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 A PROJECT: Intended to guide the officers of the Agency for International Development in evaluating and determining the technical and economic feasibility of desalination projects for which U.S. Government assistance may be sought. The original two-volume Manual -- one volume on technology and one on economics -- was prepared by Kaiser Engineers of Oakland, California in April, 1967. In October, 1972, Burns and Roe Inc., of Oradell, New Jersey produced a supplement to each volume.  
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 DEVELOPMENTS: Technical improvements and cost reductions of desalination have added a new dimension to water supply planning: This method of supplementing freshwater supplies demands prominent consideration as a means of meeting future water needs. The Manual reviews various desalination processes and presents economic and technical guidelines for gathering and analyzing data on energy and water resources and requirements -- data that must be considered in deciding whether water desalination is a viable solution to an area's water shortage problem. Volume I discusses eight desalination methods and describes a typical plant for each: Distillation processes - 1. vertical falling and rising film, 2. multistage flash, 3. multieffect multistage flash, 4. vapor compressions, and 5. solar stills; Non-distillation processes - 6. vacuum-freezing vapor-compressions, 7. electro dialysis, and 8. reverse osmosis. It includes a feasibility study on combining desalination

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plants with electric power generating plants, and a discussion on combining desalination with production of chemical by-products. Volume II gives guidelines for studies to determine if desalination is the optimum solution to an area's water shortage problem. An Appendix lists existing plants, technical data on properties of seawater and brackish water, and sample survey questionnaires. The Supplements to Volumes I & II do not present new technologies but rather refinement and commercialization of the material in the two volumes. They update technical and economic guides - often pointing to the increased viability of desalination solutions. The Supplements describe typical plants built since 1967 and provide sections on conceptual designs, water development planning, and updated budget water plant pricing. They add as well some environmental considerations, and feed treatment and brine disposal methods. Whereas the Manual provides information for evaluation and determination of the feasibility of desalination programs, it does not provide the detailed technical data required by a desalination plant designer. Volumes I & II can be used independently of each other; the Supplements, however, do require reference to Volumes I & II.

CSD-1440GTS  
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# **A MANUAL ON WATER DESALINATION**

## **VOLUME ONE — TECHNOLOGY :**

**CHAPTERS 1 - 4**

**APRIL 1967**

**PREPARED FOR**



**Department of State  
AGENCY FOR INTERNATIONAL DEVELOPMENT  
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**KAISER  
ENGINEERS . OAKLAND . CALIFORNIA**

A MANUAL ON WATER DESALINATION

VOLUME ONE

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AGENCY FOR INTERNATIONAL DEVELOPMENT

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## Notice

"This manual was prepared for the Agency for International Development (AID), to guide its officers in evaluating and determining the technical and economic feasibilities of desalination programs and projects, for which United States Government assistance may be furnished or sought. The information contained herein is not sufficient for and is not intended to be the sole basis for design or construction of a project at any particular location, or as a substitute for professional judgment, advice, and design work by competent engineers in connection with such a project."

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## I. INTRODUCTION

Many countries are experiencing a rapidly growing demand for additional freshwater sources to accommodate the anticipated growth of industry, agriculture and population. As an area's water requirements increase, the development of available freshwater sources becomes increasingly difficult and expensive. If natural sources of fresh water have already been utilized to near their ultimate capacity, it is imperative that economical alternate sources be found--otherwise a nation's development may be stifled.

During the past decade, the cost of fresh water produced by the desalination of seawater or brackish water has been steadily reduced. This cost reduction has been effected both by technological improvements in the various desalination processes and by a gradual accumulation of manufacturing and operating experience which allows larger capacity plants to be built. In some areas, desalination already has become competitive with alternative methods of supplementing freshwater supplies. In other areas, the cost differential between desalinated water and that obtained from natural sources is rapidly diminishing. Thus, desalination has added a new dimension to water supply planning, and should be given prominent consideration as a means of supplying future water needs.

The Agency for International Development recognized the need for a systematic approach to identifying those areas and communities where water desalination might be economically attractive. Kaiser Engineers was contracted to prepare a Manual on Water Desalination which would review the state of the art of the various desalination processes and would present economic and technical guidelines for gathering and analyzing data on energy and water resources and requirements. Such data are essential in deciding whether water desalination should be considered as the solution to an area's water shortage problems, in conducting feasibility and economic studies and in preparing an "Economic and Technical Soundness Analysis" of a proposed solution.

