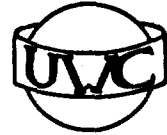


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OPTIMIZATION OF A REVERSE OSMOSIS
SEA WATER DESALINATION SYSTEM

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SUMMARY

A literature survey has been made which presents a summary review of the work previously undertaken by others in the field. In general, much of the material available in literature is theoretical in nature and serves to point out the need for practical application of basic principles. In addition, study of the literature collected provided a background for the work carried on under this contract and confirmed the soundness of the approach based on the use of formamide modified cellulose acetate membranes in flat and tubular form.

Experimental results indicate that formamide modified cellulose acetate membranes can desalinate sea water effectively. Membranes tested in flat laboratory cells have reduced the dissolved salts in sea water from 35,000 ppm to less than 500 ppm at 10 gal. sq ft-day under an operating pressure of 1250 psi in a single pass.

Results for tubular membranes have, thus far, shown a single pass reduction to only 1000 ppm. Present data, although limited, indicate that this may be due to the geometric form of the tubular support structure, the high operating pressure and module sealing difficulties.

Research on membrane production led to an improvement in membrane properties for membranes cast from a formamide-cellulose acetate-acetone casting solution containing pyridine. The membranes cast from the pyridine-containing solution showed an improvement in membrane physical properties. Successful development of the new, stronger membrane serves to verify the supposition that substantial areas for membrane improvement do exist.

While the tubular membrane may be developed to duplicate results obtained with the flat type, it seems advisable at this time to consider a two pass tubular system as an interim design to produce desired conversion for immediate applications and determination of membrane life.

In the meantime, membrane research should be continued as a logical step toward a one pass tubular membrane system. Use of pyridine in the membrane casting solution has shown substantial strength improvement, and this is important under rigorous sea water operating conditions. This effect should be further explored and other membrane improvement possibilities investigated to provide best possible effectiveness in the membrane itself.

As a parallel effort, further developmental work is needed to determine the optimum operating parameters and modifications of support structures to obtain full benefit from the potential of most advanced membrane technology.

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GENERAL INTRODUCTION

Interest in the demineralization of saline water has increased during the past decade. Of particular interest has been the reverse osmosis process, in which a semipermeable membrane is used to desalinize saline water with pressure as the driving force. The term osmosis is used to describe spontaneous flow of solvent into a solution, or from a dilute to a more concentrated solution when separated from each other by a semipermeable membrane. In order to obtain fresh water from saline water, the flow must be reversed, i.e., from the solution into a fresh water stream. Hence the term "reverse osmosis".

Reverse osmosis, as a process, is dependent on a semipermeable membrane. Thus the practical application of the concept as a desalting process will largely depend on the characteristics and properties of the membranes utilized.

Early work at the University of Florida resulted in the discovery of cellulose acetate as a suitable membrane material. In 1960, membranes modified by magnesium perchlorate were prepared at the University of California. These membranes possessed much improved water transmission rates in addition to high selectivity. Further improvements were made at the University of California in 1965 when formamide modified membranes were fabricated at ambient temperatures.

Reverse osmosis has now been successfully operated and shown to be a basically useful commercial process, with many possibilities for improvement and applications to be explored.

LITERATURE SURVEY

I. GENERAL REVIEW

1. Development of Cellulose Acetate Membranes

Reid and Breton (1), at the University of Florida discovered the selective properties of cellulose acetate membranes after screening a large number of commercially available polymeric films. Commercial cellulose acetate films and laboratory prepared membranes of Breton had the necessary selectivity; however, their water transmission rates were prohibitively low.

In 1960, Loeb and Sourirajan(2), at the University of California, took up the development of cellulose acetate membranes. They applied earlier findings of Dobry (3), who had been working on miscibility of aqueous magnesium perchlorate and cellulose acetate. By utilizing an aqueous solution of magnesium perchlorate as a modifying agent in acetonetic solutions of cellulose acetate and, by modifying the fabrication procedure they succeeded in increasing the apparent throughput of cellulose acetate membranes while retaining the high selectivity of the unmodified films. Aqueous magnesium perchlorate modified membranes were used at the University of California until 1965 when Manjikian (4) introduced an all organic casting solution consisting of cellulose acetate, formamide and acetone.

Since 1962, a concentrated search has been directed toward the discovery or development of suitable polymers as replacement for cellulose acetate. The objective was a membrane material with the selectivity of cellulose acetate but with higher water transmission rates and longer life. No membrane material superior to cellulose acetate has thus far been discovered.

Major efforts of groups such as Aerojet General, General Atomic, M.I.T. and others working with the Office of Saline Water have been aimed at the understanding of the mechanism of cellulose acetate selectivity, and the investigation of the parameters of the process as a whole.

2. Major Contributions

Membrane materials studied by Reid and co-workers (1) (5) (6) at the University of Florida resulted in their discovery of the selective properties of cellulose acetate. An additional major contribution was Breton's (7) efforts toward understanding the fundamental of the process.

Recent work on new polymer systems for reverse osmosis membranes was described by Saltonstall et al(8). They selected poly(vinylene carbonate) and polyacrylonitrile as candidates for study. Francis, P. S.(9) has studied the behaviour of ultra-thin membranes cast from polymers of differing structures in

an attempt to improve membrane performance. Baddour et al (10) have developed new techniques for preparing semipermeable membranes. These include thin film polymerization, salt inclusion, and solvent control. Michaels et al (11) after making a thorough study of the mechanism of salt and water flux through cellulose acetate membranes, used their findings as a guide in their search for new membrane materials. These included poly(sodiumstyrene sulfonate) and poly(vinylbenzyl trimethyl ammonium chloride). In addition, Lonsdale et al (12) have investigated nylon and complex cellulose compounds as membrane materials.

None of the materials investigated in these studies have shown any significant improvement over cellulose acetate.

Modifying agents were investigated by Loeb and Sourirajan⁽²⁾ at the University of California. They accomplished the successful modification of cellulose acetate membranes to achieve a 100 fold increase in membrane water transmission rates while retaining the selectivity of unmodified films. The original casting solution was a mixture of cellulose acetate, acetone and an aqueous solution of magnesium perchlorate. By proper control of fabrication variables, they succeeded in preparing a membrane with a very thin, dense surface layer and a relatively porous substructure. The high flux of these membranes was attributed to the lowered resistance to water flow through this thin surface layer. This has since been confirmed by studies at General Atomic and Aerojet General.

Since the initial work was based on empirical methods, various attempts were made to backtrack and determine the function of casting solution constituents and the effect of each fabrication step on membrane characteristics. Loeb and McCutchan (13), after an exhaustive study of electrolytic additives in casting solutions, concluded that the electrolyte, by virtue of its anion, served to "break" the residual ice structure of water present in the casting solution which, in turn, determined the proper structurization of the membrane. In the fabrication process, the evaporation period was given credit for the creation of the thin upper layer after which the film was immersed in ice water to stop further development of the skin and to form the porous substructure. Finally the film was cured to obtain the required membrane semipermeability.

In 1965, a major change was introduced in the modification and preparation of cellulose acetate membranes. Manjikian⁽⁴⁾ introduced an all organic casting system comprising cellulose acetate, formamide and acetone. The prevailing picture was changed radically in that aqueous inorganic electrolytes were replaced by organic non-electrolytes as modifying agents. This led to the hypothesis that modifying agents did not contribute to the desalinating ability of cellulose acetate membranes and that their only function was to reduce the resistance to water flow through the membrane by structurally modifying the film.

Keilin and his group (14) at Aerojet General have carried out an intensive investigation of the role of the "membrane salt" in the fabrication of high flow cellulose acetate membranes. They have shown that the membrane salt does not modify cellulose acetate chemically and that it is completely removed from the membrane during the fabrication process. It is stated that the membrane salt acts as a swelling agent and as such contributes directly to the amount and nature of water retained in the finished membrane.

Mechanisms of salt rejection of cellulose acetate membranes was first studied at the University of Florida. The classic investigative work of Breton (7) on the phenomenon of cellulose acetate semipermeability has served as a guide in nearly every aspect of hyperfiltration developmental work undertaken since 1957. A modified version of his solution/diffusion mechanism is still the most widely accepted explanation of cellulose acetate permeability, regardless of intermediate reasoning processes.

The selectivity mechanism was also studied by Merten and co-workers (15) at General Atomic who have been instrumental in the advancement of osmotic membrane technology in recent years. Their initial contribution was the derivation of a modified equation for water flow through cellulose acetate membranes. The diffusivity of water was measured in an unmodified membrane and used in calculating the apparent thickness of the active surface layer of a modified membrane. It has been shown experimentally that the modified cellulose acetate membrane is asymmetric in nature, i. e. one surface is semipermeable while the other is not selective. Thus it was hypothesized that the modified membrane consisted of a very thin, dense surface layer and a relatively porous sublayer.

In a related study, electron micrographs of a modified cellulose acetate membrane were taken by Lonsdale et al (16) showing distinctly the predicted asymmetry. From these micrographs, the thickness of the active surface was measured and found to be very close to the value obtained from the diffusion equation. This led to the conclusion that the high flux of a modified membrane was due to the lowered resistance of a thin active layer and that this layer in a modified membrane had essentially the same characteristics of an equivalent layer of an unmodified cellulose acetate membrane.

Wasilewsky (17) investigated the nature of changes that occur in cellulose acetate membranes on heating at elevated temperatures. By taking microwave spectra of cellulose acetate membranes, he succeeded in showing that changes brought about by the curing process resulted from liberated rotational motion of segments and side chains of cellulose acetate molecules. In unheated membranes, most of the oxygen atoms of the carbonyl groups are intra-molecularly hydrogen bonded. During the heating at elevated temperature, enough energy is absorbed to break this bond and to cause the group to rotate about a single bond, bringing two segments from different cellulose

acetate molecules close together to form a new inter-molecular bond. This bond, being stronger than the original intra-molecular bond, permanently immobilizes the segments involved. The formation of inter-molecular bonds results in smaller intra and inter-molecular spaces, thus decreasing the size of "pores" in the active skin layer of cellulose acetate membrane.

Keilin and co-workers (14) have generally accepted, with some refinements, the Breton (7) hypothesis as to the mechanism of cellulose acetate semipermeability. In addition, they postulate that cellulose acetate membranes are completely semipermeable and that any dissolved salts present in the treated water is contributed by pore flow through defective sites in the thin surface layer.

Banks and Sharples (18) have taken the simplest and possibly the most reasonable view on the mechanism of water and salt flow through osmotic membranes. They assume that the dense surface layer is free of pores and that both water and salt are transmitted through the active layer by a true diffusion process, and that pure water flow is directly proportional to the net applied operating pressure while salt flow is not. Thus a 100 percent salt rejection is asymptotically approached at high operating pressures.

Boundary layer effects were investigated by Sherwood and co-workers (19) (20) at the Massachusetts Institute of Technology. The magnitude of the boundary layer effect was determined theoretically and experimentally by Sherwood et al (21). Equations presenting turbulent region performance of tubular reverse osmosis desalination units were investigated experimentally by Resenfeld et al (22). Additional data on this subject has been compiled by Brian (23). The effect of change in interface salt concentration and precipitation of insoluble salts on boundary layer conditions has been studied by Merten et al (24).

The above studies indicate that salt build up at the membrane-brine interface might present a future problem in limiting the performance of high flux membranes. In addition, boundary layer effects limit the design of the membrane support structure in that turbulent flow of brine across the membrane surface might be a necessary condition for effective membrane performance.

Membrane life has been investigated in the laboratory and under field conditions. Extended use of cellulose acetate membranes has resulted in most cases, in partial deterioration of membrane desalinating properties. A number of postulated causes and cures of membrane failure have been advanced by various investigations. Most active have been groups at Aerojet General (14) and General Atomic (25). The first group tends to ascribe membrane failure to microbial decomposition, while the second suggest hydrolysis of cellulose acetate as the cause of failure. In addition

to the above, some evidence is presented indicating a direct relationship between brine concentration and membrane life.

pH of feed water was found to influence the useful life of cellulose acetate membranes by Hatcher and Merten (25). Rapid decline in salt rejection properties was noted in membranes exposed to high pH solutions. However, they postulate a theoretical membrane life of 4.3 years at a pH of 4.8.

Banks and Sharples (18) have examined commonly proposed causes of membrane failure and conclude that at present, the nature of membrane failure is not fully understood.

Thus far, six month membrane life has been demonstrated under field conditions at a brackish water site (26).

In general, the above studies indicate that membrane life is determined largely by the environmental characteristics of the system to which the membrane is exposed.

Design of membrane support structures have taken three general forms: (1) the flat plate and frame concept, (2) spirally wound flat membranes in capsules and (3) tubular modules.

Early reverse osmosis units utilized the plate and frame concept. Loeb and Milstein (27) describe the first such unit to be built and tested at the University of California. Aerojet General (29) has since optimized this approach for use in commercial desalination units.

Spirally wound membrane capsules have been developed by General Atomic (30). These capsules are inserted in cylindrical pressure vessels and connected together to form the basic unit of a desalting plant.

Tubular structures were first disclosed by Havens Industries (31). The design provided for porous fiberglass tubes lined with membranes. In 1965, University of California efforts shifted from flat to tubular membranes. Their design as described by Loeb (28) comprised a metal outer tube, perforated at intervals, with a fabric nylon liner into which a tubular membrane is inserted.

Universal Water Corporation (32) has followed in principle the University of California tubular design approach, with basic modifications directed at the modular grouping of tubes and the use of plastics throughout.

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MEMBRANE STUDY

I. PROCEDURES

1. Membrane Fabrication Procedure

Cellulose acetate was dissolved in a mixture of solvent and modifying agent. For a standard membrane, cellulose acetate type E-398-3 was dissolved in a mixture of acetone and formamide. In general, any of the above casting solution components could be replaced by a suitable substitute. However, it is possible to add a fourth component to the casting mixture to enhance the role of either the solvent or the modifying agent.

After proper mixing of the casting solution, films were cast on plate glass with 0.005 - 0.015 side runners by use of a doctor blade, to produce flat membranes of variable thickness. Tubular membranes were cast in 0.435 inch I.D. stainless steel tubes with an as cast thickness of 0.008 - 0.015 inches.

In general, there is a time lapse between the casting of the film and immersion in water. For flat membranes prepared from formamide modified acetic solutions of cellulose acetate, a time lapse of 0 to 30 seconds is advisable. However, in the preparation of tubular membranes, the lapse between the above fabrication steps is not necessary. The accepted terminology of this time lapse is evaporation period. This time period is determined largely by the properties of the solvent and the modifying agent.

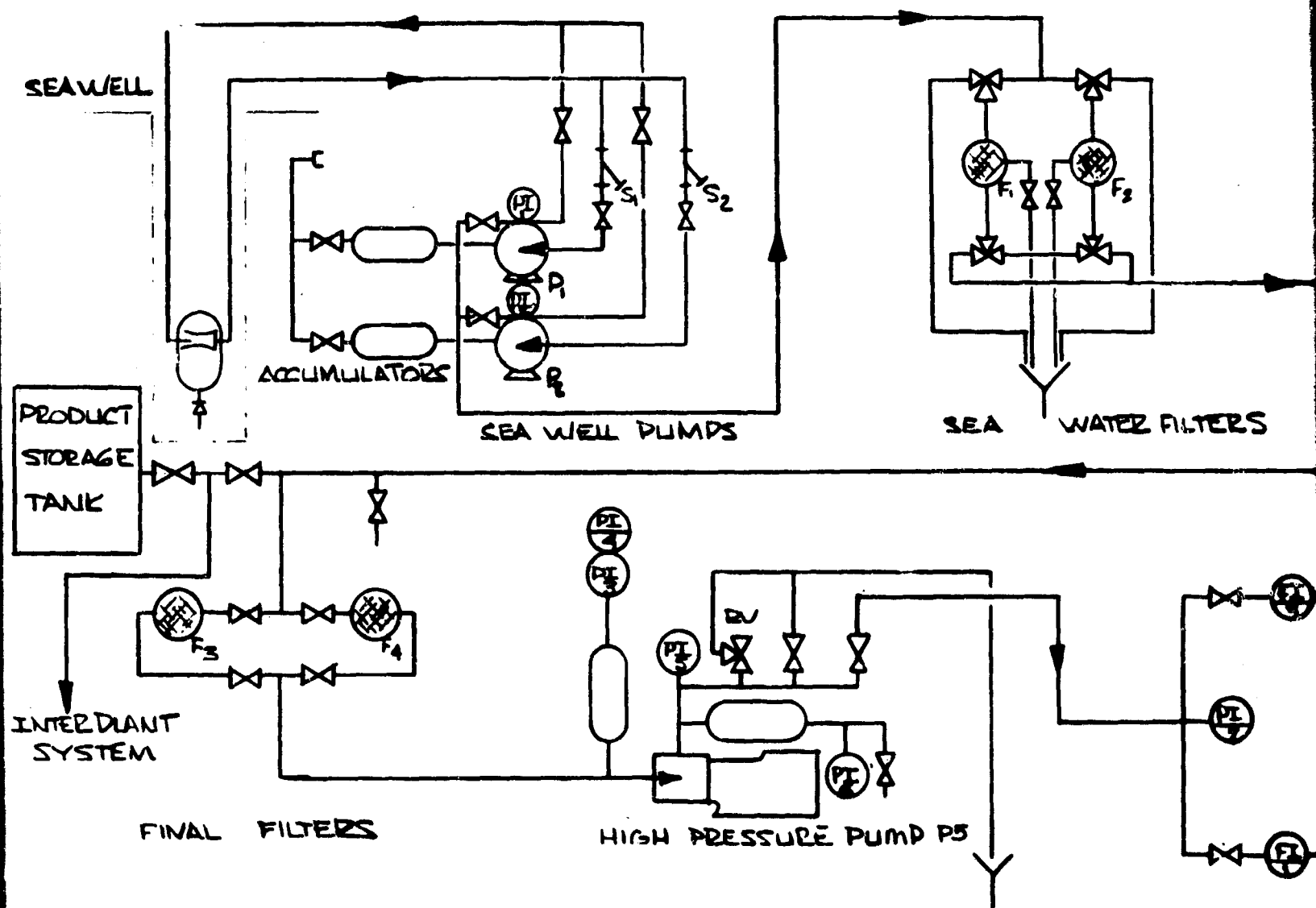
During the water immersion period the membrane achieves its final composition by exchanging the solvent and the modifying agent for water. However its structure is too "open" i.e., it is not selective in application. Up to this point the fabrication procedure has produced a structurally asymmetric membrane with a very thin, dense upper layer and a relatively porous substructure. This condition satisfies one of the two performance criteria, namely flux. Selectivity is achieved by curing the membrane at elevated temperatures which serves to consolidate the membrane and reduces the inter-intra chain spaces of cellulose acetate. The curing temperature is determined by performance requirements and fabrication and operational variables. Flat membranes are generally heated at 75-85°C. Tubular membranes are heated at 85 to 95°C. These temperature ranges are based on standard formamide modified membrane requirements.

