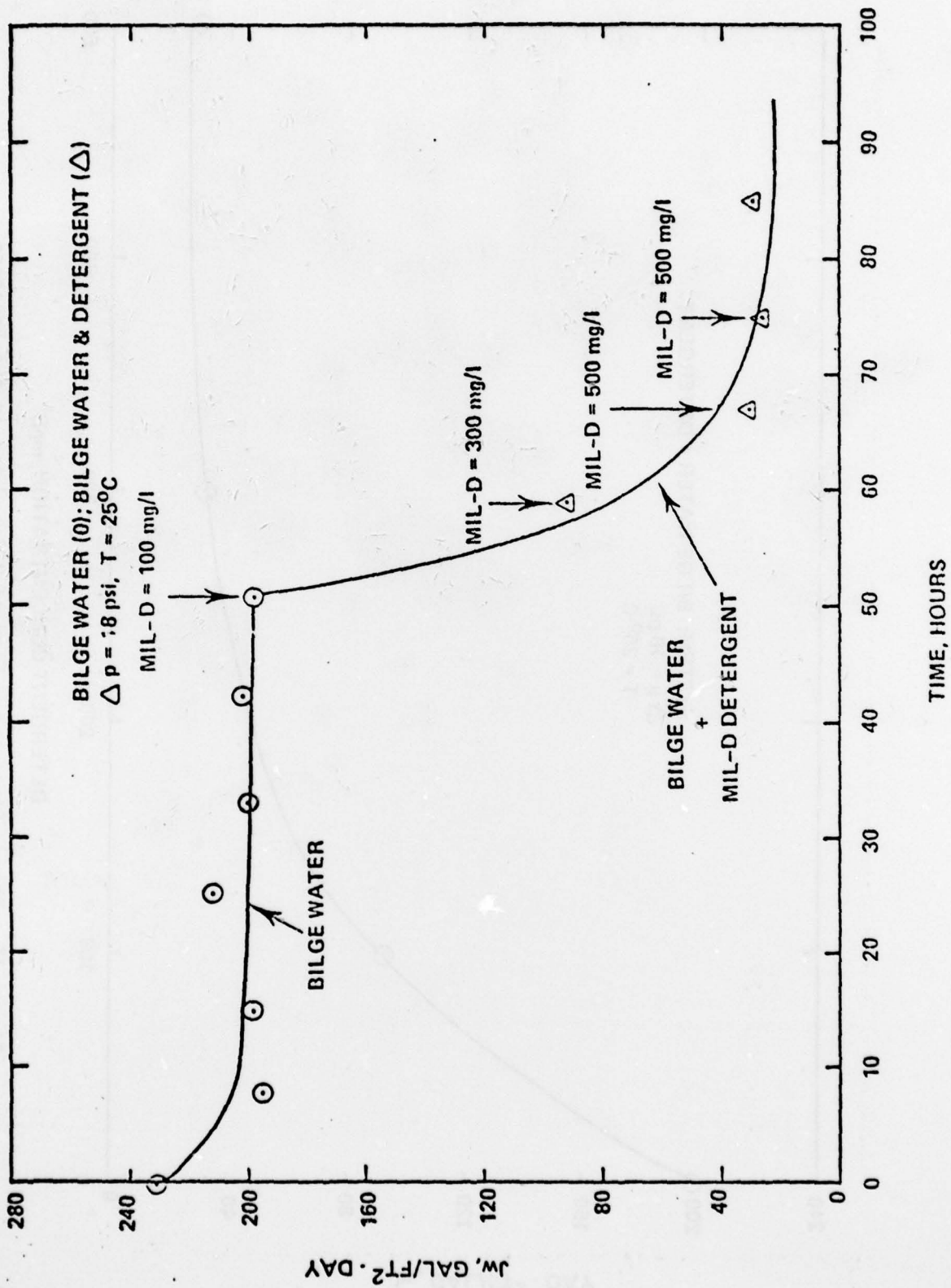


Figure 14. Time Dependence of Water Flux for Bilge Water Systems.