The primary purpose of the Manual is to provide information which the Agency for International Development can use in evaluating and determining the technical and economic feasibility of proposed desalination programs in less developed countries. Generally, less developed countries will require desalination plants with capacities of 100,000 to 10 million gallons per day, and the Manual was intended for use in

considering plants in this range. The process descriptions in this Manual are applicable to sizes beyond this range, but for plants above 10 million gallons per day a nuclear power plant should be considered for a heat source (see Section VI, Dual Purpose Plant Discussion). The Manual also provides much useful information for those interested in acquiring a general background on desalination technology. However, the Manual is not intended to contain the detailed technical data which would be required by a desalination plant designer. It is anticipated that those countries seriously considering a desalination plant would engage a qualified architect-engineer to perform the technical and economic analyses required to establish the criteria for the desalination program and subsequently to perform the engineering design of the plant.

The Manual on Water Desalination is divided into two parts -- Volume One is a discussion of desalination processes and plant designs and Volume Two provides the recommended technical and economic guidelines for solving water shortage problems. The two parts of the Manual can be used independently. A user whose requirement involves the application of the technical and economic guidelines contained in Volume Two can proceed directly to that portion of the Manual without first reading Volume One. On the other hand, a reader who desires to obtain a general familiarity with the state of the art of the various desalination processes, or of any particular process, can refer to the appropriate portion of Volume One.

Many features of the desalination processes described in the Manual are covered by patents held by various organizations. Since desalination is one of the most rapidly developing technological areas, the patent situation is somewhat unsettled and the validity of many patents has yet to be tested. No attempt has been made herein to explore comprehensively the patent situation with regard to the various processes. Anyone who contemplates building a desalination plant should make a full determination of all proprietary rights relating to the particular process or design, and should procure any necessary licenses. The desalination facility owner should obtain a "hold harmless" clause from equipment suppliers indemnifying him against liability or loss from patent infringements.

## II. SUMMARY

Advances in desalination technology have reduced the cost of desalting seawater and brackish water to where in certain areas it is competitive with the cost of water obtainable from new natural water supplies. This Manual on Water Desalination has been prepared as a guide in evaluating the feasibility of desalination in water-short areas where desalination may be competitive with other water sources.

The Manual is divided into two volumes. VOLUME ONE, DESALINATION PROCESS TECHNOLOGY, includes a discussion of the state of the art of the major desalination processes and VOLUME TWO, WATER SHORTAGE PROBLEMS, includes technical and economic guidelines and an outline of studies required to determine the optimum approach towards resolving the water shortage problems of a country or region.

### Volume One - Desalination Process Technology

From the standpoint of commercial application, the leading seawater desalination process today is the multistage flash distillation process (MSF)--there being more than 100 such plants in commercial operation. Sixteen of the MSF plants have capacities of 1,000,000 gallons per day (gpd) or more.

Other seawater distillation processes such as the multieffect multistage flash process (MEMS), the falling and rising film processes (including the long tube vertical process--LTV), and solar distillation, have been utilized in demonstration and small commercial plants and, in certain applications, may offer advantages over the MSF process. In sunny and warm climates the solar distillation process is sometimes the most economical process for installations of 25,000 gpd and under.

The vapor compression distillation process, while suitable for seawater, requires very little cooling water and is, therefore, well suited to inland locations where cooling water is in short supply. Other than the 1,000,000 gpd Vapor Compression Demonstration Plant constructed at Roswell, New Mexico, and a 692,000-gpd plant in the Marshall Islands, vapor compression plants have been limited in capacity to 200,000 gpd. The leading brackish water process (where brackish water salinity ranges from 1,000 to 5,000 parts per million of total dissolved solids) is electrodialysis, there being more than 100 of these plants in commercial operation, including plants of 250,000 gpd at Webster, South Dakota and Port Mansfield, Texas, and a 650,000-gpd plant at Buckeye, Arizona.

Processes still under development for both seawater and brackish water installations are the several freezing processes (the leading process being vacuum-freezing vapor-compression) and the reverse osmosis process. In the case of vacuum-freezing vapor-compression and reverse osmosis, pilot plant units have been operated and commercial size units may soon be available.