2. Testing Procedures

Testing of developmental membranes was carried out in small flat laboratory cells as shown in Fig. 1. Fig. 2 is a flow diagram of the sea water test unit. Advanced membranes were prepared and tested in tubular form. Fig. 3 presents assembly details of a single tubular unit.

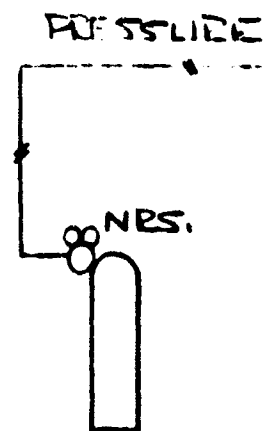
In general, with a feed water of 5,000 ppm TDS, membranes were tested at an operating pressure of 600 psig. When sea water was used as feed, operating pressure varied from 800 to 1400 psig. In all cases feed water flow across the membrane was kept in the turbulent range.

A



LEGEND

1. NRS NITROGEN REGULATORS
2. BPR BACK PRESSURE REGULATORS
3. NV NEEDLE VALVE
4. (PI) PRESSURE INDICATOR LOCALLY MOUNTED
5. (PI) PRESSURE INDICATOR PANEL MOUNTED
6. (ΔPI) DIFFERENTIAL PRESSURE INDICATOR
7. (FI) FLOW INDICATOR LOCALLY MOUNTED
8. ALL VALVES - BALL VALVES EXCEPT AS SHOWN



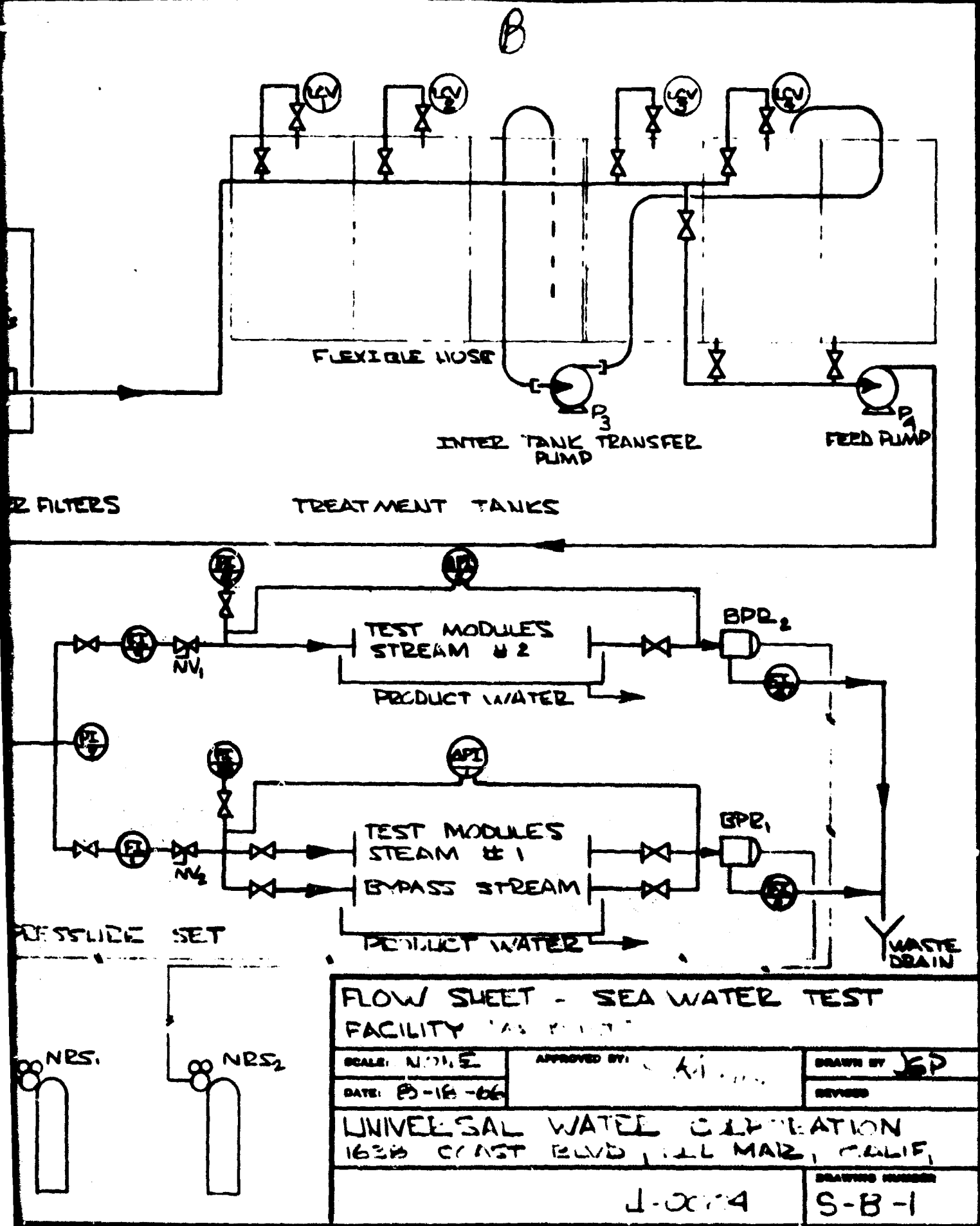
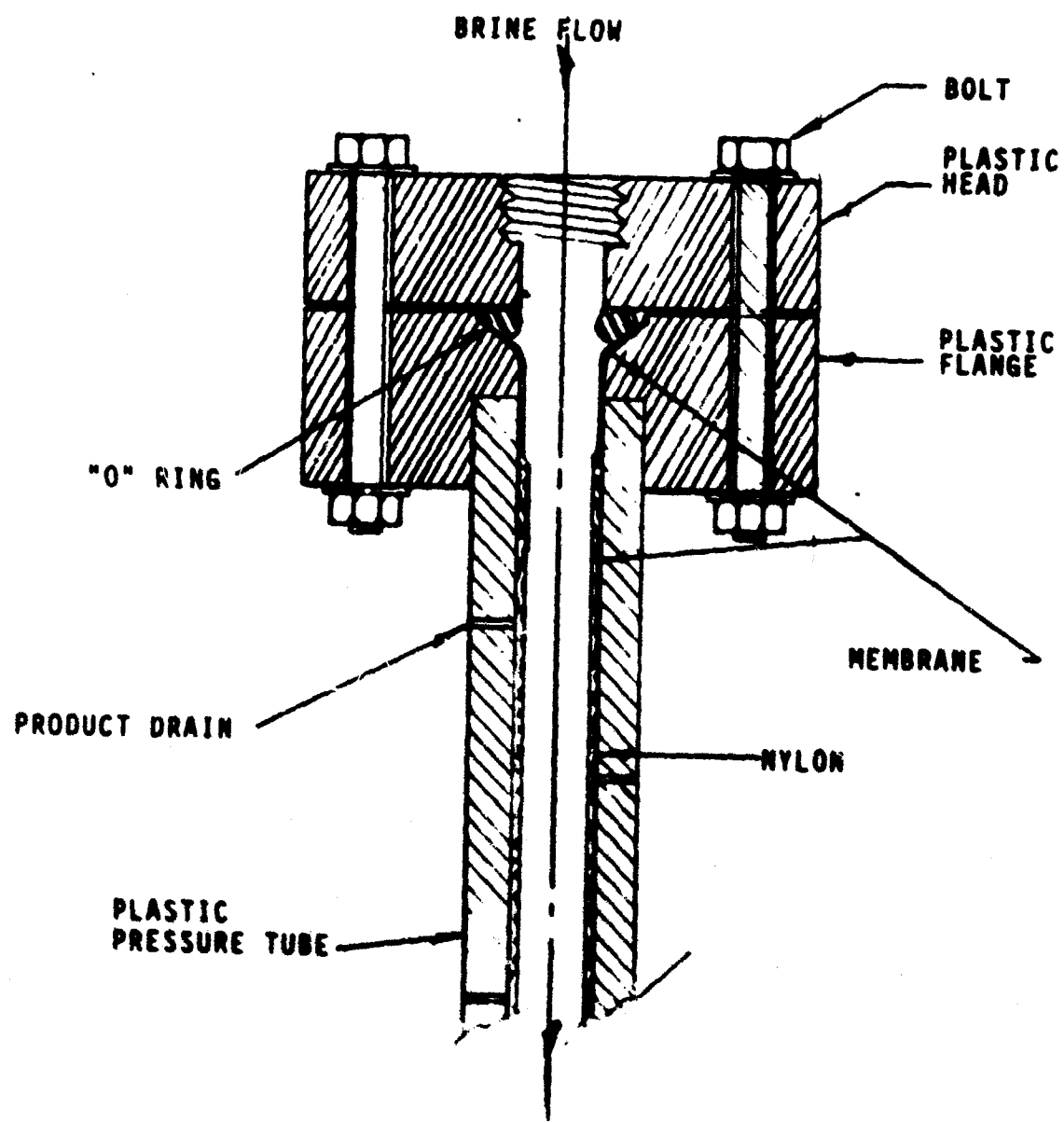


FIGURE 2



SINGLE TUBE ASSEMBLY DETAIL

FIGURE 3

II. CASTING SOLUTION CONSTITUENTS

A. Membrane Material

The most successful membrane material used in the preparation of reverse osmosis membranes is cellulose acetate. In optimizing semipermeable membranes for practical application, three major criteria are taken into consideration: (a) membrane performance (selectivity and flux), (b) membrane physical properties and, (c) operating conditions.

Experimentally it was found that cellulose acetate type E-398-3 was best suited for the preparation of flat membranes. However, short chain length cellulose acetate powders were found to be inadequate for the fabrication of tubular membranes. In general, membranes prepared from cellulose acetate type E-398-10 or E-400-25 were found to be more suitable for the fabrication of tubular membranes and were, in addition, physically superior to those made from E-398-3.

B. Solvents

The main function of the organic solvent utilized in a membrane casting solution is to provide a suitable system from which membranes can be fabricated. In general, solvent characteristics must be compatible with the requirements of the system in that the solvent should be miscible with water and the modifying agent used. Availability and cost are practical factors to be considered, as well as safety and ease of handling. Thus far, acetone has proven to be the best choice.

C. Modifying Agents

The main requirements for a modifying agent are that it be miscible with the cellulose acetate-solvent system and be soluble in water. It is hypothesized that the function of the modifying agent is to help determine the proper structurization of the membrane during fabrication.

After the film is cast, it is immersed in water where the solvent and the modifying agent are replaced by water. The rate of this exchange is determined by the characteristics of the solvent and modifying agent and by the temperature of the immersion water. Since the final membrane is a gel of cellulose acetate and water, it may be concluded that the main function of the modifying agent is to help create a membrane with a very thin, relatively dense surface layer and a very porous substructure. In addition to high selectivity, the formation of this very thin surface layer and the porous substructure reduces the resistance to water flow through the membrane.

III. RESULTS AND DISCUSSION

1. Formamide Modified Membranes

Significant test results are summarized in Tables I, II and III. These tests were run on raw sea water without filtering, pH adjustment, or pre-treatment of any kind. The data is for a single pass through a flat laboratory test cell. It is concluded from the results tabulated that:

(a) Formamide modified membranes are capable of practical desalination of sea water down to less than 500 ppm TDS in one pass at pressures between 800 and 1,200 psig.

(b) Comparative tests show that higher pressures increase production rate and salt rejection. Curing of membranes at low temperature (78°) results in high flux, and poor selectivity, while membranes cured at high temperature (88°) have good selectivity but unacceptably low flux. Optimum curing temperature appears to be between 81 and 85°C for flat membranes and this will be about 88 to 94°C for tubular membranes.

(c) Operating pressure must first overcome the osmotic pressure of sea water and, second, must provide sufficient driving force for adequate fresh water flow through. The optimum range is 1000 to 1200 psig.

TABLE I

Sea Water Tests - Formamide modified E- 8-3 membranes

Pressure psig	Product rate gal/sq ft-day	Product Salt ppm	Curing Temp. °C	% Salt Rejection
600	12.0	1950	78	94.43
800	25.0	3500	78	90.00
800	23.0	2940	78	91.60
800	17.0	1820	78	94.80
1000	26.0	2310	78	93.40
1000	19.0	1190	78	96.60
1200	21.0	1080	78	96.91
600	8.0	1330	81	96.20
800	15.7	1050	81	97.00
800	15.6	1330	81	96.20
1000	12.8	504	81	98.56
1000	17.0	755	81	97.64
1200	16.2	532	81	98.48
1200	18.0	560	81	98.40
800	8.8	730	82	97.94
1000	12.0	935	82	97.90
1000	11.5	655	82	98.13
1200	11.7	595	82	98.30

Table I , continued

Sea Water Tests - Formamide modified E-398-3 membranes

Pressure psig	Product rate gal/sq ft-day	Product Salt ppm	Curing Temp. °C	% Salt Rejection
600	6.0	560	83	98.14
600	7.0	700	83	97.67
600	6.2	840	83	97.20
800	9.6	380	83	98.74
800	10.9	480	83	98.40
800	9.6	540	83	98.20
1200	13.0	270	83	99.10
1200	18.5	340	83	98.87
1200	14.6	390	83	98.70
800	8.0	595	84	98.30
1000	11.0	504	84	98.56
1200	11.0	530	84	98.49
1200	11.0	475	84	98.65
600	4.3	833	85	97.63
800	7.5	525	85	98.50
800	8.0	413	85	98.82
1000	8.9	336	85	99.05
1000	12.9	490	85	98.60
1200	10.6	560	85	98.40
1200	11.6	343	85	99.02
1200	12.6	413	85	98.82
1200	10.5	210	85	99.40

Table I , continued

Sea Water Tests - Formamide modified E-398-3 membranes

Pressure psig	Product rate gal/sq ft-day	Product Salt ppm	Curing Temp. °C	% Salt Rejection
600	.17	445	88	98.73
800	2.9	280	88	99.20
1000	5.1	308	88	79.12
1000	4.8	203	88	99.42
1200	5.5	196	88	99.44

TABLE II

Sea Water Tests - Formamide modified E-398-6 Membranes

Pressure psig	Prod.rate gal/sq ft-day	Prod.salt ppm	Curing Temp. °C	% Salt Rejection
800	8.8	740	82	97.88
1000	11.5	660	82	98.13
1200	11.7	590	82	98.33
800	8.3	590	84	98.33
1000	10.9	500	84	98.57
1200	10.9	480	84	98.63

TABLE III

Performance of membranes prepared from E-398-10
cellulose acetate

Pressure psig	Product rate gal/sq ft/day	Product Salt ppm	Curing Temp. °C	% Salt Rejection
800	9.3	840	82	97.6
1000	11.0	630	82	98.2
1200	13.5	660	82	98.1
800	6.9	650	84	98.1
1000	8.3	560	84	98.4
1200	9.4	420	84	98.8
800	3.4	450	86	98.7
1000	5.7	390	86	98.9
1200	7.8	350	86	99.0

* Sea water as feed, single pass

2. Pyridine Type - Developmental Membranes

Table IV shows performance data for membranes cast from solutions of cellulose acetate, acetone, formamide and pyridine. Flat membranes were cast from solutions containing 15% and 20% pyridine, and these were produced with solvent evaporation periods from 1/4 to 1 minute. Curing temperatures were varied from 70 to 78°C. Membranes were tested for product flux and salt rejection.

Performance results indicate that for a given selectivity the required curing temperature for pyridine membranes is about 5°C lower than that normally required for standard formamide modified membranes. Performance with respect to product rate and selectivity is comparative. The mechanical properties of the pyridine membrane, particularly strength, are superior.

As yet no substantial sea water tests have been made with pyridine type membranes. However, tubular pyridine membranes were fabricated and used in tubular modules for the treatment of brackish water with considerable success.

The appearance of tubular membranes is significantly changed by the presence of pyridine in the casting solution. Instead of an opalescent appearance, membranes cast from pyridine solutions are clear and transparent. The clarity is considered to indicate a more uniform or homogeneous membrane. It is postulated that the presence of pyridine in the casting solution favorably affects the fabrication conditions, specifically during the water immersion period when the solvent and modifying agent are replaced by water in the cast film. The fineness and uniformity of distribution of the water content of the finished membrane appear to be greatly improved by the presence of pyridine.

Physical and mechanical properties are important in the overall membrane production process. Physically stronger membranes are easier to handle and assemble into units and modules with their supporting structures. They are less likely to develop structural failures both during production, assembly and curing, as well as during the membrane operating life. While life tests are not yet available, it would appear reasonable to assume that a stronger and tougher membrane might be a longer lasting membrane.

Clarity and homogeneity are also important in membrane production. Defective sites are much more readily observed and thus enable more effective quality control of membrane production.

Exploration of the effect of pyridine has as yet been limited, and only the initial indications of improvement have been discovered. A much larger scale effort would be required to optimize the casting system cellulose acetate-acetone-formamide-pyridine and to develop better methods of processing cast films into finished membranes. The successful use of pyridine also opens a new field of

investigation of casting solution additives that could possibly improve the function of pyridine, or result in other important advantages in better membrane production, performance and life.

3. Storage Effects on Membrane Performance

Sections of a standard membrane were stored in sea water and in plain water for a period of approximately five months. Some membrane sections were stored in the uncured condition while other sections were stored after curing at 87° C. The uncured sections were heated to 87°C prior to testing.