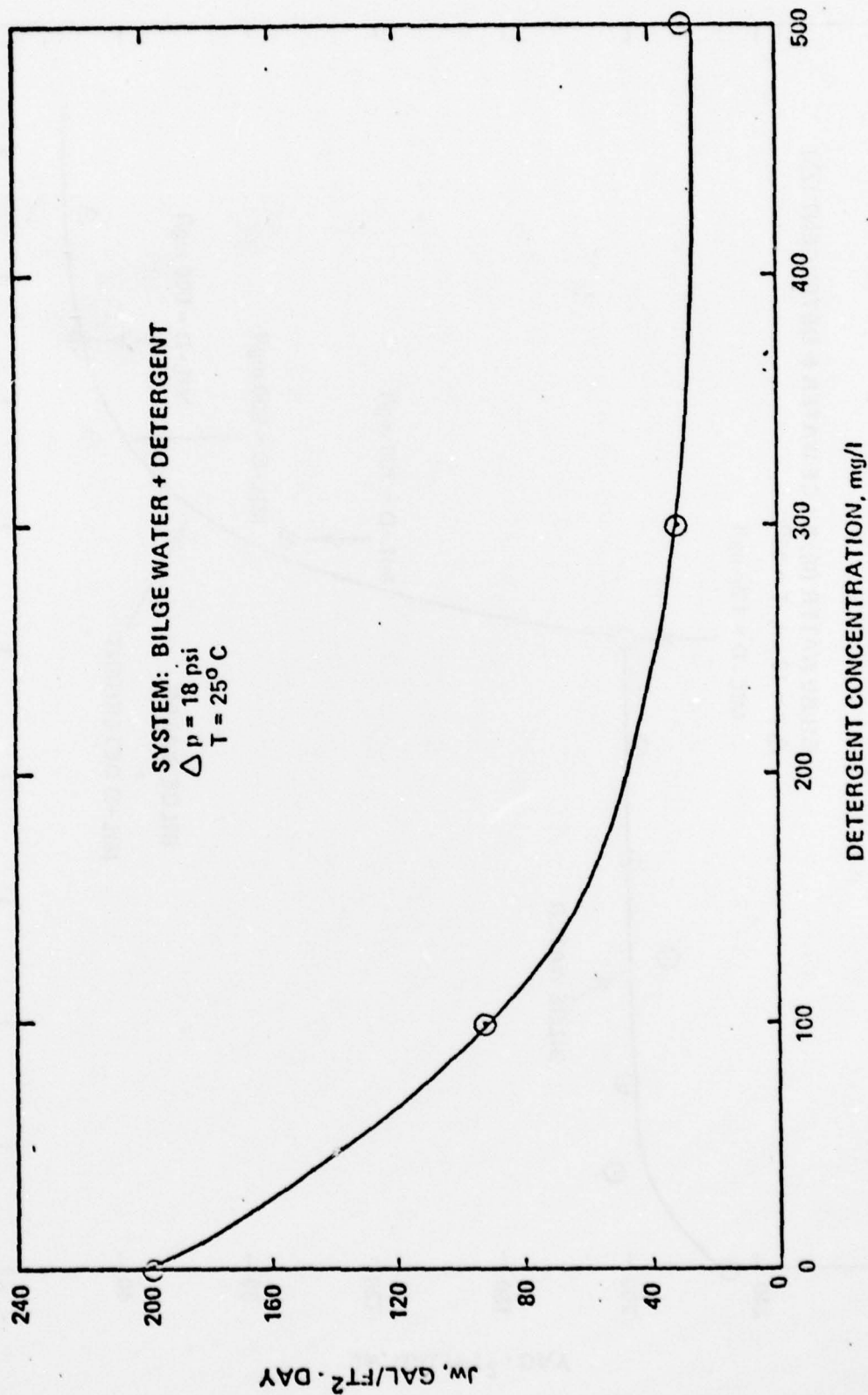


Figure 15. Steady-State Water Flux of Bilge Water in the Presence of Detergent at Various Concentrations.