A discussion of seawater and brackish water composition, description of process phenomena and definitions of terms which are used in the literature in discussing impurities present in water have been included in Section III - Saline Water Phenomena and Definitions. A discussion of the state of the art of the above processes together with a discussion of the now-obsolete submerged-tube single and multieffect processes is presented in Section IV - Desalination Process State of the Art. Each process description includes a process flow diagram and a discussion of process principles.

Typical plants were selected for the five distillation processes--vertical falling and rising film, MSF, MEMS, vapor compression and solar stills; and three nondistillation processes--vacuum-freezing vapor-compression, electro dialysis and reverse osmosis. In each case, the typical plant is described in Section V - Description of Typical Plants. The ratio of product water-to-initial steam of the typical distillation process plants ranges from 10 pounds of water per pound of steam for the OSW Demonstration Plant No. 2 at San Diego (Pt Loma) to 20 pounds of water per pound of steam for the Clair Engle Plant being constructed at San Diego, California. In these plants a staff of 13 or 14 people is required for continuous round-the-clock operation. The solar still plant at Symi, Greece, however, requires only one part-time operator because of its simplicity. The staff requirements of the electro dialysis plant at Webster, South Dakota, is six people.

During 1966, two major engineering feasibility studies were made to determine the cost of desalted water from large dual-purpose electric power and seawater desalting plants--one for a 200 megawatt electrical, 100 million gpd dual-purpose plant for the Government of Israel, and the other for a 1,500 megawatt electrical, 150 million gpd dual-purpose plant for the Metropolitan Water District in southern California. In each case, the most economical plant which could be placed in operation by the early 1970's was found to be a dual-purpose complex using a light-water moderated-and-cooled nuclear reactor and a multistage flash evaporator. The aspects of combining desalination plants with electric power generation plants such as was done in the above dual-purpose plant feasibility studies are described in Section VI - Dual-Purpose

Plant Discussions. In addition, Section VI contains a discussion of the possibility of combining desalination with some other objective such as producing chemical by-products. Summaries of these two major conceptual feasibility studies, together with the results of 15 other conceptual design studies, are reported in Section VII - Summary of Major Conceptual Design Studies.

## Volume II - Solution of Water Shortage Problems

It is necessary to conduct a number of surveys and perform a number of studies to determine if desalination is the optimum solution to the water shortage problems of an area. Guidelines for structuring a study organization, discussion of study objectives and an outline of the recommended plan of action for the study organization is described in Section VIII - Solution of Water Shortage Problems. The plan of action includes performing a number of surveys to define a country's water and energy sources and requirements and to define possible alternative solutions to the water shortage problems. The results of these surveys may be utilized in preparing a "water development plan" as described in Section IX - Water Development Plan.

To select the most promising solution(s) to the area's water shortage problems, it is necessary to conduct preliminary feasibility studies on all possible alternative solutions. The procedure recommended for conducting these feasibility studies on desalination solutions is described in Section X - Selection of Most Promising Solutions.

When the most promising solution to the water shortage problem has been identified by the preliminary feasibility studies, a detail engineering feasibility and economic study should be performed. The objectives and scope of this detail study are outlined in Section XI - Detailed Feasibility Study of Selected Solution.

## Appendix

The Appendix contains a list of existing desalination plants (excluding distillation plants with less than 100,000 gallon per day capacity), selected technical data on the properties of seawater and brackish waters, estimating aids for assistance in performing desalination feasibility studies, and sample questionnaires to be used in soliciting information and data during the surveys of water and energy resources and requirements.

### III. SALINE WATER PHENOMENA AND DEFINITIONS

#### A. General

Any water containing more than 1,000 parts per million (ppm), by weight, of dissolved solids is considered saline. Each of the two types of saline water, i. e., seawater and brackish water, is discussed in this section. Also included is a section on salinity terminology.

Generally, brackish waters include those saline waters with dissolved solid contents above 1,000 ppm and less than that of seawater (about 35,000 ppm). The term brackish water is most frequently applied to saline waters containing less than 10,000 ppm. However, occasionally saline ground waters containing more than 10,000 ppm also are referred to as brackish. Thus, there is no precise upper limit on the solids content of those waters classified as brackish. Saline waters having higher salt concentrations than seawater are classified as brines.