Results, as shown in Table V, indicate that exposure of a membrane to sea water as such does not affect its desalinizing properties; and, second, storage of a membrane in fresh water as well as sea water for a prolonged period does not have a deleterious effect on membrane performance. Results were similar for membranes cured before or after storage.

TABLE IV

Performance of membranes prepared from casting solutions containing pyridine.

Casting solution composition %				Evap. Period Min.	Cure Temp °C	Operating Pressure psig	Product Rate gal/sq ft-day	Salt Rejection %
Cellulose Acetate	Acetone	Formamide	Pyridine					
25	30	30	15	1/2	78	600	17.7	97
25	30	30	15	1/2	74	600	20.8	94
25	30	30	15	1/4	78	600	19.2	97
25	30	30	15	1/4	74	600	24.0	93
25	30	30	15	0	74	600	22.6	95
25	30	25	20	1/2	78	600	15.1	97
25	30	25	20	1/2	74	600	18.2	96
25	30	25	20*	1/4	78	600	18.0	97
25	30	25	20	1/4	74	600	21.8	95
25	30	25	20	0	74	600	28.0	94
25	30	25	20	1.0	70	600	28.0	88
25	30	25	20	1.0	74	600	18.0	93
25	30	25	20	3/4	74	600	23.4	94

TABLE V
Comparative performance of fresh and stored membranes

Storage period	Nature of storage liquid	Operating pressure psig	Feed salinity micromhos/cm	Product salinity micromhos/cm	Product rate gal/sq ft/day	Curing temp. °C
6-1-66 to 10-24-66	Sea water	300	6100	110	5.2	<u>b</u> 87° C
6-1-66 to 10-24-66	Fresh water	600	6100	145	4.4	<u>b</u> 87° C
6-1-66 to 10-24-66	Sea water	600	6100	200	5.0	<u>a</u> 87° C
6-1-66 to 10-2-66	Fresh water	600	6100	200	4.0	<u>a</u> 87° C
Control (no storage)	---	600	6100	95	4.0	87° C

a 87° C - membranes cured before storage

b 87° C - membranes cured after storage

MEMBRANE STRUCTURAL PROPERTIES

Structural properties of the membrane are of great importance in reverse osmosis systems. Substantial stresses and strains are developed as the membrane is deformed under pressure to conform to its structural backing. Such strains could possibly cause micro-cracks in the desalting surface layer of the membrane and thus reduce its operating efficiency.

The objective of this set of experiments was to study the stress-strain relationships in membranes, and particularly to evaluate the effect of the addition of pyridine to a cellulose acetate-acetone-formamide membrane casting solution. Equipment and procedures were arranged to obtain relative and practical performance data and were not necessarily designed to follow standard procedures suggested for obtaining basic data. A special tensile tester was designed which exerted stress at a relatively constant rate, and specimen elongations were measured for given stresses. The apparatus was designed to keep the membrane wet during tests to insure reproducible results.

Casting solutions were prepared by dissolving cellulose acetate in a mixture of acetone, formamide, and pyridine. Standard fabrication procedures were followed for both flat and tubular membrane preparation. After casting, some membranes were cured by treating at elevated temperatures and then tested, while others were tested in the uncured condition.

Results have shown a definite increase in strength for membranes cast from a pyridine-containing solution. Such strength increase could be sufficient to significantly affect fabrication procedures and membrane operations.

1. Experimental

A. Equipment

A tensile tester was designed and constructed for determining membrane strength. A sketch of this apparatus is shown in Fig. 4. A test specimen is held between rubber-lined clamps immersed in water in a container. A flexible, thin cable has one end attached to the top clamp and passes over a pair of horizontally spaced pulleys. Its other end is attached to a water receptacle. A burette is set to deliver water at a constant rate to the receptacle thus applying a uniformly increasing tensile load on the membrane specimen. Membrane elongation to final fracture is indicated by a pointer attached to the wire cable which travels along a scale on the horizontal pulley support.

B. Preliminary tests

Preliminary work was carried out with the newly designed tester to establish the best operating procedures. Variations in the rate of load application were studied to determine the effect of this variable on the characteristics of the stress-strain diagram. The width and length of the membrane specimen were determined largely by the physical limitations of the testing unit. This phase of the work also enabled the operator to become familiar with operation of the apparatus. Optimum rate of water addition to increase load was found to be between 17 and 20 milliliters per minute. Most convenient specimen size was found to be about 12 cm. long and about 0.8 cm. wide. Thickness of specimens varied from 0.010 cm. to 0.020 cm.

C. Procedure

Test specimens were prepared with a cutter having two spaced blades to insure uniform width and defect-free edges. Tubular membranes were first split open, then held flat and strips cut in the same manner as with flat membranes. The strips were then cut to length and thickness determined by micrometer. Care was taken to keep the specimen straight and flat while handling and setting in the tester. The initial load, the empty water receptacle, was suspended at the end of the cable to keep the specimen under some slight initial tension. After a period of time for stabilization, the length of the specimen between the clamps was measured and the elongation pointer set to zero on the scale. Water flow at a pre-set rate was then started from the burette into the water receptacle.

Elongation measurements were taken at the end of each 50 ml. load application. As the specimen approached its breaking point, more frequent readings were taken to accurately determine the breaking point.

A generally representative curve for a standard flat uncured membrane cast from a solution of 25% cellulose acetate 45% acetone and 30% formamide is shown as Fig. 5. The curve shows an initial stress of about 8 Kg/cm² resulting from the tare weight of the water receptacle. This initial stress is required to set up the specimen in position and maintain it just taut between the clamps. If the curve is extrapolated down to zero stress, the "negative" strain at the intercept would be a correction to be applied to the strain values shown to produce absolute values. The initial stress as shown will not, however, affect the elastic modulus or values of stress.

Referring to the curve in Fig. 5, the specimen deforms elastically until a yield point is reached at 27 Kg/cm². The elastic

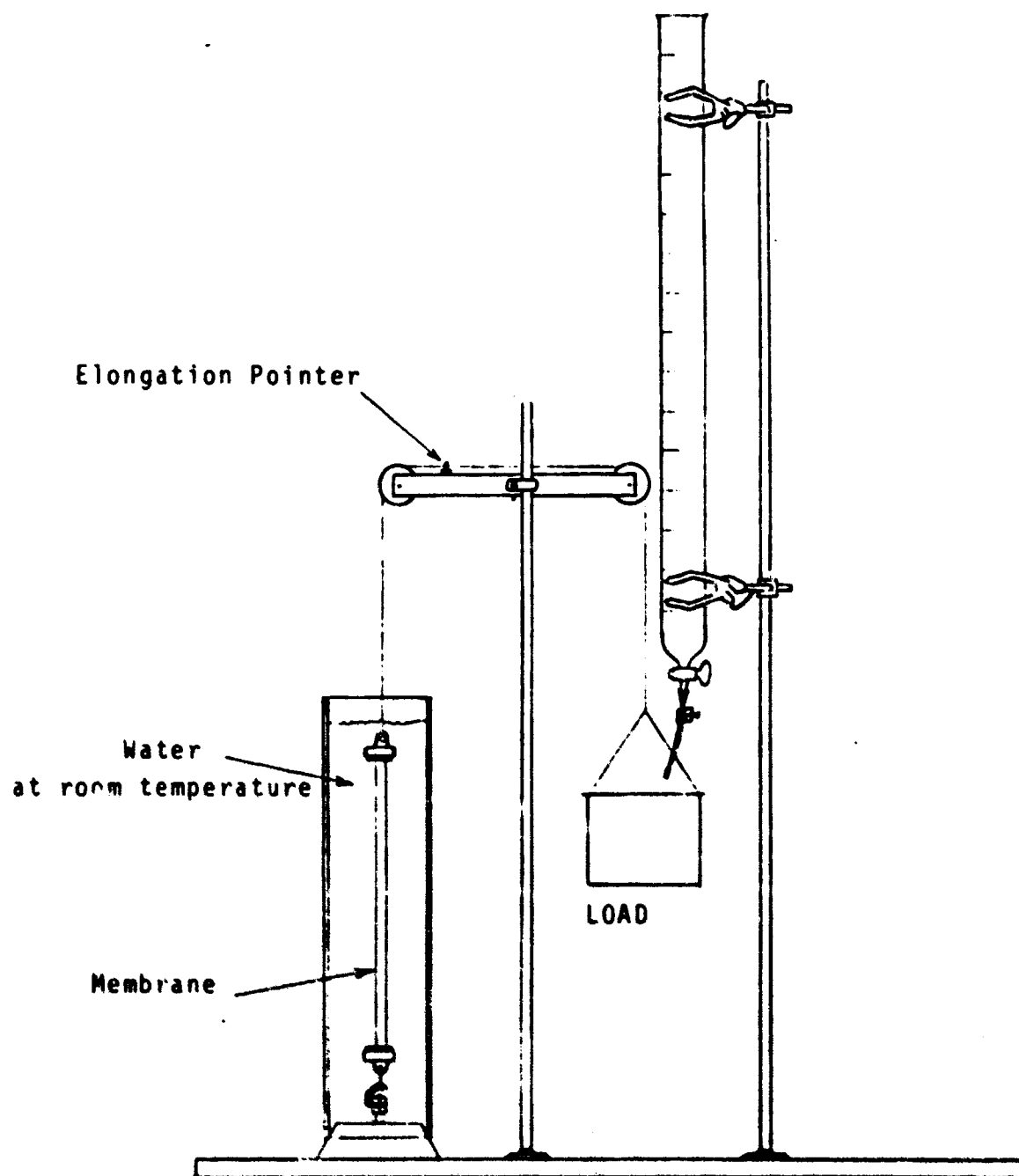


Figure 4 , Tensile Tester

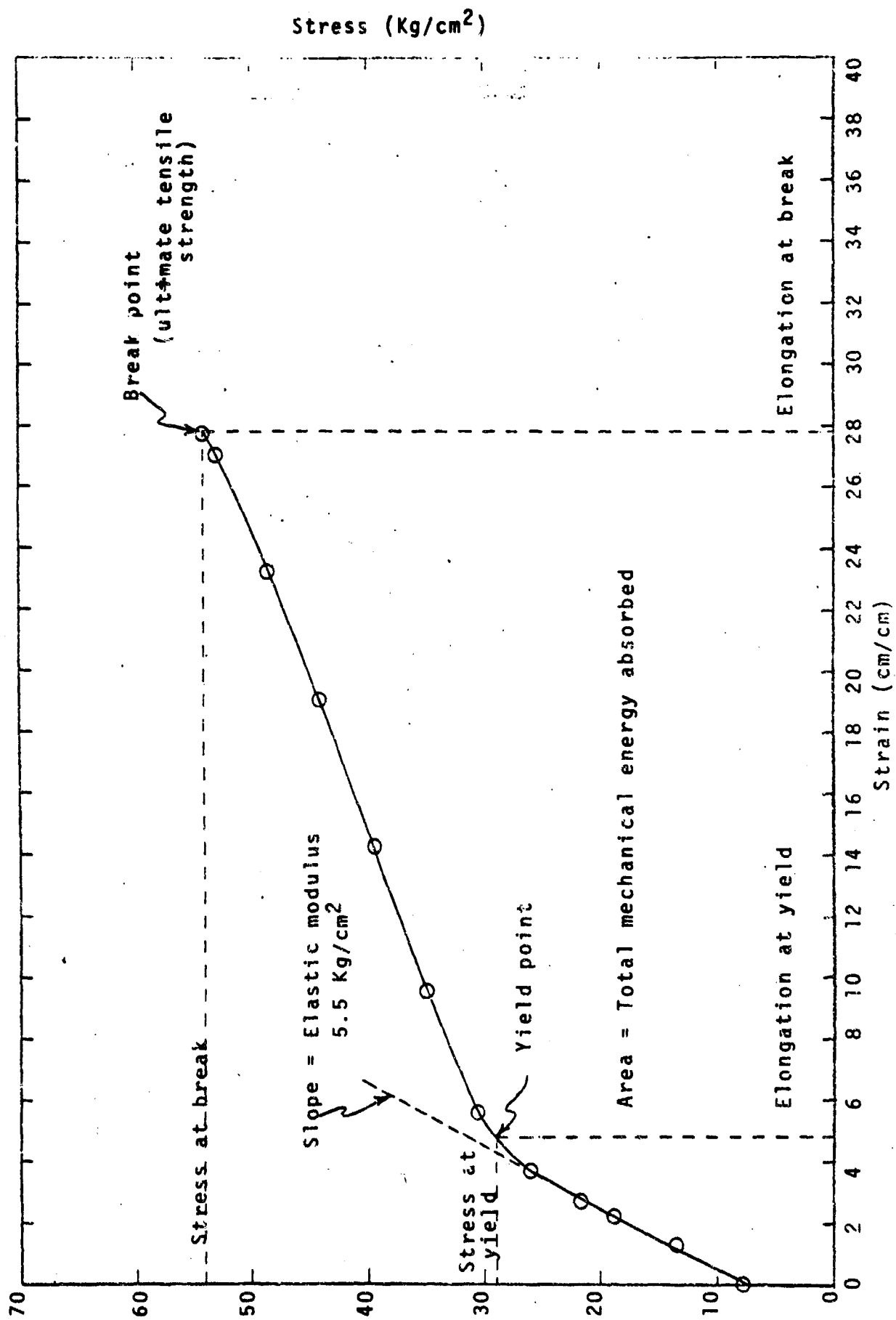


Figure 5 , Typical Stress-Strain Diagram

modulus, determined by the slope of the curve, being 5.5 Kg/cm². Application of additional load at an average rate of 0.018 Kg per minute produces permanent deformation until the specimen fractures at 54.3 Kg/cm². Total elongation at fracture is 28.5%.

D. Results and Discussion

Stress-strain diagrams were plotted for flat and tubular membranes, cast from solutions with and without pyridine, in cured and uncured condition. Table VI gives composition of these solutions. Curves were also determined for three types of cellulose acetate used in casting solutions.

Table VII shows average mechanical properties determined for various specimens tested, the original values being taken from stress-strain diagrams shown in Figures 6 through 11.

The most significant effect of pyridine on the strength properties of membranes is its ability to increase the ultimate tensile strength. In a comparative example of flat membranes cured at 78°C, ultimate tensile strength was raised from 56.6 Kg/cm² to 69.4 Kg/cm² when pyridine was included in the membrane casting solution. In cured tubular membranes, ultimate tensile strength was raised from 57.4 Kg/cm² to 64.8 Kg/cm². Uncured tubular membranes showed an appreciable strength increase for pyridine, while uncured flat membranes showed only a slight increase.

Elongation, that is ultimate strain at final fracture, increased for flat cured pyridine membranes to 31% compared to 22% without pyridine. For cured tubular membranes the increase was from 27.8% to 35.2%. Uncured tubular membranes showed an appreciable increase in elongation for pyridine, while uncured flat membranes showed only a slight increase.

The elastic modulus and yield strength of membranes appeared to be substantially unaffected by pyridine in both cured and uncured conditions.

Stress-strain diagrams were determined for membranes prepared from formamide modified casting solutions made with three different types of cellulose acetate. Fig. 12 gives these results, indicating that membrane ultimate strength is substantially higher when cellulose acetate of longer chain length was used (E-398-6 or E-398-10) and that elongation at break-point was approximately 50% greater than for the shorter chain cellulose acetate (E-398-3).

TABLE VI

Casting Solution Composition of Membranes
Used in Stress-Strain Measurements

<u>Membrane</u>	<u>Cellulose Acetate</u>	<u>Acetone</u>	<u>Formamide</u>	<u>Pyridine</u>
Flat Standard	25% (E-398-3)	45%	30%	---
Tube Standard	24.6% (E-398-10)	45.8%	29.6%	---
Flat Pyridine	25% (E-398-3)	25%	25%	25%
Tube Pyridine	25% (E-398-10)	30%	25%	20%

E. Conclusions

Pyridine in the casting solution favorably affects the strength of membranes produced from such solution, while elasticity and yield point are not materially affected. The strengthening effect of pyridine could be especially valuable for sea water treatment where higher pressures and more rigorous operating conditions will be encountered. The tests reported here, however, cover only a limited range of casting solution compositions and fabrication procedures. Various proportions of pyridine as well as other constituents of the casting solution should be further investigated, as well as curing temperature and duration of curing period. This would provide data for optimization of the pyridine effect to provide the strongest possible membrane, having required selectivity and flux, and with the potential of longest life in service.