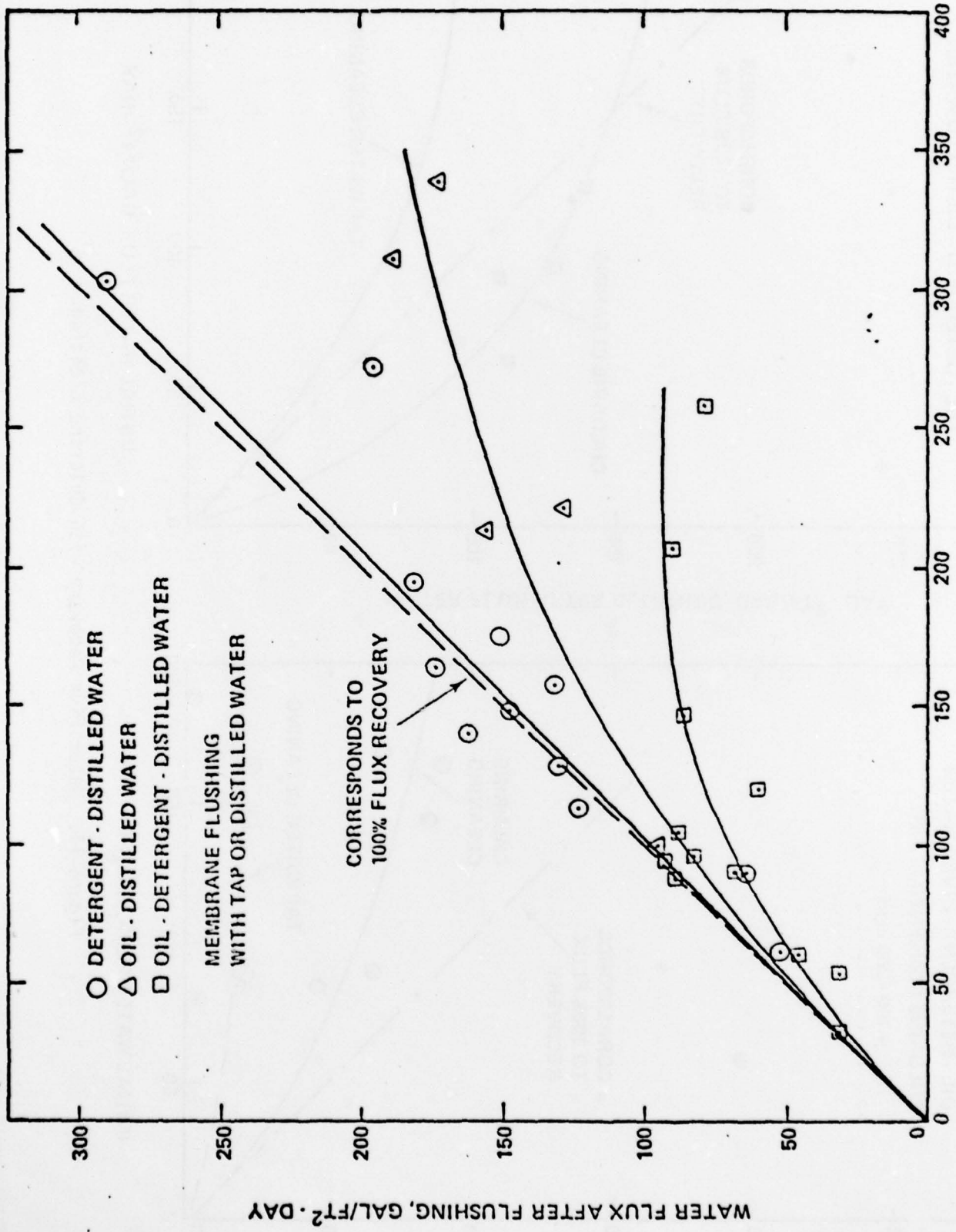


Figure 16. Water Flux Recovery with Tap Water Flushing.