#### B. Typical Seawater Analysis

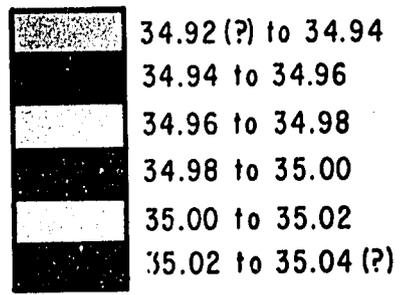
Approximately 97% of the earth's inventory of water resides in the oceans. The world's major oceans (Atlantic, Pacific and Indian Ocean) are all interconnected by the Antarctic Ocean surrounding the Antarctic continent, thereby forming one continuous world ocean. In the open ocean the average amount of dissolved solids varies only slightly from 3.5% by weight (35,000 ppm).

Locally, however, there are minor compositional variations which reflect the movement of various water masses. Figure III-1 shows the variation of composition in the North Atlantic. Note that the flows from the Mediterranean and Norwegian Seas have a higher salinity than that of the open ocean surrounding these flows(1). Increases in salinity are brought about both by evaporation and freezing, whereas decreases are caused by precipitation and melting. These salinity variations are most pronounced in relatively isolated bodies of water. For instance, in the Baltic Sea the concentration of dissolved solids reaches as little as 3,000 parts per million (ppm) since the freshwater inflow and the precipitation together exceed the evaporation(2). Conversely in areas where solar evaporation is relatively high, the concentration of dissolved solids in seawater exceeds the oceanwide average. Some typical values are:

FIGURE III-  
VARIATION IN SALINITY  
NORTH ATLANTIC



SALINITY, g/kg



SOURCE: TILSON, S., "THE OCEAN"  
 INTERNATIONAL SCIENCE AND TECHNOLOGY,  
 FEBRUARY 1966

Red Sea(2)	41,000 ppm
Eastern Mediterranean Sea(3)	38,600 ppm
Arabian Gulf(4)	42,000 ppm

Near the mouths of the world's large rivers, such as the Amazon and the Congo, the flow of fresh water extends many miles into the ocean, reducing the salinity in these locations. These two rivers, the Amazon and the Congo, together account for more than 10% of the total runoff of all rivers into the sea(5).

In certain regions, such as Antarctica, the salinity of coastal waters varies markedly with the seasons. During the summer, melting ice and increased precipitation reduce seawater salinity, whereas during the winter the salinity increases because of the salt left behind when seawater freezes.

Because of previously described seawater compositional variations, no universally accepted seawater analysis exists. Two well-known seawater analyses are "normal seawater" and "seawater," as presented in Table III-1. These analyses are presented in the form of ionic composition, since essentially all of the dissolved salts are present as dissociated ions. "Normal seawater" is prepared by the Hydrographic Laboratories, Copenhagen, Denmark and its analysis was reported by Office of Saline Water Report No. 25(20). The "seawater" analysis shown in Table III-1 was reported by Sverdrup, Johnson and Fleming in their book The Ocean(21). The dominant ionic species are sodium and chloride ions, which together represent approximately 86% by weight of all the dissolved solids. More significant from the standpoint of designing desalination plants are those ions such as calcium, magnesium, carbonate, and sulfate which may produce relatively insoluble scale deposits on the heat exchange surfaces in distillation plants. The principal insoluble scale-forming compounds are calcium carbonate, magnesium hydroxide and calcium sulfate.

Seawater contains practically all of the known elements; however, most are present in trace quantities only. Table III-2 is a listing of some of the elements present in seawater; it excludes the hydrogen and oxygen which comprise the water, and the dissolved gases. Although of no significance in the consideration of desalination processes, many of the minor constituents such as copper, zinc, nickel, iron and vanadium play important roles in the life processes of ocean flora and fauna. The body structures of some sea organisms contain these elements in concentrations which are hundreds to tens of thousands times those present in seawater.