TABLE VII

Average values of measured membrane mechanical properties

Membrane	Curing Temp. °C	Stress at yield Kg/cm ²	Strain at yield cm/cm x 10 ⁻²	Ultimate stress Kg/cm ²	Ultimate strain cm/cm x 10 ⁻²	Elastic modulus Kg/cm ² x 10 ²
<u>FLAT</u>						
Std. unheated	R.T.	27.0	4.0	54.3	28.5	5.2
Std. heated	78	36.0	3.9	56.6	22.0	8.8
Pyr. heated	78	35.5	4.3	96.4	32.4	8.3
Pyr. unheated	R.T.	27.5	3.4	57.1	31.0	6.5
<u>TUBE</u>						
Std. unheated	R.T.	28.2	2.8	51.4	25.4	8.6
Pyr. unheated	R.T.	26.2	3.6	61.6	35.3	7.8
Std. heated	90°	34.8	3.8	57.6	27.8	9.4
Pyr. heated	90°	36.0	3.4	64.8	35.2	10.2

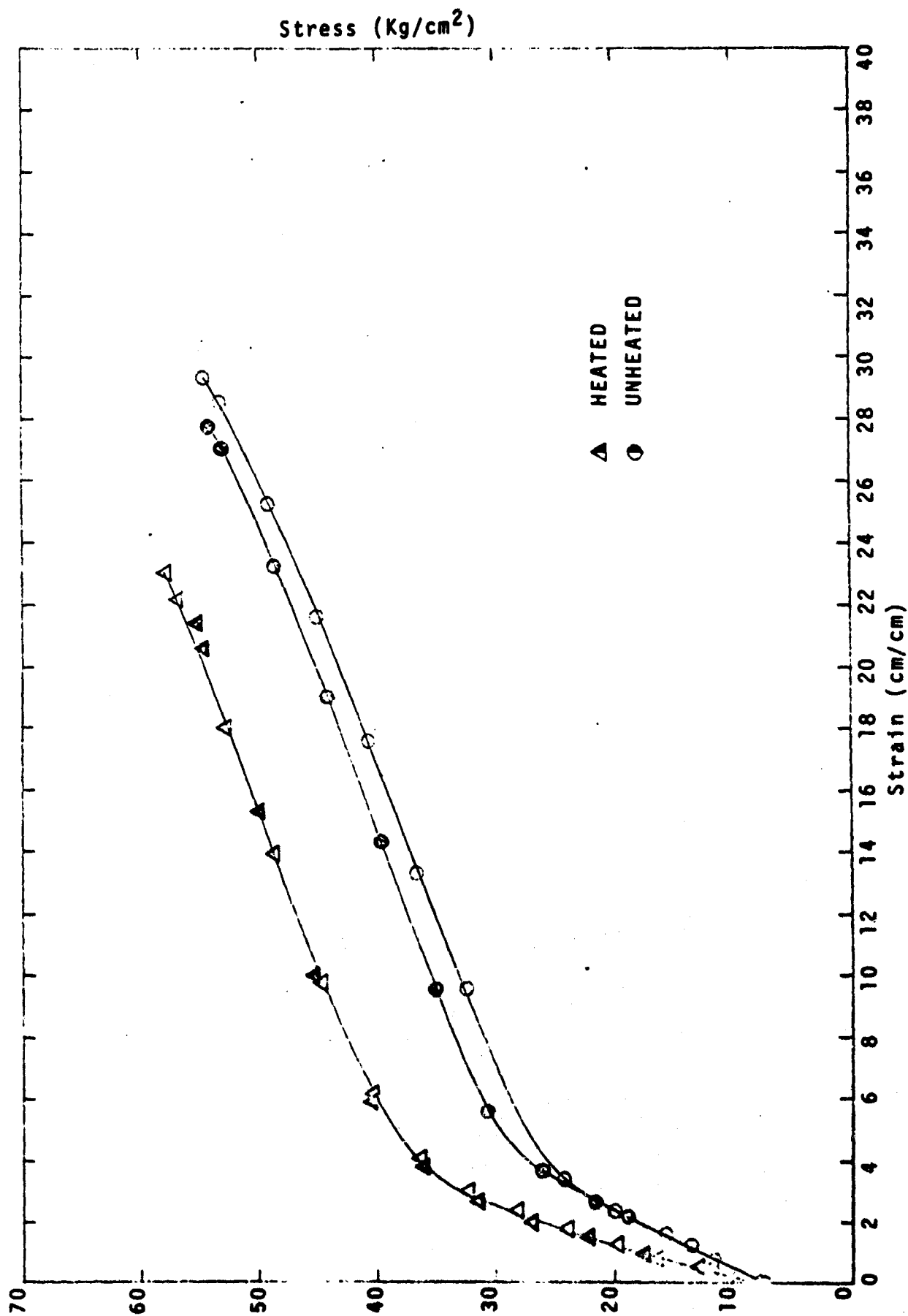


Figure 6 , Stress-Strain Diagram of Heated and Unheated Flat Standard Membranes

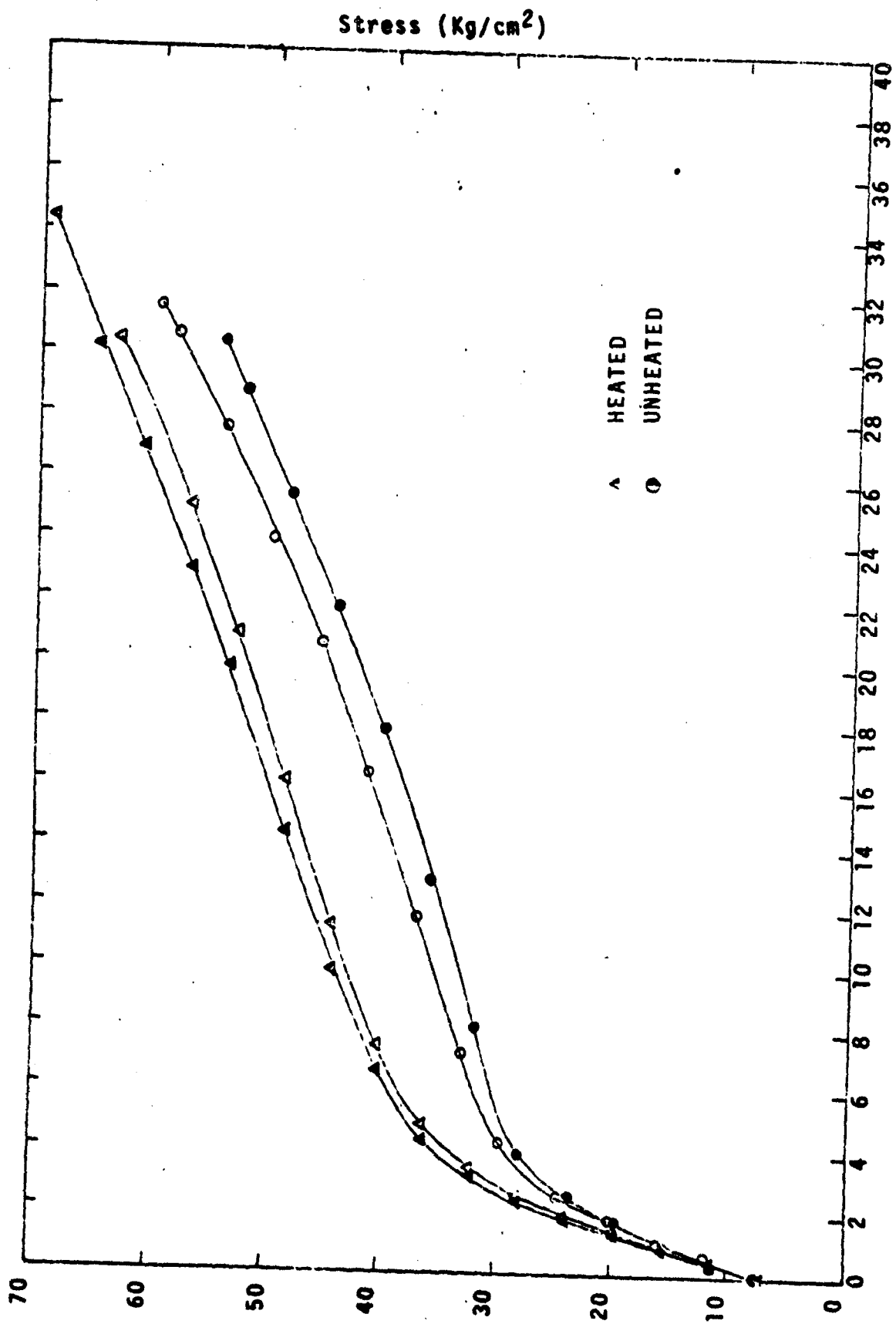


Figure 7 Stress-Strain Diagram of Heated and Unheated Flat Pyridine Membranes

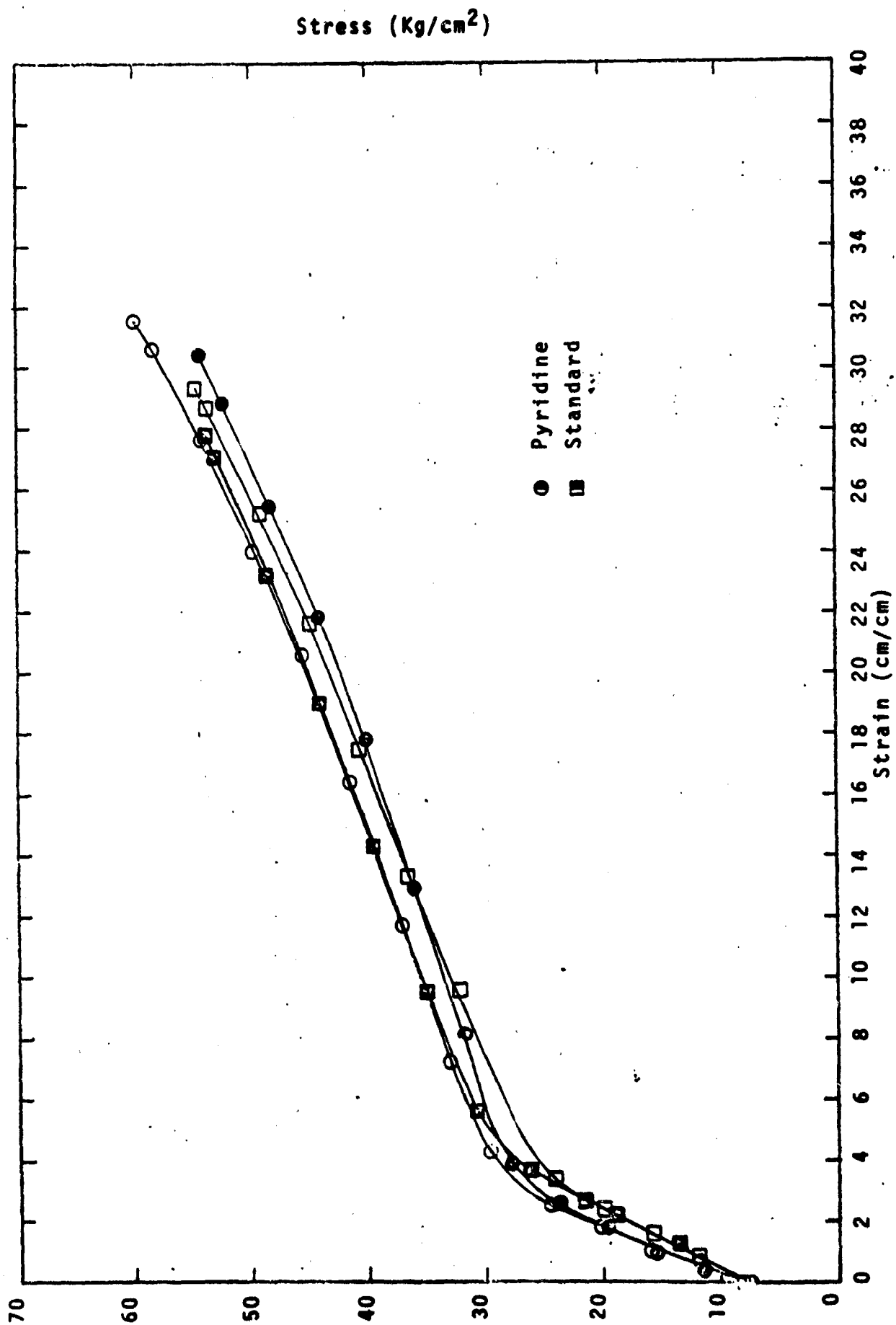


Figure 8 Stress -Strain Diagram of Standard and Pyridine Flat Membranes Unheated

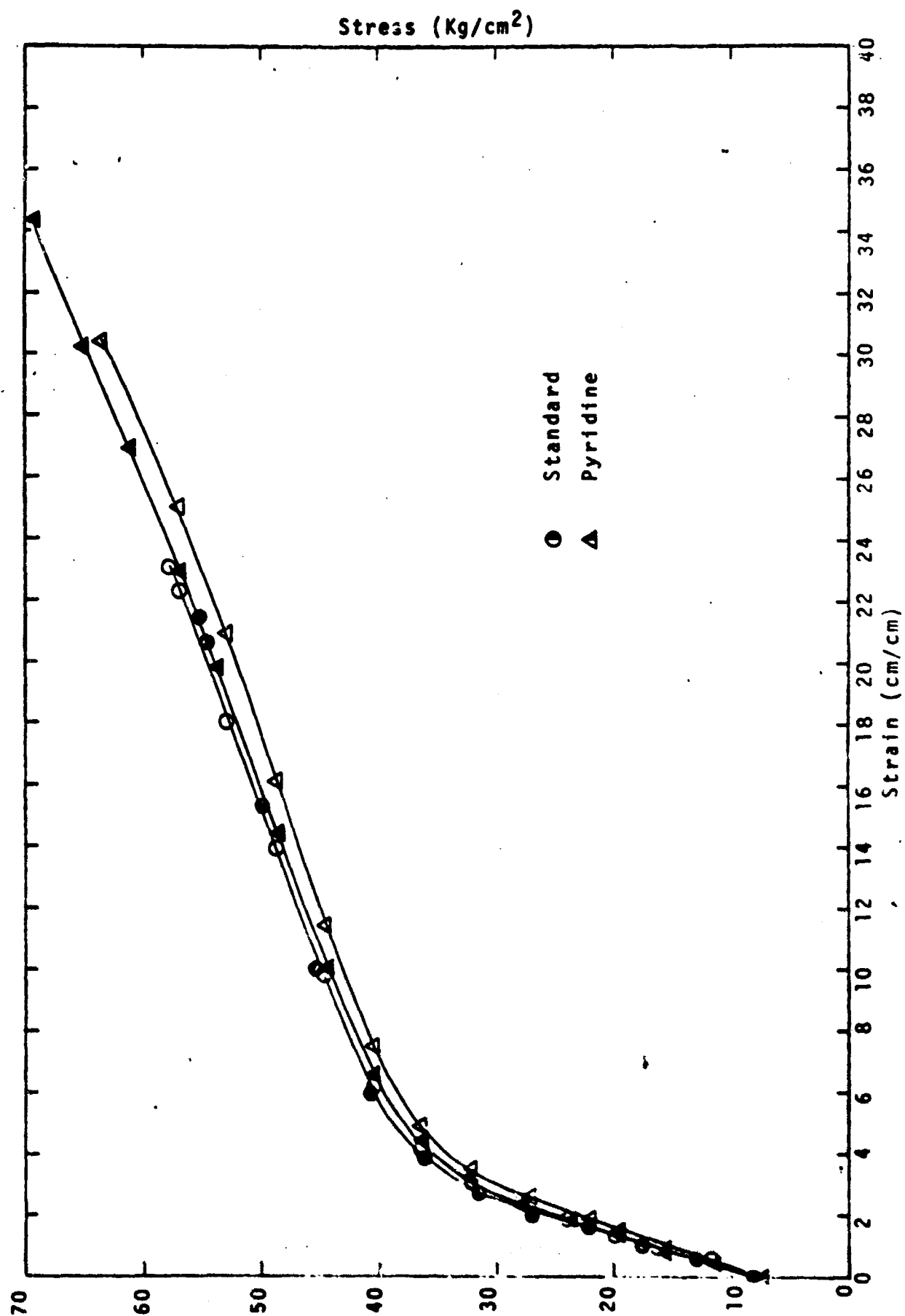


Figure 9 . Stress-Strain Diagram of Standard and Pyridine Flat Membranes Heated

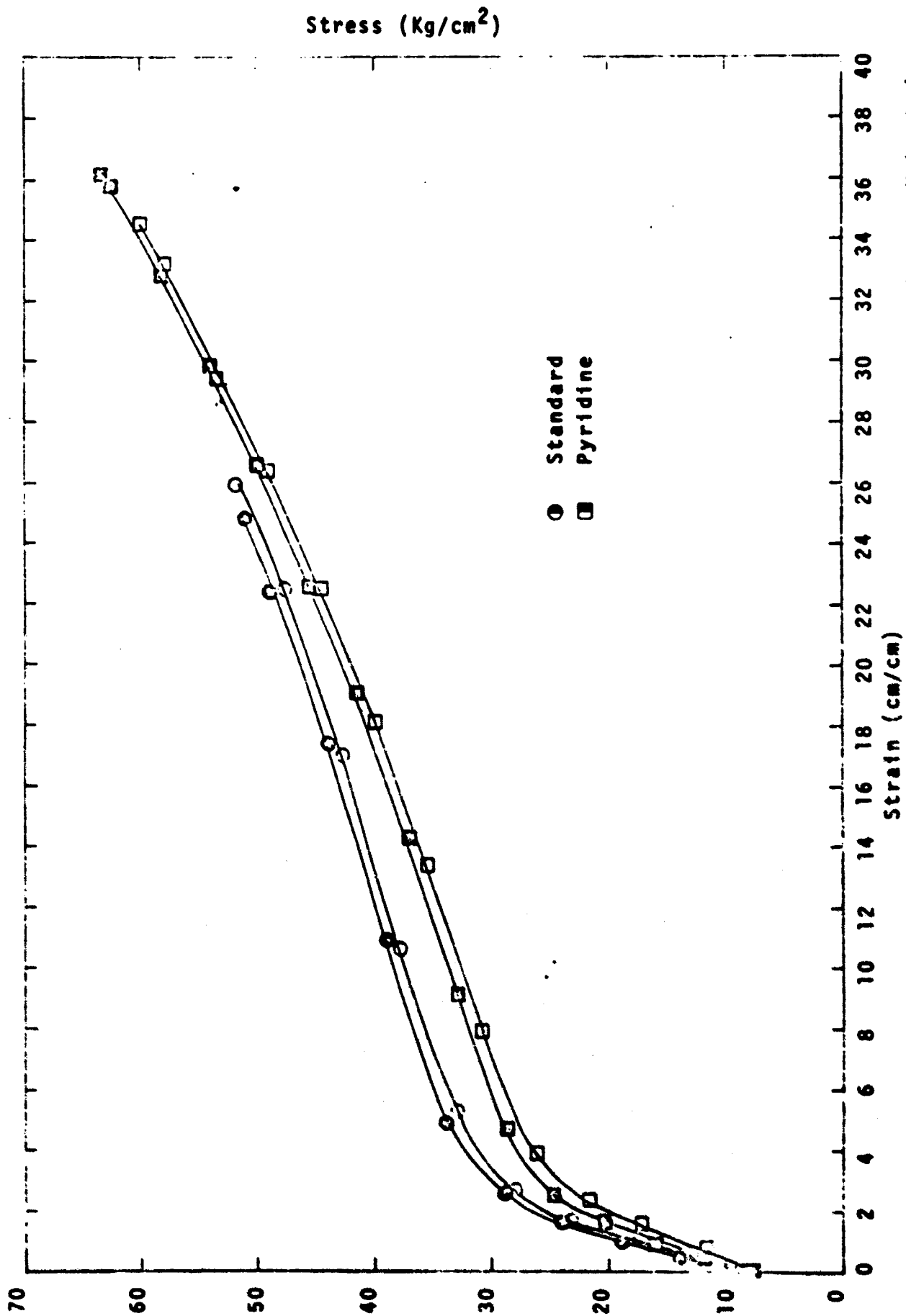


Figure 10. Stress-Strain Diagram of Standard and Pyridine Tubular Membranes Unheated