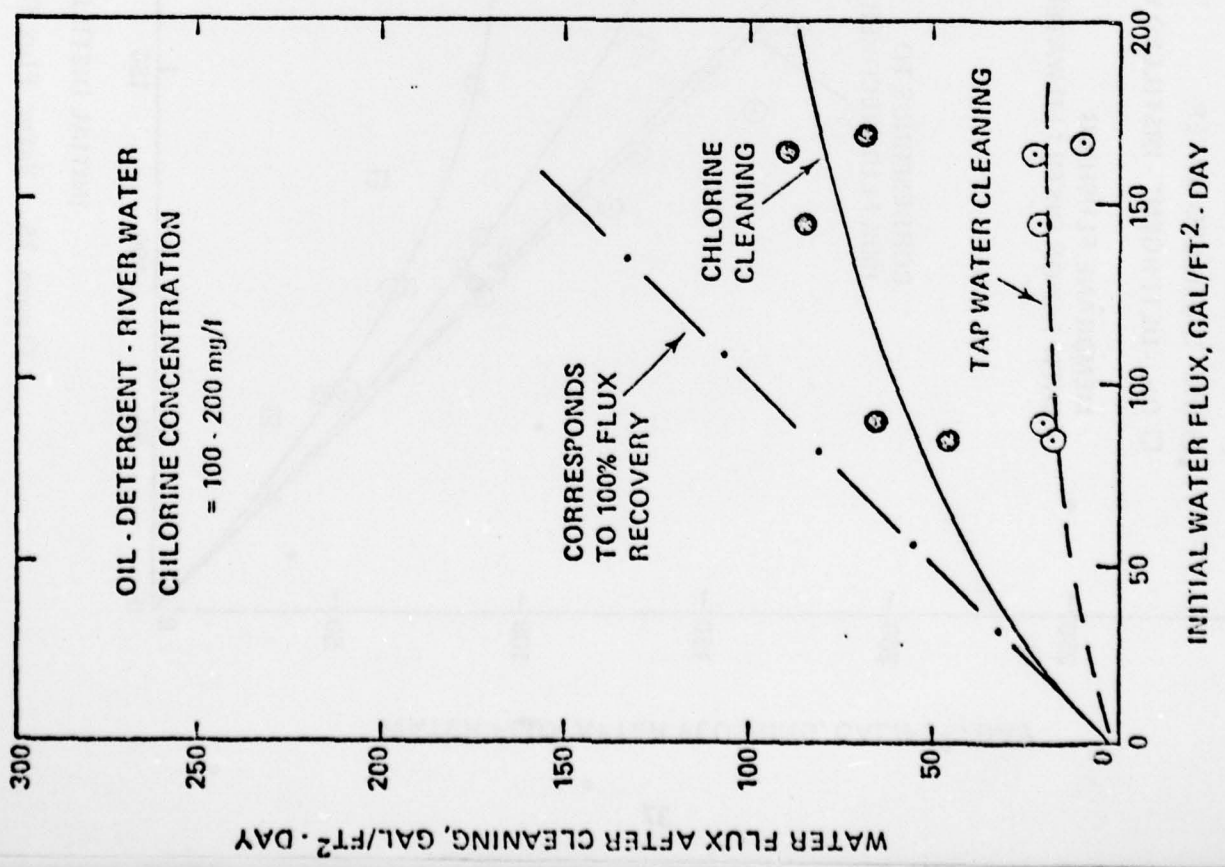
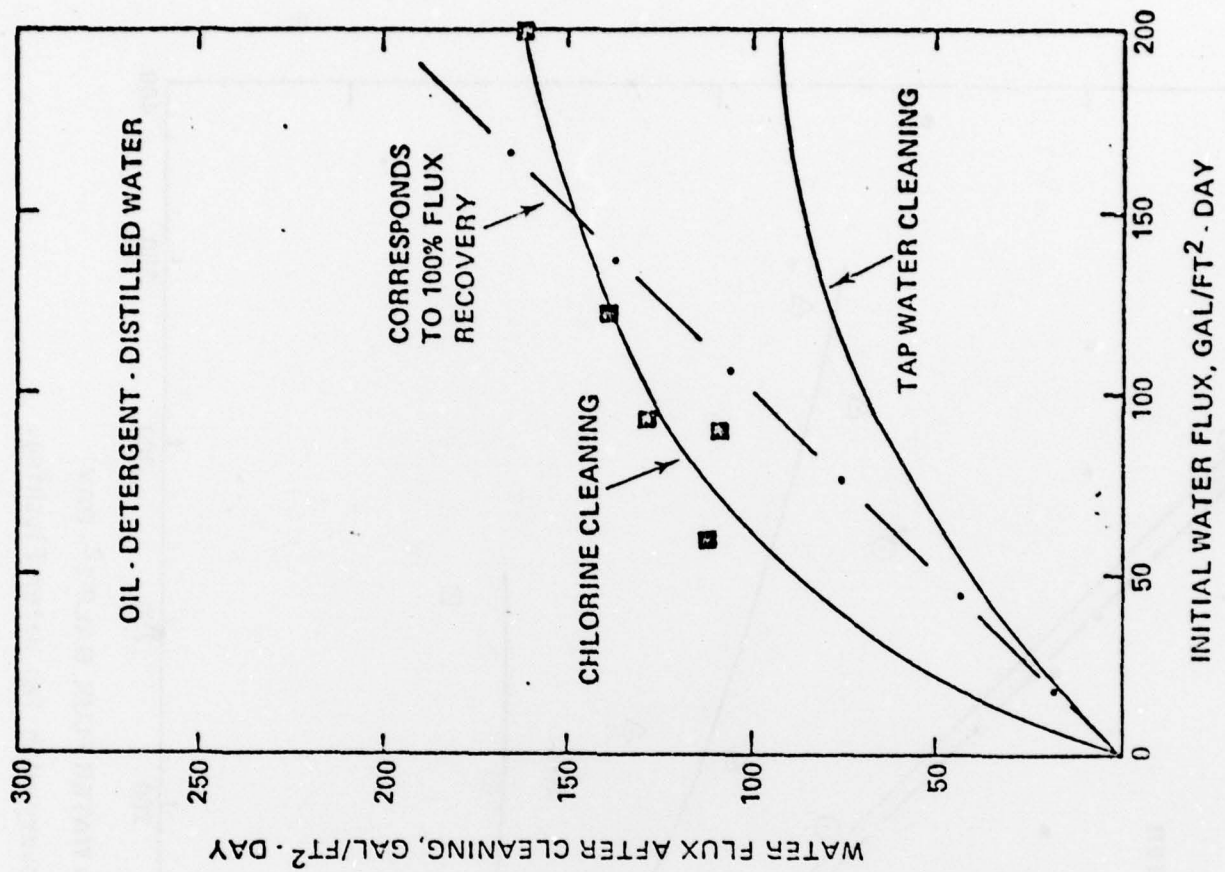


Figure 17. Water Flux Recovery with Chlorine Cleaning.