TABLE III - 1

PRINCIPAL IONS IN "NORMAL SEAWATER" AND "SEAWATER"(6)

<u>Constituent</u>	<u>Normal Seawater*(20)</u> <u>(mg/kg or ppm)</u>	<u>Seawater(21)</u> <u>(mg/kg or ppm)</u>
Total Dissolved Solids	35,174	34,482
Chloride (Cl <sup>-</sup> )	19,360	18,980
Sulfate (SO <sub>4</sub> <sup>- -</sup> )	2,702	2,649
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	142	140
Bromide (Br <sup>-</sup> )	66	65
Fluoride (F <sup>-</sup> )	1	1
Iodide (I <sup>-</sup> )	1	-
Sodium (Na <sup>+</sup> )	10,768	10,556
Magnesium (Mg <sup>++</sup> )	1,298	1,272
Calcium (Ca <sup>++</sup> )	408	400
Potassium (K <sup>+</sup> )	388	380
Strontium (Sr <sup>++</sup> )	14	13
Silicon (Si <sup>++++</sup> )	1 (to 4 )	-
Boric acid (H <sub>3</sub> BO <sub>3</sub> )	26	26
Others	1	-
<hr/>		
Chlorinity (g/kg)	19.38	19.00
Chlorosity (g/liter)	19.86	19.46
Salinity (g/kg)	35.01	34.33
Specific Gravity at 20 C	1.025	1.024

\*Based on "Normal Seawater" prepared by the Hydrographic Laboratories, Copenhagen, Denmark

TABLE III-2

ELEMENTS IN SEAWATER(7)\*  
(Excluding Dissolved Gases)

<u>Element</u>	<u>Amount in Seawater (mg/kg or ppm)</u>
Chlorine	18,980
Sodium	10,561
Magnesium	1,272
Sulphur	884
Calcium	400
Potassium	380
Bromine	65
Carbon	28
Strontium	13
Boron	4.6
Silicon	0.02-4.0
Fluorine	1.4
Nitrogen	0.01-0.7
Aluminum	0.5
Rubidium	0.2
Lithium	0.1
Phosphorus	0.001-0.10
Barium	0.05
Iodine	0.05
Arsenic	0.01 -0.02
Iron	0.002-0.02
Manganese	0.001-0.01
Copper	0.001-0.01
Zinc	0.005
Lead	0.004
Selenium	0.004
Cesium	0.002
Uranium	0.0015
Molybdenum	0.0005
Thorium	0.0005
Cerium	0.0004
Silver	0.0003
Vanadium	0.0003
Lanthanum	0.0003
Yttrium	0.0003
Nickel	0.0001
Scandium	0.00004
Mercury	0.00003
Gold	0.000006
Radium	0.2-0.3x10 <sup>-10</sup>
Cadmium	Trace
Chromium	Trace
Cobalt	Trace
Tin	Trace

\*Based on Sverdrup, H. V., Johnson, M. W., and Fleming, R. H. The Oceans, pp. 176-177, Prentice-Hall, Inc., New York, N. Y., 1942

Most of the ocean's dissolved solids have come from two sources. The first source has been the weathering and eroding of materials from the earth's surface. This surface runoff has contributed salts of sodium, calcium, magnesium and potassium. The second source was volcanic activity which released volatiles such as hydrogen chloride, hydrogen fluoride, hydrogen sulfide, carbon dioxide and nitrogen from rocks in the earth's interior.

Each year the rivers of the world carry an impressive quantity of dissolved material into the sea (4 billion tons of inorganic and 400 million tons of organic matter). In addition, approximately five times as much undissolved matter is washed into the ocean in the form of sediment(5). Nevertheless, the composition of seawater has remained relatively constant for a long time. Much of the dissolved salts in stream runoff have been recycled from the sea. This occurs when tiny salt particles are formed from drops of sea spray, and later act as nuclei on which condensation occurs, forming rain clouds. It is interesting to note that while in seawater the ionic concentration of sodium exceeds that of magnesium, which in turn exceeds that of calcium, in river water the order is reversed.

An important property of seawater is its pH, which is a measure of the balance between acids and alkalies. The pH of seawater varies from 7.8 to 8.4, with an average value of 8.2, which is a little on the alkaline side of neutral (7.0 on a pH scale ranging from 0 to 14).

But the sea is more than just a repository of dissolved inorganic material. It abounds in living organisms, whose life processes, over long periods of geologic time, have had a profound effect on its composition. For instance, calcium carbonate is extracted by coral polyps and small marine animals called globigerina, and the skeletons and shells of these creatures have formed large calcium carbonate deposits in shallower water. Silica is extracted by tiny diatoms and radiolarians; the deep ocean deposits of siliceous materials are made up of the skeletal remains of these creatures. Other important biochemical processes are the carbon cycle which starts with the production of organic matter by photosynthesis in small marine plants near the surface, the production of oxygen by sulfate reducing bacteria, and nitrogen-fixation by bacteria.