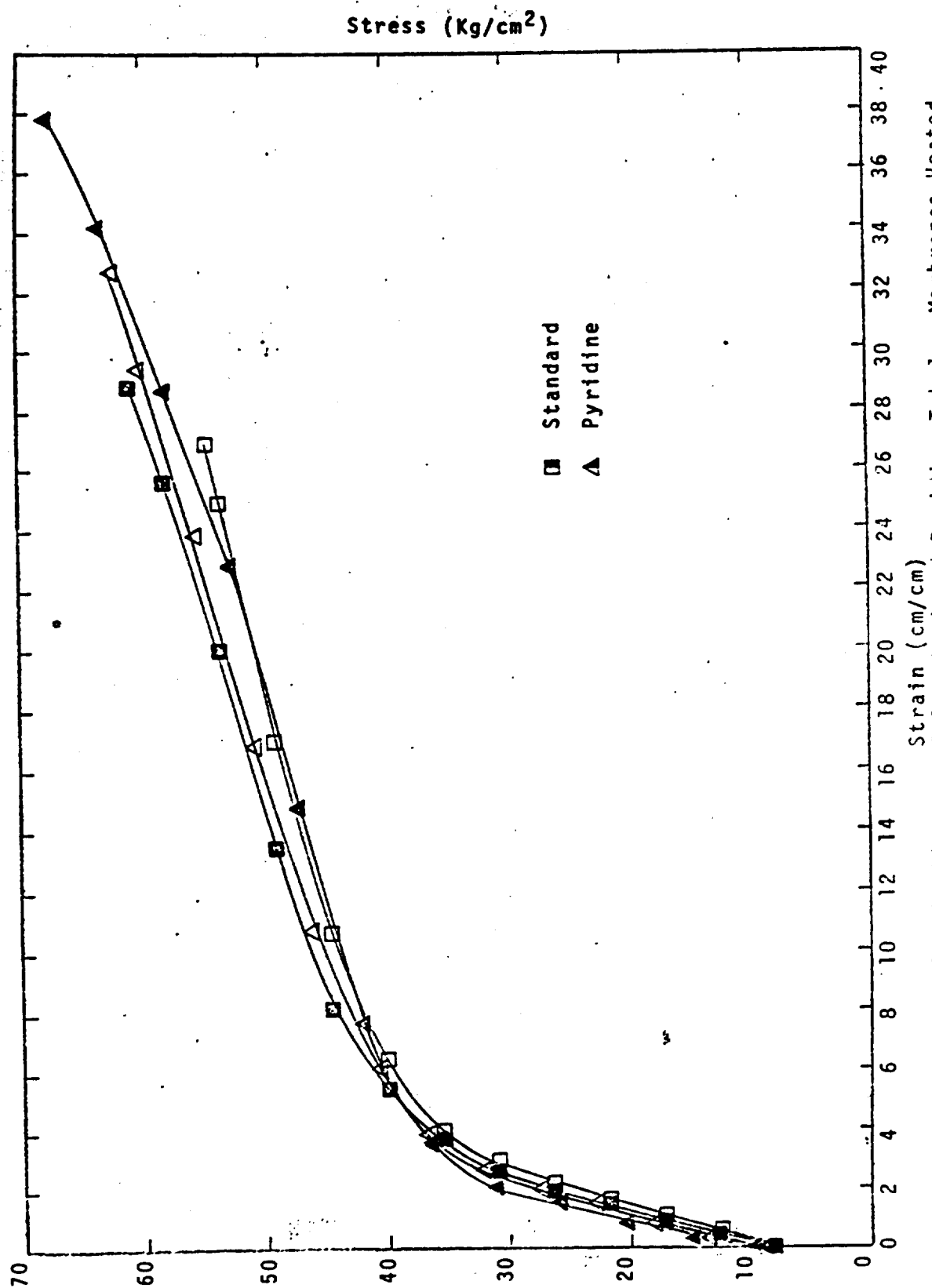


Figure 11, Stress-Strain Diagram of Standard and Pyridine Tubular Membranes Heated

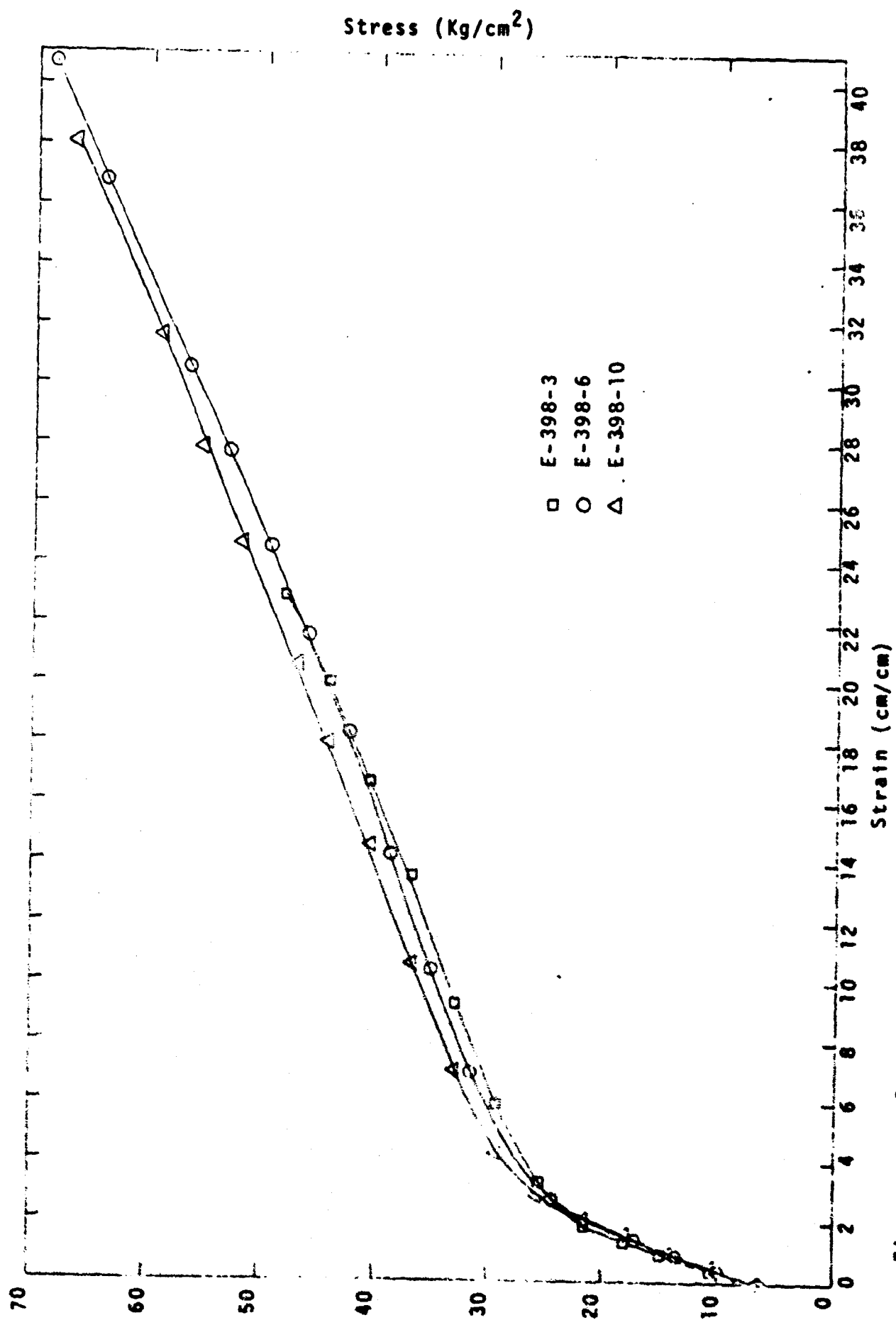


Figure 12. Stress-Strain Diagram for E-398-3, E-398-6 and E-398-10 Membranes Unheated

PROTOTYPE SYSTEM DESIGN

Four factors principally influence the design of a 360 gallon per day prototype reverse osmosis system.

First, it is important to obtain operational data concerning the complete membrane-machine system as soon as possible. Therefore, the design should be based on present technology which is sufficiently advanced to provide a good basis for a reliable operating unit.

Second, the design should be simple and economical to produce and operate consistent with production of dependable and pertinent data.

Third, the design should provide versatility so that reasonable changes in operating conditions can be made without exceeding the design limitations of any of the system components.

Fourth, the design should be capable of incorporating advances in technology and utilization, as these become available as the result of parallel programs, with a minimum amount of system modification.

Presently developed modular systems utilizing tubular membranes, while capable of desalting brackish waters, have not been developed sufficiently to permit sea water desalination to the 500 ppm level in a single pass. Therefore, multiple pass and multiple stage systems were considered for the prototype system.

1. The Proposed Prototype Design

The chosen design comprises a single stage two pass system. Sea water is first passed through a tubular module unit at 1250 psig. This will produce an intermediate product i.e., water of 5000 ppm TDS which would be stored in a suitable tank. After a specified period of operation on sea water feed, the unit would be switched to treat the stored intermediate product. In this second pass the TDS will be reduced to less than 500 ppm. The process flow contemplates operation for 19.2 hours on sea water with 25% recovery of 5,000 ppm intermediate product water, followed by a 4.8 hour operation with the intermediate production as feed to produce water of less than 500 TDS at 50% recovery.

Advantages of this design for the required purpose are:

1. Simplicity in that only one module bank, pump, pressure regulator and set of auxilliary equipment is required together with a storage tank.

2. Versatility in that it can be modified to operate as a single pass system as better membranes and modules are developed.

3. Individual steps have been well proven. Reduction of sea water to 5,000 ppm and conversion of this to 500 ppm product is unquestionably operable and feasible.

Process Description

Fig. 13 presents the details of the selected design. A system flow description follows.

Sea water is first screened through intake strainer F-1 to remove large debris and is then taken up by feed pump P-1 which raises its pressure to 40 psig. After P-1, dual ceramic filters F-2A and F-2B remove particulate matter above 100 micron size. After filtering, sulfuric acid is added by the acid proportioning system A-1 to adjust the pH of the sea water to 6.0. The high pressure pump P-3 raises the pressure of the acidified sea water to 1250 psig and the pressurized water is then fed to the module bank M-1 containing 8 modules equipped with tubular desalination membranes. First pass product water containing 5000 ppm TDS is collected and stored in Tank T-2. The concentrated brine passes through the modular unit and back pressure regulator BPR-1 where the pressure is reduced to atmospheric and the brine purged.

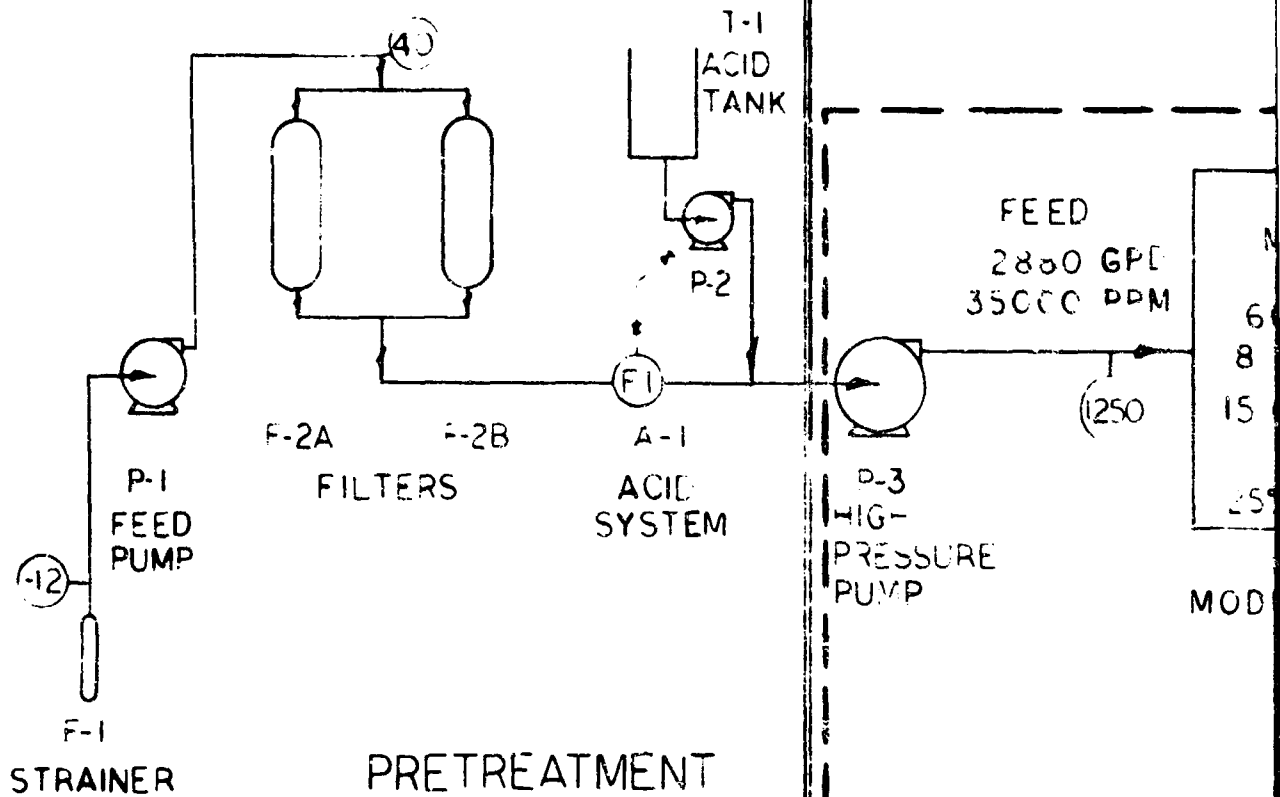
After 19.2 hours operation under Pass I conditions, sea water feed is cut off and water from tank T-2 is fed to pump P-3, pressurized to 1250 psig and passed through the same bank of desalination Modules M-1. In this second pass, 50% of the feed water is converted to product water containing less than 500 ppm TDS and is collected in tank T-3.

In short, the system will operate 80% of the time under Pass I condition and 20% of the time under Pass II condition in each 24 hour period. Operation will be made continuous and automatic by the incorporation of a suitable control system for the change over from Pass I to Pass II. Operation and performance of the system will be monitored by the installation of appropriate instruments and recorders. Fig. 14 presents a general outline dimensions of the system and Fig. 15 shows the basic desalination module to be employed.

A list of major pieces of equipment together with general specifications is given in Appendix B.

Alternative design considerations are presented in Appendix C.

A



NOTES

PRESSURE 10 PSIG

EQUIPMENT ITEMS WITHIN
DASHED LINES COMMON TO
BOTH PASSES I & II

FEED
720 GPD
5000 PPM

P-3
HIGH
PRESSURE
PUMP

(1250)

MEM

8

30

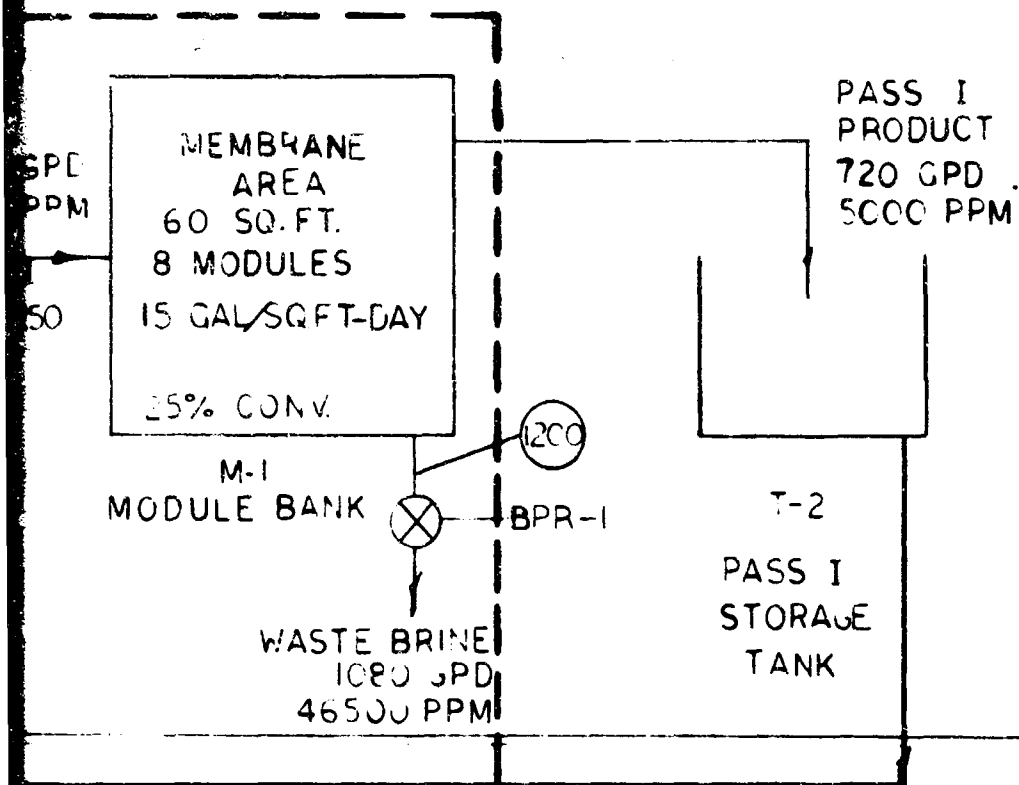
MOD

FIGURE 13

B

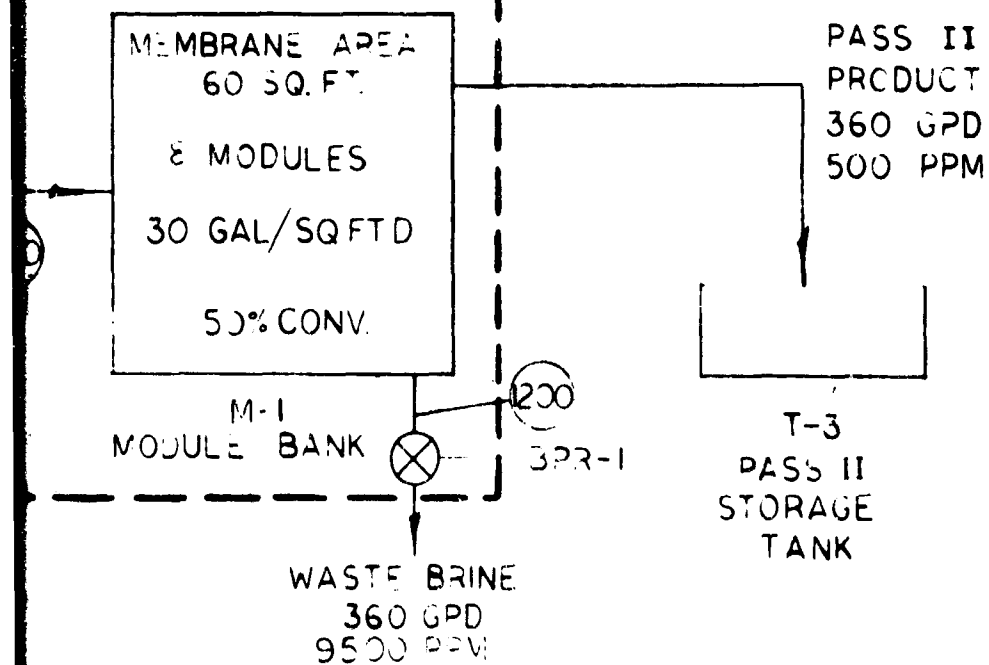
PASS I

19.2 HOURS PER DAY

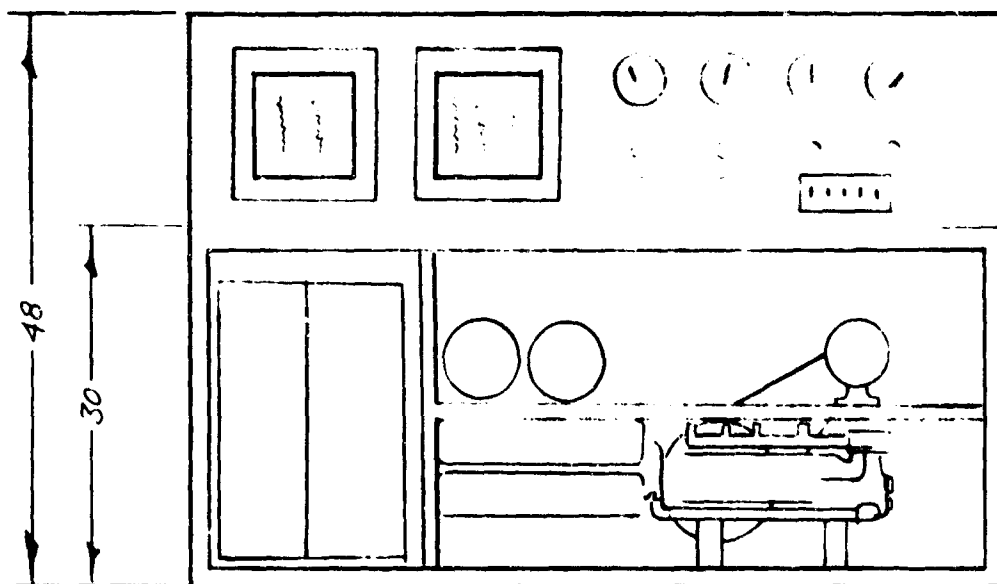
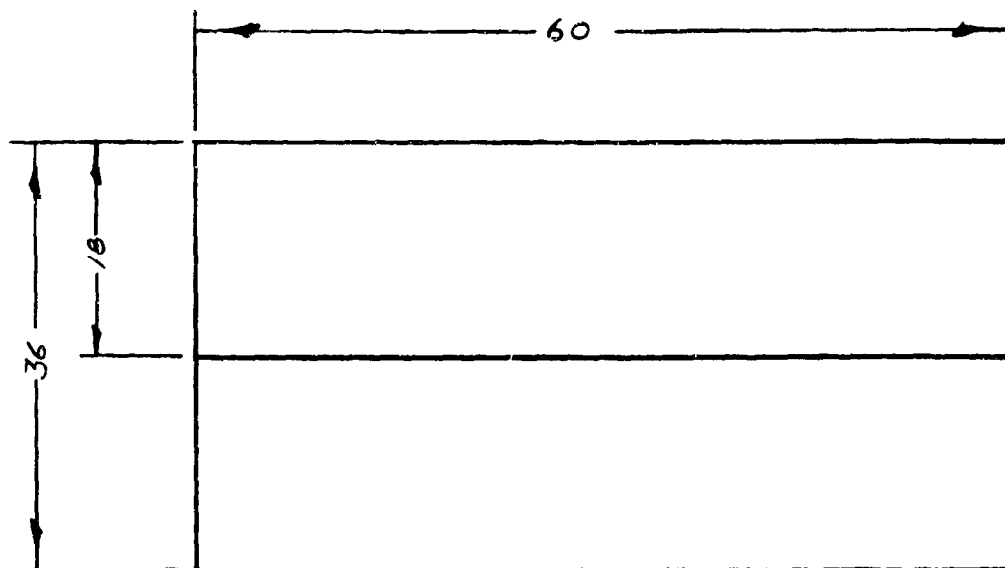


PASS II

4.8 HOURS PER DAY



A



B

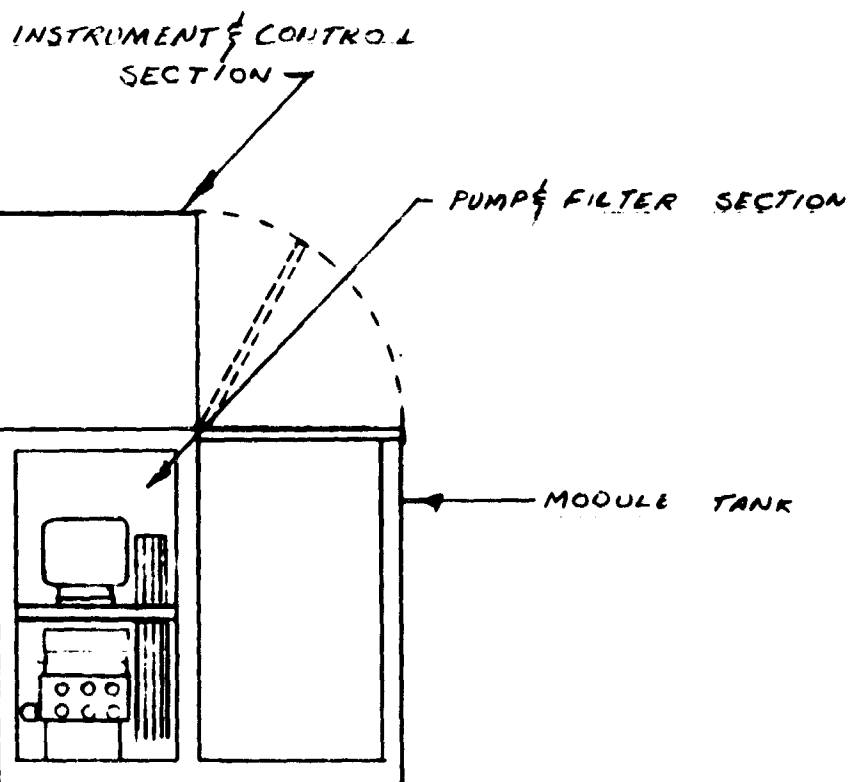
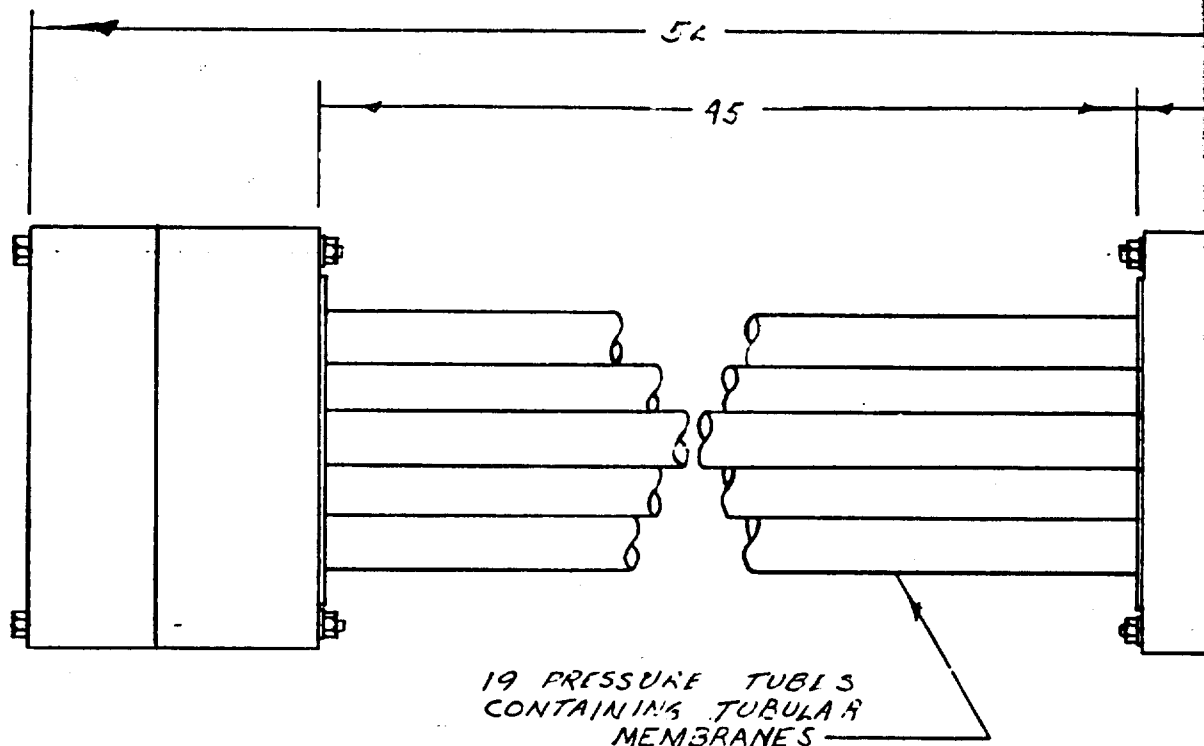


FIGURE 14
GENERAL OUTLINE 360 GALLON PER DAY SYSTEM

SCALE: $3/4" = 1'$	APPROVED BY:	DRAWN BY: <i>CK</i>
DATE: 10-25-66		REVISED:
		DRAWING NUMBER

A



<u>MATERIALS</u>		
TUBES	ABS	FLANGES & DISTRIBUTOR HEADS 1/2" 304 LOKK
HARDWARE		TYPE 316 SS

B

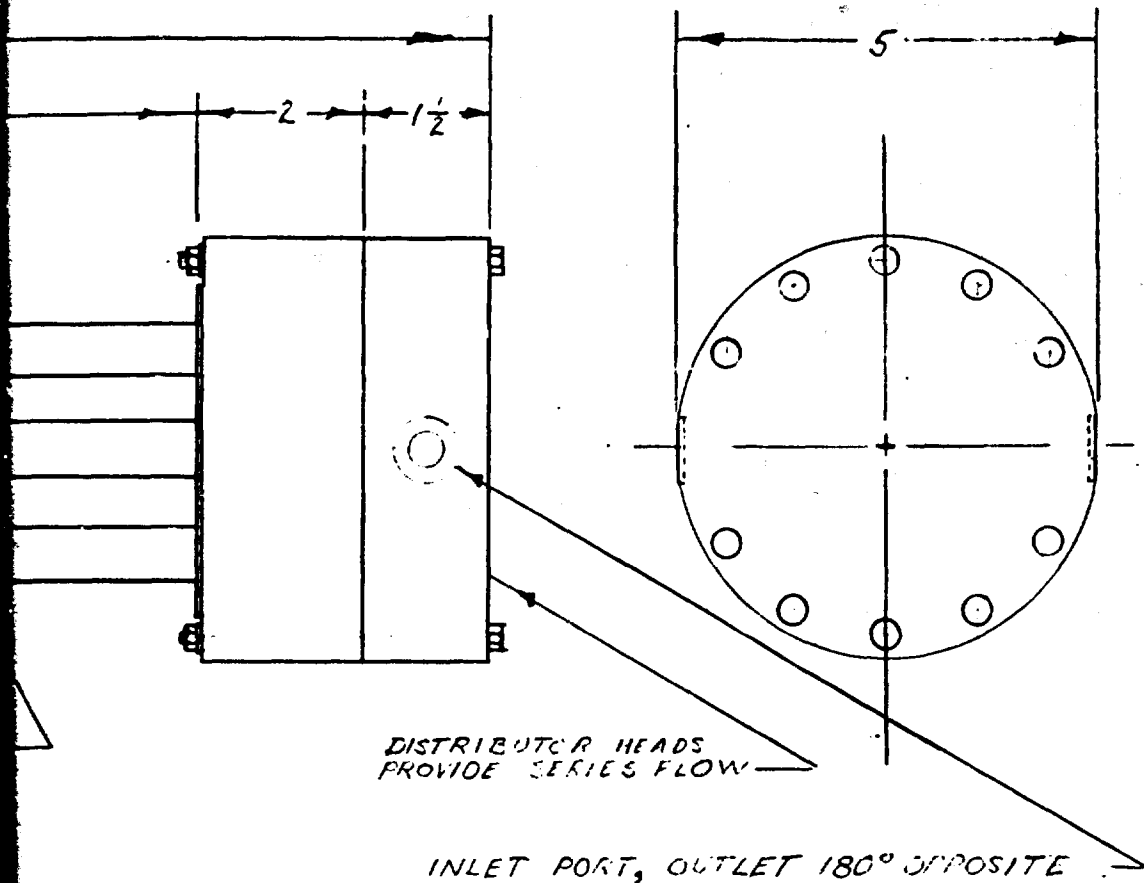


FIGURE 15
BASIC DESALINATION MODULE

FIGURE 15 BASIC DESALINATION MODULE		
SCALE: 1/4" = 1"	APPROVED BY:	DRAWN BY <i>CK1</i>
DATE: 10-25-66		REVISED
UNIVERSAL WATER CORPORATION 10,500 EAST 13TH AVE., DENVER, CO 80231		
		DRAWING NUMBER

APPENDIX A

Stress-strain measurements of cellulose acetate membranes

This section contains data compiled in testing the physical properties of cellulose acetate membranes. The rate of addition of water was recorded as the total volume added, divided by time. The stress was computed by dividing the total weight of water and tare by the initial cross sectional area of the specimen. The density of water was taken as 1.0 gm/ml. The dimension of stress was recorded as Kg/cm². It was found that the cross sectional area decreased by about 19% from start to break. Strain was arrived at by dividing the measured elongation by the initial length of the sample. The dimensions were cm/cm (ℓ/ℓ).

The elastic modulus was determined graphically as the slope of the curve for the elastic portion of the test. The yield point was considered as the approximate center of the arc at the elbow of the curve. Experimental data are given in Tables X through XXV.

TABLE X

Membrane description: Standard flat E-398-3, heated to 78°C

Length: 12.0 cm

Width: 0.76 cm

Thickness: 0.0160 cm

Cross sectional area: 0.0121 cm²

Total time of test: 31 minutes

Average rate of water addition: 19.6 mL/min. (load application)

Volume of Water (mL)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain- ℓ/L (cm/cm)
0	0	89	7.4	0.0
50	0.7	139	11.6	0.006
100	1.0	189	16.3	0.008
150	1.5	239	19.7	0.013
200	2.1	289	23.9	0.018
250	2.8	339	28.0	0.023
300	3.6	389	32.2	0.030
350	4.9	439	36.3	0.041
400	7.4	489	40.4	0.062
450	11.7	539	44.5	0.098
500	16.7	589	48.6	0.139
550	21.6	639	52.8	0.180
600	26.6	689	56.9	0.222
610	----	699	57.9	(0.230)

TABLE XI

Membrane Description: Standard flat E-398-3, heated to 78°C

Length: 11.7 cm

Width: 0.76 cm

Thickness: 0.014 cm

Cross sectional area: 0.0108 cm²

Total time of test: 32 minutes

Average rate of water addition: 15.9 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	8.2	0.0
50	0.6	139	12.9	0.005
100	1.1	189	17.5	0.009
150	1.8	239	22.1	0.015
200	2.3	289	26.8	0.020
250	3.1	339	31.4	0.026
300	4.4	389	36.0	0.038
350	6.9	439	40.6	0.059
400	11.7	489	45.3	0.100
450	17.9	539	49.9	0.153
500	24.1	589	54.5	0.206
508	25.0	597	55.2	0.214

TABLE XII

Membrane Description: Standard flat E-398-3, unheated

Length: 12.0 cm

Width: 0.75 cm

Thickness: 0.0160 cm

Cross sectional area: 0.0120 cm²

Total time of test: 28 minutes

Average rate of water addition: 17.2 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain- ℓ/L (cm/cm)
0	0.0	89	8.4	0.0
50	0.3	139	13.1	0.002
100	1.0	189	17.8	0.008
150	1.9	239	22.5	0.015
200	2.5	289	27.3	0.020
250	3.3	339	31.8	0.026
300	4.8	389	36.7	0.038
350	7.8	439	40.6	0.061
400	13.5	489	46.2	0.107
450	22.2	539	50.8	0.168
500	30.0	589	55.5	0.238
550	37.0	639	60.02	0.294
568	----	657	62.0	(0.327)

TABLE XIII

Membrane Description: Standard flat E-398-3, unheated

Length: 11.5 cm

Width: 0.75 cm

Thickness: 0.0147 cm

Cross sectional area: 0.0111 cm²

Total time of test: 26 minutes

Average rate of water addition: 19.6 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - $\Delta L/L$ (cm/cm)
0	0.0	89	8.0	0.0
60	1.4	149	13.4	0.012
120	2.5	209	18.8	0.022
150	3.0	239	21.5	0.026
200	4.2	289	26.0	0.036
250	6.4	339	30.6	0.056
300	9.9	389	35.0	0.095
350	16.5	439	39.5	0.143
400	21.9	489	44.1	0.190
450	26.7	539	48.6	0.232
500	31.0	589	53.0	0.270
511	----	600	54.0	(0.277)

TABLE XIV

Membrane Description: Standard flat E-398-3, unheated

Length 12.0 cm

Width: 0.75 cm

Thickness: 0.0160 cm

Cross sectional area: 0.0120 cm²

Total time of test: 28 minutes

Average rate of water addition: 20 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	7.4	0.0
50	0.9	139	11.6	0.008
100	1.9	189	15.7	0.016
150	2.8	239	19.9	0.023
200	4.0	289	24.1	0.033
300	11.5	389	32.4	0.096
350	16.0	439	36.6	0.133
400	21.0	489	40.6	0.175
450	25.9	539	45.0	0.216
500	30.2	589	49.1	0.252
550	34.2	639	53.2	0.285
568	35.2	657	54.7	0.293

TABLE XV

Membrane Description: Pyridine flat E-398-3, heated to 78°C

Length: 12.5 cm

Width: 0.76 cm

Thickness: 0.0160 cm

Cross sectional area: 0.0121 cm²

Total time of test: 37 minutes

Average rate of water addition: 18.4 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	7.4	0.0
50	0.5	139	11.5	0.004
100	1.1	189	15.6	0.009
150	1.8	239	19.7	0.014
200	2.3	289	23.9	0.018
250	3.2	339	28.0	0.026
300	4.3	389	32.2	0.034
350	6.1	439	36.3	0.049
400	9.3	489	40.4	0.074
450	14.3	539	44.5	0.114
500	20.1	589	48.6	0.161
550	26.1	639	52.8	0.209
600	31.2	689	57.0	0.250
680	38.0	769	63.5	0.304

TABLE XVI

Membrane Description: Pyridine flat E-398-3, heated to 78°C

Length: 12.6 cm

Width: 0.76 cm

Thickness: 0.0160 cm

Cross sectional area: 0.0121 cm²

Total time of test: 50 minutes

Average rate of water addition: 15.0 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	7.4	0.0
50	0.5	139	11.5	0.004
100	1.0	189	15.6	0.008
150	1.7	239	19.7	0.014
200	2.2	289	23.9	0.018
250	2.9	339	28.0	0.023
300	4.0	389	32.2	0.032
350	5.5	439	36.3	0.044
400	8.3	489	40.4	0.066
450	12.5	539	44.5	0.099
500	18.2	589	48.6	0.144
560	24.9	649	53.6	0.198
600	28.9	689	57.0	0.229
650	33.8	739	61.1	0.269
700	38.3	789	65.2	0.302
750	43.0	839	69.3	0.344

TABLE XVII

Membrane Description: Pyridine flat E-398-3, unheated

Length: 11.0 cm

Width: 0.75 cm

Thickness: 0.0163 cm

Cross sectional area: 0.0122 cm²

Total time of test: 32 minutes

Average rate of water addition: 18.0 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain- ℓ/L (cm/cm)
0	0.0	89	7.3	0.0
50	0.3	139	11.4	0.003
100	1.0	189	15.5	0.009
150	1.9	239	19.6	0.017
200	2.8	289	23.7	0.025
250	4.3	339	27.8	0.039
300	8.9	389	31.8	0.081
350	14.2	439	36.0	0.129
400	19.6	489	40.1	0.178
450	24.0	539	44.2	0.218
500	28.0	589	48.3	0.254
550	31.6	639	52.4	0.288
573	33.5	662	54.3	0.304

TABLE XVIII

Membrane Description: Pyridine flat E-398-3, unheated

Length: 12.1 cm

Width: 0.75 cm

Thickness: 0.0157 cm

Cross sectional area: 0.0118 cm²

Total time of test: 36 minutes

Average rate of water addition: 17.2 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain- ℓ/L (cm/cm)
0	0.0	89	7.5	0.0
50	0.8	139	11.8	0.007
100	1.2	189	16.0	0.010
150	2.1	239	20.2	0.017
200	3.0	289	24.5	0.025
260	5.1	349	29.6	0.042
300	8.7	389	33.0	0.072
350	14.2	439	37.2	0.117
400	19.9	489	41.4	0.164
450	25.0	539	45.6	0.206
500	29.1	589	49.9	0.240
550	33.4	639	54.1	0.276
600	37.0	689	58.4	0.306
620	----	709	60.0	(0.315)

TABLE XIX

Membrane Description: Standard tubular E-398-10, heated to 90°C

Length: 12.5 cm

Width: 0.76 cm

Thickness: 0.0145 cm

Cross sectional area: 0.0110 cm²

Total time of test: 30 minutes

Average rate of water addition: 17.0 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	8.1	0.0
50	0.7	139	12.6	0.006
100	1.3	189	17.2	0.010
150	2.0	239	21.7	0.016
200	2.7	289	26.3	0.022
250	3.7	339	30.8	0.030
300	5.0	389	35.4	0.040
350	8.0	439	39.9	0.064
400	13.3	489	44.5	0.106
450	22.2	539	49.0	0.170
500	31.1	589	53.5	0.249
510	----	599	54.5	(0.269)

TABLE XX

Membrane Description: Standard tubular E-398-10, heated to 90°C

Length: 12.6 cm

Width: 0.76 cm

Thickness: 0.0145 cm

Cross sectional area: 0.0110 cm²

Total time of test: 34 minutes

Average rate of water addition: 17.0 mL/min.

Volume of Water (mL)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	8.1	0.0
50	0.5	139	12.6	0.004
100	1.0	189	17.2	0.008
150	1.8	239	21.7	0.014
200	2.4	289	26.3	0.019
250	3.3	339	30.8	0.026
300	4.7	389	35.4	0.037
350	6.8	439	39.9	0.054
400	10.2	489	44.5	0.081
450	16.9	539	49.0	0.134
500	25.2	589	53.5	0.200
550	32.2	639	58.0	0.256
580	36.3	669	60.8	0.288

TABLE XXI

Membrane Description: Standard tubular E-398-10, unheated

Length: 12.5 cm

Width: 0.76 cm

Thickness: 0.0132 cm

Cross sectional area: 0.0100 cm²

Total time of test: 22 minutes

Average rate of water addition: 19.1 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - $\Delta L/L$ (cm/cm)
0	0.0	89	8.9	0.0
50	0.5	139	13.9	0.004
100	1.2	189	18.9	0.010
150	2.0	239	23.9	0.016
200	3.2	289	28.9	0.026
250	6.1	339	33.9	0.049
300	13.6	389	38.9	0.109
350	21.8	439	43.9	0.174
400	28.1	489	48.9	0.224
421	31.0	510	51.0	0.248

TABLE XXII

Membrane Description: Standard tubular E-398-10, unheated

Length: 12.7 cm

Width: 0.76 cm

Thickness: 0.0135 cm

Cross sectional area: 0.0103 cm²

Total time of test: 24 minutes

Average rate of water addition: 18.5 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress ₂ (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	8.6	0.0
50	0.8	139	13.5	0.006
100	1.3	189	18.3	0.010
150	2.1	239	23.2	0.016
200	3.4	289	28.0	0.027
250	6.7	339	32.9	0.053
300	13.5	389	37.8	0.106
350	21.6	439	42.6	0.170
400	28.6	489	47.5	0.225
444	33.0	533	51.8	0.259

TABLE XXIII

Membrane Description: Pyridine tubular E-398-10, heated to 90°C

Length: 12.7 cm

Width: 0.76 cm

Thickness: 0.0122 cm

Cross sectional area: 0.0093 cm²

Total time of test: 30 minutes

Average rate of water addition: 18.0 mL/min.

Volume of Water (mL)	Elongation (mm)	Tran Weight (gm)	Stress (Kg/cm ²)	Strain- ℓ/L (cm/cm)
0	0.0	85	9.6	0.0
50	0.3	139	14.9	0.002
100	1.0	189	20.3	0.008
150	1.9	239	25.7	0.015
200	2.6	289	31.0	0.020
250	4.5	339	36.4	0.035
300	9.7	389	41.8	0.076
350	18.8	439	47.2	0.145
400	29.0	489	52.5	0.228
450	36.5	539	58.0	0.287
500	43.5	589	63.4	0.342
540	----	629	67.6	(0.378)

TABLE XXIV

Membrane Description: Pyridine tubular E-398-10, unheated

Length: 12.7 cm

Width: 0.76 cm

Thickness: 0.0145 cm

Cross sectional area: 0.0110 cm²

Total time of test: 30 minutes

Average rate of water addition: 19.0 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	8.1	0.0
50	1.0	139	12.6	0.008
100	2.0	189	17.2	0.016
150	3.0	239	21.7	0.024
200	4.9	289	26.2	0.038
250	10.0	339	30.8	0.079
300	17.0	389	35.4	0.134
350	23.0	439	39.9	0.181
400	28.6	489	44.5	0.225
450	33.5	539	49.0	0.264
500	37.4	589	53.5	0.294
550	42.2	639	58.0	0.332
572	----	661	60.0	(0.345)

TABLE XXV

Membrane Description: Pyridine tubular E-398-10, unheated

Length: 12.5 cm

Width: 0.76 cm

Thickness: 0.0155 cm

Cross sectional area: 0.0118 cm²

Total time of test: 39 minutes

Average rate of water addition: 16.9 ml/min.

Volume of Water (ml)	Elongation (mm)	Total Weight (gm)	Stress (Kg/cm ²)	Strain - ℓ/L (cm/cm)
0	0.0	89	7.5	0.0
50	0.4	139	11.8	0.003
100	1.0	189	16.0	0.008
150	2.0	239	20.2	0.016
200	3.1	289	24.5	0.025
250	5.8	339	28.7	0.046
300	11.4	389	32.9	0.091
350	17.9	439	37.2	0.143
400	23.9	489	41.4	0.191
450	28.2	539	45.6	0.226
500	33.3	589	49.9	0.266
550	37.2	639	54.0	0.298
600	41.0	689	58.3	0.328
650	44.8	739	62.5	0.358
658	45.2	747	63.3	0.361

APPENDIX B

TABLE XXVI

MAJOR EQUIPMENT LIST

Item	Description	Duty	Materials
P-1	Feed Pump	5.0 GPM @ 120' TDH NPSH: 27' NP: 2.34 Motor HP: 3.0 TEFC	All bronze Teflon packing
P-2	Acid Feed Pump	Proportioning pump driven by water pressure upon command of flow totalizer. (Integral) with (A-1)	Inert plastic in contact with acid. Teflon, polyethylene, Kel-F, Kynar, etc.
P-3	High Pressure Pump	3.0 GPM 3500 TDH HP: 3.5 Motor HP: 5 TEFC	Monel or Ni Resist
F-1	Intake Strainer	5 GPM 1/8" mesh attached to intake hose	Ceramic attached to neoprene hose
F-2	A & B Filters	5 GPM each 100 Micron Provide backwash plumbing	Ceramic cartridge permanent Type I PVC low pressure plumbing
A-1	Acid Proportioning System	Adjust pH to 6.0 Driven by water pressure	Pump P-2 above polyethylene tubing. Acid tank - plastic carboy
M-1	Module bank	Tubular Modules Sea water - 15G/sq ft-D Brackish - 30G/sq ft-D Max. operating pressure 1500 psig Membrane salt rejection 8-10:1	All plastic in contact with sea water. Mounting hardware: type 316 ss intermodular connections: Delrin

APPENDIX BContd.

TABLE XXVI Contd.

<u>Item</u>	<u>Description</u>	<u>Duty</u>	<u>Materials</u>
BPR-1	Back Pressure Regulator	Gas dome headed Max. operating pressure 2000 psig. Max. flow - 5 GPM	Monel or type 316 ss
T-1	Acid Tank	13 Gallons	Polyethylene carboy
T-2	Pass I Product Storage	800 Gallons	Steel, plastic lined
T-3	Pass II Product Storage	400 Gallons	Steel, plastic lined

General

Miscellaneous fittings in contact with sea water will be of Monel; in contact with product water only brass or bronze. All interconnections of dissimilar metals will be insulated electrically wherever feasible. System to be skid mounted, capable of being moved by fork lift truck.

APPENDIX C

Alternative System Designs Considered

In addition to the system chosen, several alternative systems were considered as being technically feasible utilizing available technology. The final selection was made considering that system which best met the overall program objectives. Following is a brief description of the other systems which were studied during the design effort.

Two Stage Single Pass System with Dual Pressure (Fig. 16)

In this system, two separate desalination stages are utilized in series. In the first stage sea water is mixed with the lower salinity stage II waste, thus lowering the salinity of the mixed stream to 29,656 ppm. This stream is pressurized by Stage I pump P-3 to 1250 psig and fed to the Stage I module bank M-1. Product from M-1, containing 5000 ppm TDS, is repressurized by Stage II pump P-4 to 750 psig and fed to Stage II module bank M-2, which produces 360 GPD of 500 ppm product. This system would require thirteen modules in Stage I and four modules in Stage II for a total of 17 modules in addition to the two high pressure pumps.

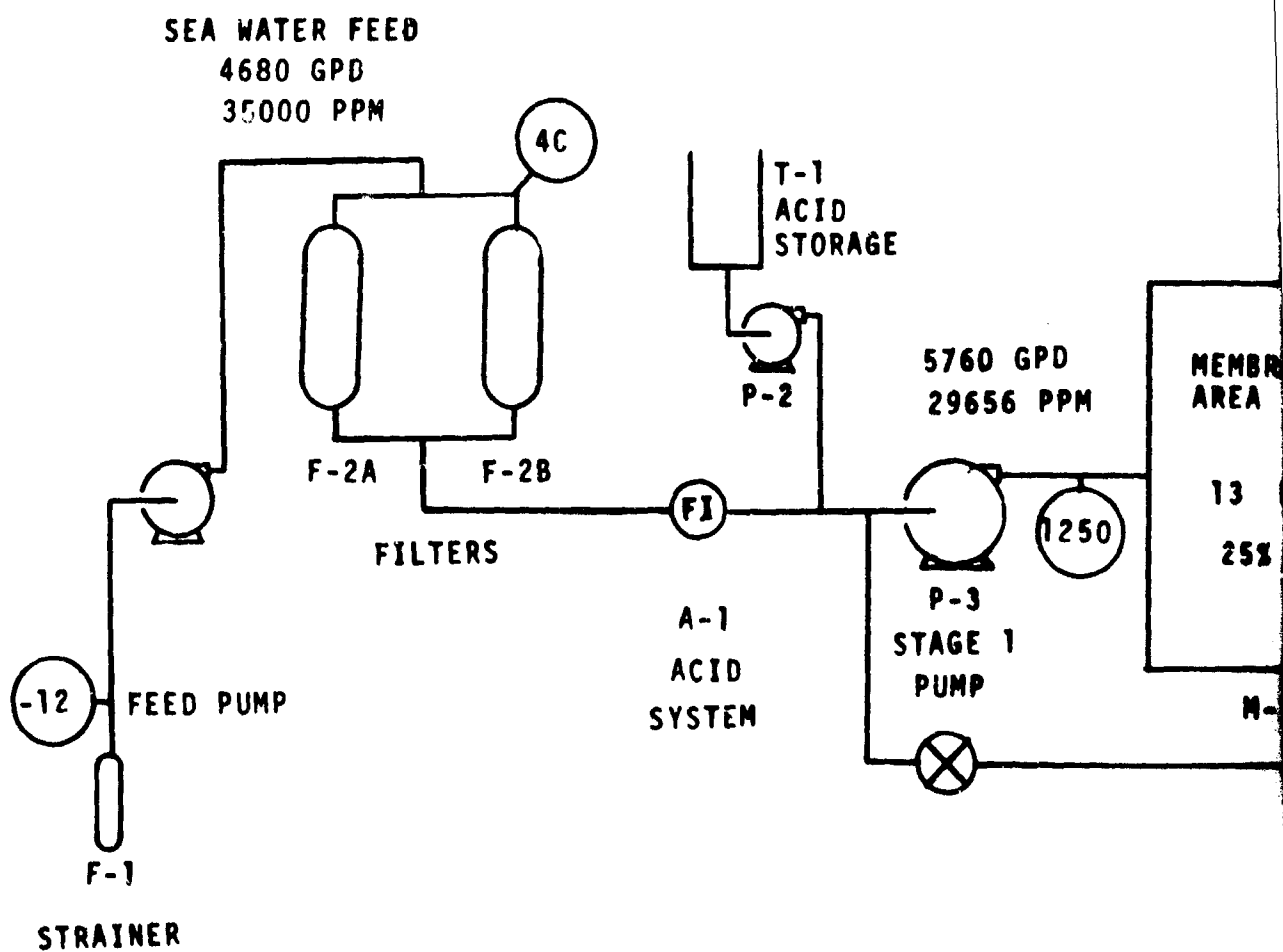
Two Stage Single Pass Single Pressure System (Fig. 17)

This system is identical with the preceding dual pressure system with the exception that both stages operate at an identical intermediate pressure, 1000 psig. This causes a slight decrease in Stage I flux and increase in Stage II flux. While the material balance remains constant, Stage I requires 16 modules and Stage II requires 3 for a total of 19 modules.

Single Stage One Pass System with 1000 ppm Product (Fig. 18)

Presently available tubular desalination modules can reduce the salinity of sea water in one pass to 1000 ppm. While this system is presently technically feasible, it did not satisfy the requirements of the design and is presented to indicate that a single stage-single pass system should result in the near future as a consequence of present development programs.

A



PRESSURE



PSIG

B

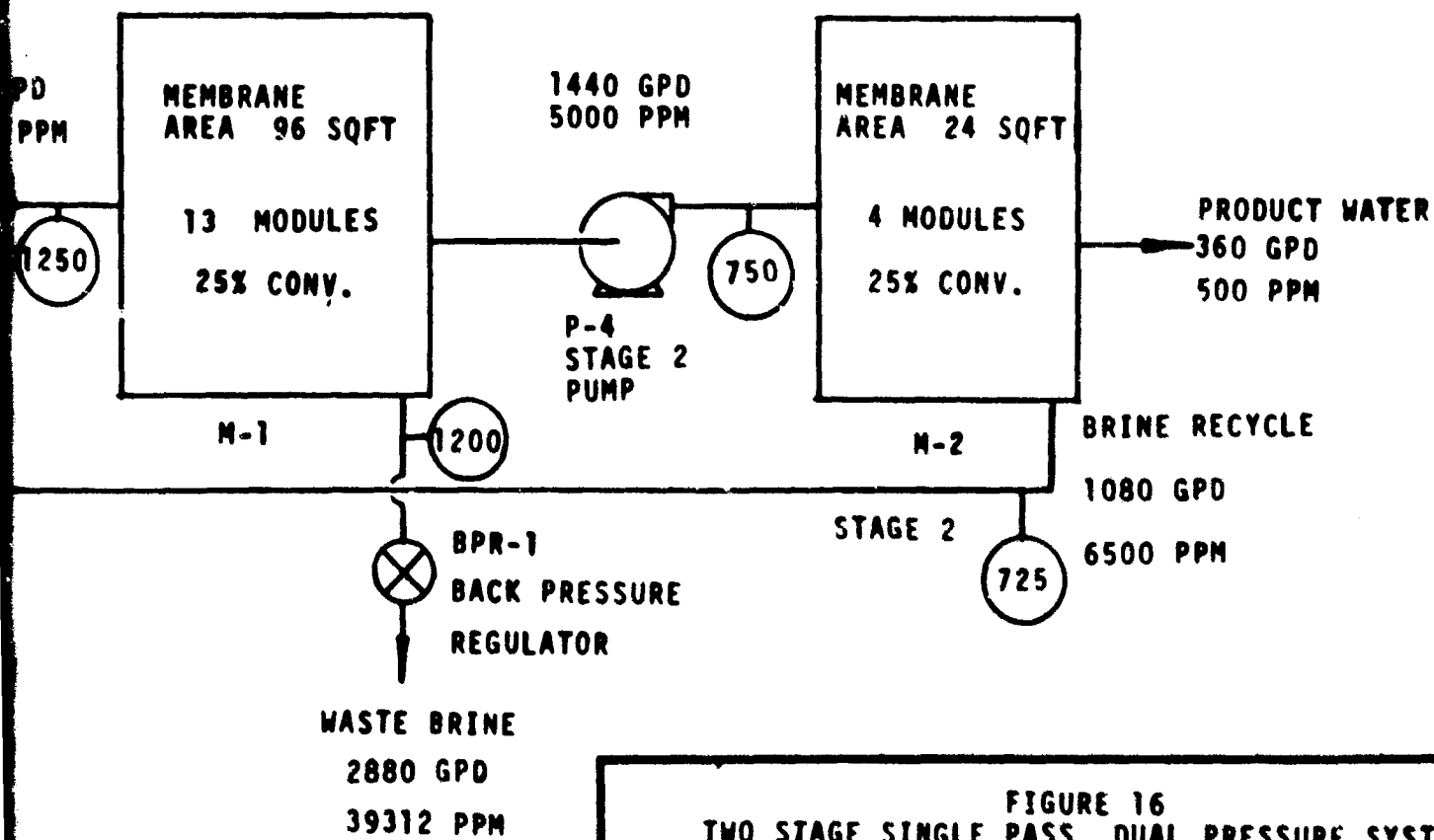


FIGURE 16
TWO STAGE SINGLE PASS DUAL PRESSURE SYSTEM

SCALE: NONE

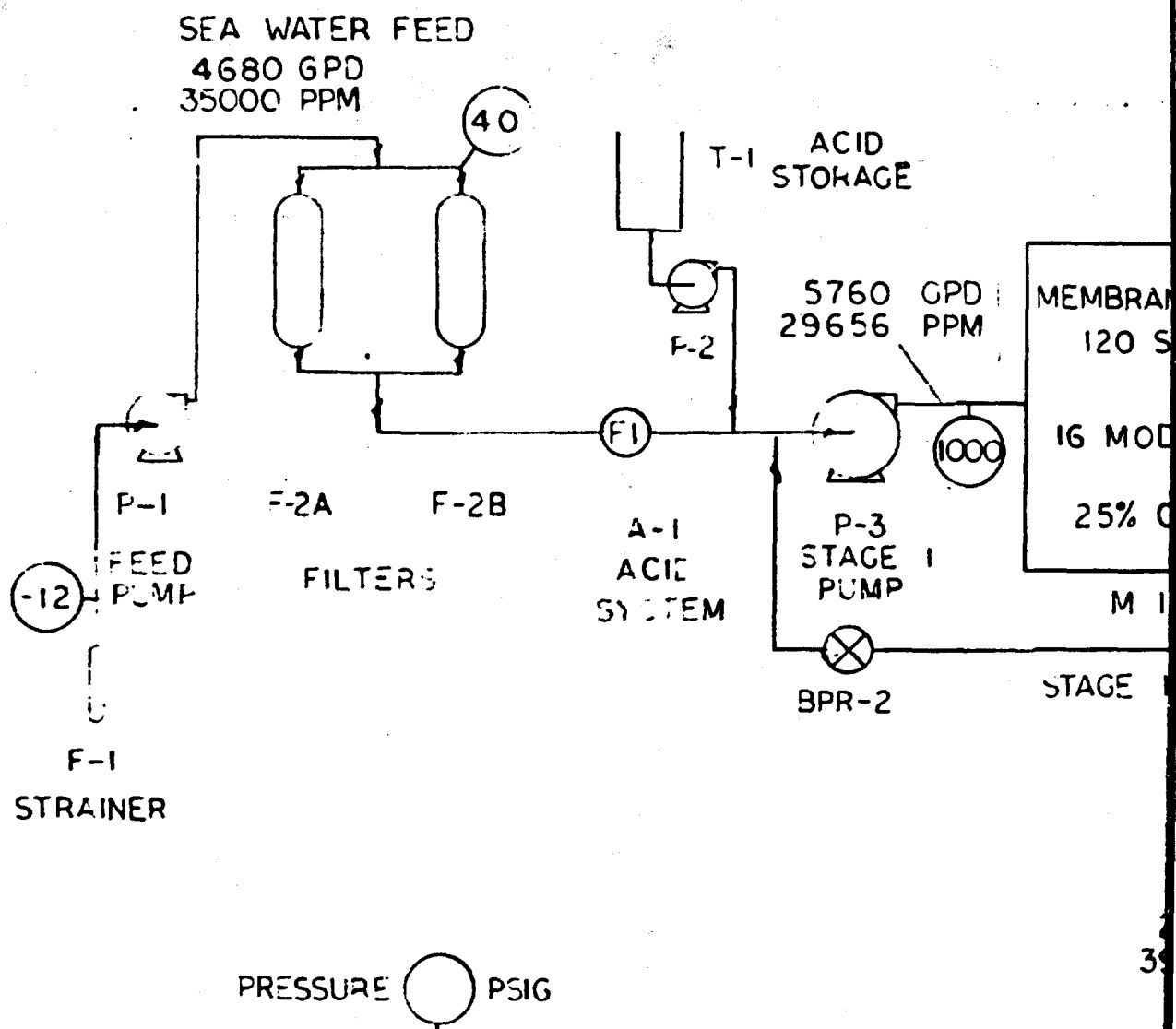
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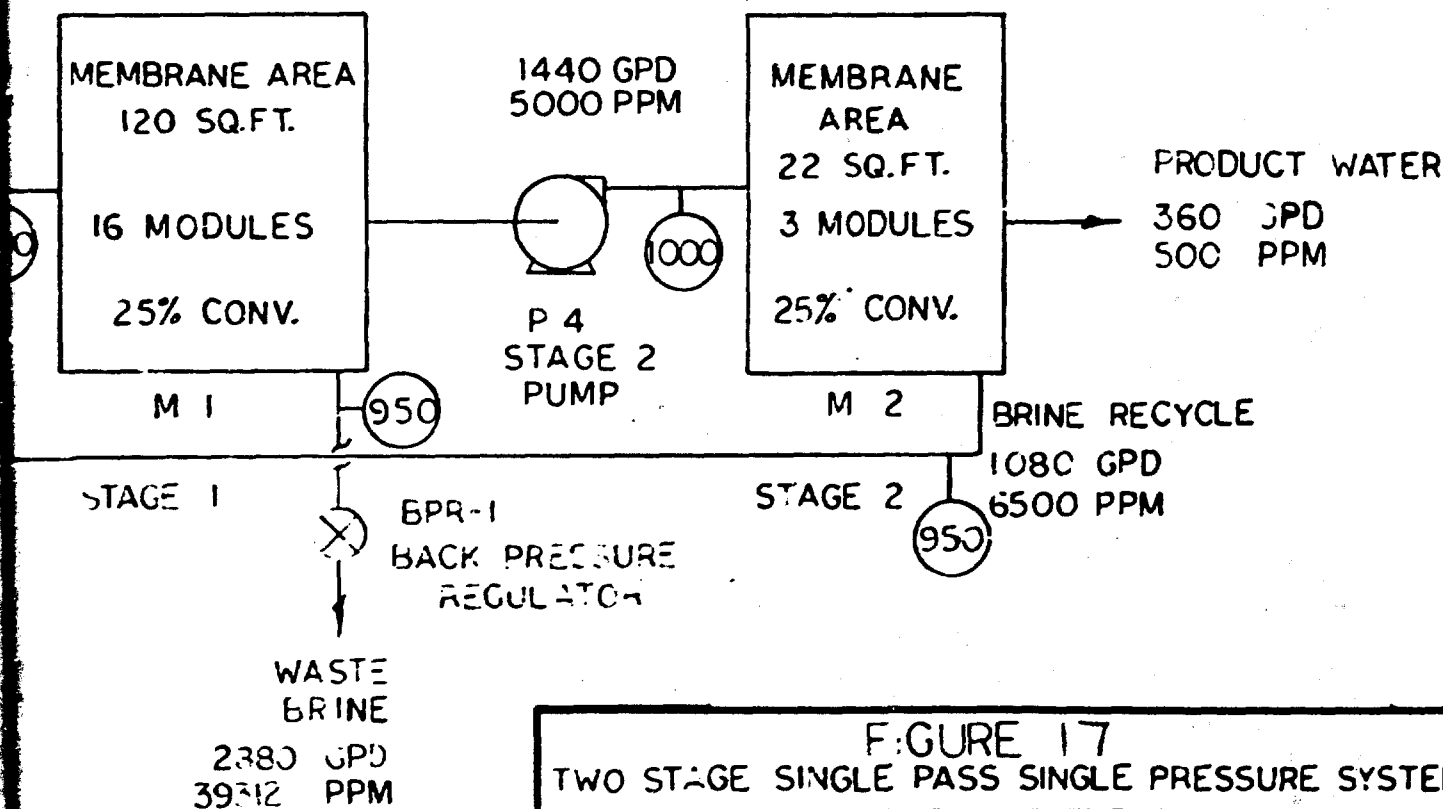
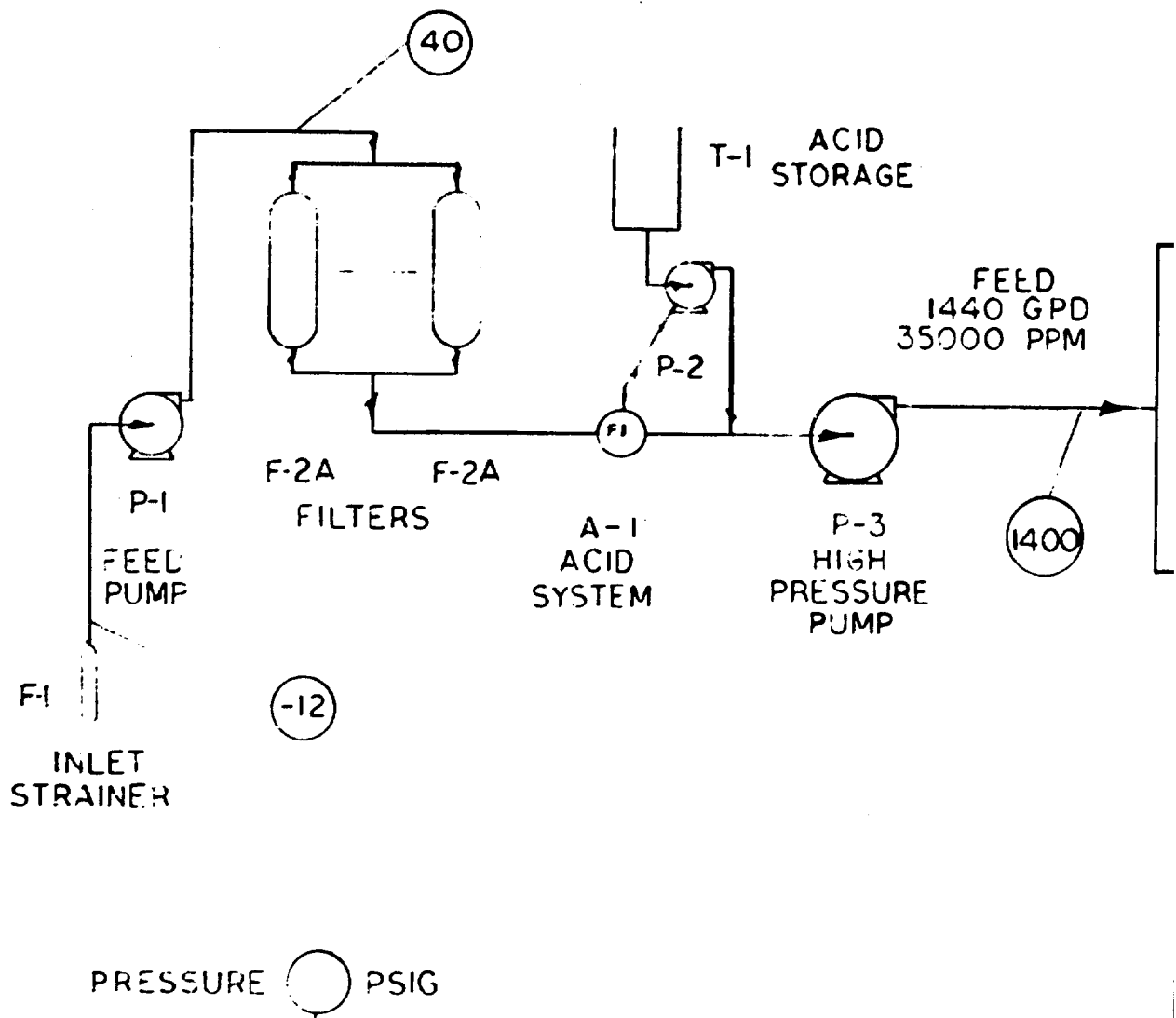


FIGURE 17
TWO STAGE SINGLE PASS SINGLE PRESSURE SYSTEM

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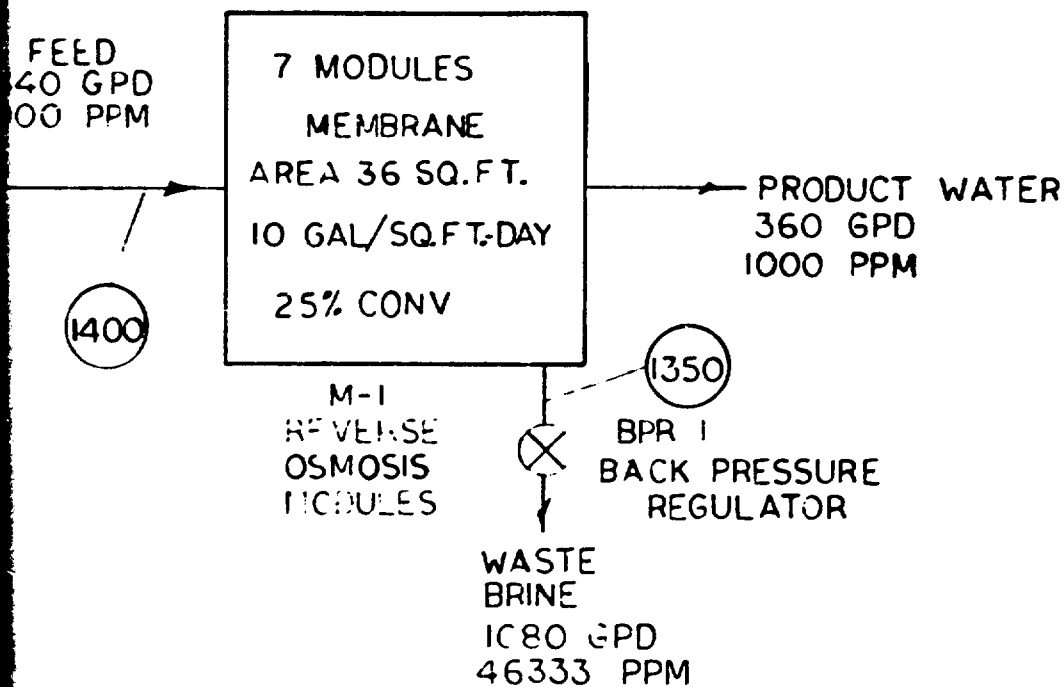


FIGURE 18		
SINGLE STAGE SINGLE PASS WITH 1000 PPM		
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13. ABSTRACT Work has been directed toward improvement of semipermeable membranes for use in reverse osmosis desalination systems. Inclusion of pyridine as a constituent in the membrane casting solution has resulted in appreciable increased membrane strength. Design criteria for various systems for desalting sea water, based on present technology, were evaluated. It is proposed to use a two pass system with sea water initially passed through membranes at 1200 psi to produce an intermediate water of about 5,000 ppm. This intermediate water is stored as produced and, in a predetermined time cycle, is used as feed for the same membrane units on a time shared basis, to produce product water of less than 500 ppm TDS.		

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
1. Water 2. Desalination 3. Reverse osmosis 4. Membranes, semipermeable 5. Sea water desalination						

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