Table III-3 lists the ionic composition of seawater from the Eastern Mediterranean, the Arabian Gulf, Kwajalein Atoll Lagoon in the Pacific, the Dead Sea, the Great Salt Lake and the Caspian Sea. For comparison purposes, the principal ionic constituents of seawater are also shown. For those bodies of water which are connected with the open ocean, the total amount of dissolved solids varies appreciably from that of seawater; however, the relative abundance of the different ionic species remain fairly constant.

The inland seas and salt lakes in arid areas have no outlet or communication with the major oceans. In these bodies of water, the salts contained in the influent rivers are left behind when the water evaporates. The ratio between the concentrations of different ions in these waters may differ markedly from that in seawater. For instance, although the total dissolved solids content in the Caspian Sea is lower than in seawater, the sulfate ion concentration is higher. Note also that in the Dead Sea the concentration of magnesium is somewhat greater than that of sodium, whereas in seawater the sodium ion concentration is approximately eight times that of magnesium.

### C. Brackish Water Analysis

Vast quantities of brackish ground water are available in many areas of the world. Knowledge concerning the distribution and extent of these brackish water resources is somewhat incomplete. Much of the available information has been derived as a by-product of the investigation of saltwater intrusion into freshwater aquifers.

The analysis of brackish water sources varies widely with location. Not only the total dissolved solids content, but also the ratio of various ionic impurities shows large variations from one brackish water source to another (see Table III-4). The proportions of calcium, magnesium, sulfates or bicarbonates in the total dissolved solids may be much higher in inland sources than in seawater. In coastal areas, where the source of salinity may be due to seawater intrusion, the relative concentrations of various ionic impurities tends to be closer to that present in seawater. Generally, the salinity increases with depth, although this is by no means a universal rule. In some areas, highly saline water is found at shallow depth, with fresh potable water occurring at greater depth in the same formation.

It is important to note that certain impurities, such as iron, manganese and silica, which may be present in relatively small quantities, may have detrimental effects on the operation of certain desalination processes.

TABLE III-3

IONIC COMPOSITION OF SELECTED SALTWATER BODIES  
(mg/kg or ppm)

<u>Constituent</u>	<u>Eastern Mediterranean(3)</u>	<u>Kwajalein Atoll Lagoon(8)</u>	<u>Arabian Gulf Shuaiba, Kuwait(4)</u>	<u>Seawater(6)(21)</u>	<u>Dead Sea(2) (100 m Below Surface)</u>	<u>Great Salt Lake Utah(2)</u>	<u>Caspian Sea(2)</u>
Total Dissolved Solids	38,600	38,200	42,000	34,482	271,000***	203,300***	12,858***
Chloride (Cl <sup>-</sup> )	21,200	22,000	23,100	18,980	178,600	112,900	5,500
Sulfate (SO <sub>4</sub> <sup>--</sup> )	2,950	2,300	3,100	2,649	400	13,600	2,970
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	155	62*	-**	140	-	-	-
Bromide (Br <sup>-</sup> )	72	-**	80	65	5,200	Trace	-
Fluoride (F <sup>-</sup> )	2	-	-	1	-	-	-
Iodide (I <sup>-</sup> )	-	-	-	-	-	-	-
Nitrate (NO <sub>3</sub> <sup>-</sup> )	1	1	-	-	-	-	-
Carbonate (CO <sub>3</sub> <sup>--</sup> )	-	10	-	-	Trace	200	48
Sodium (Na <sup>+</sup> )	11,800	11,200	-**	10,556	32,000	67,300	3,200
Magnesium (Mg <sup>++</sup> )	1,403	82	1,665	1,272	35,700	5,600	773
Calcium (Ca <sup>++</sup> )	423	742	500	400	12,700	300	297
Potassium (K <sup>+</sup> )	463	-**	-**	380	6,400	3,400	70
Strontium (Sr <sup>++</sup> )	-	-	-	13	-	-	-
Silicon (Si <sup>++++</sup> )	-	-	-	-	-	-	-
Iron (Fe <sup>+++</sup> )	-	1	-	-	-	-	-
Manganese (Mn <sup>++</sup> )	-	1	-	-	-	-	-
Boric Acid (H <sub>3</sub> BO <sub>3</sub> )	-	-	-	26	-	-	-
Silica (SiO <sub>2</sub> )	-	7	5	-	-	-	-
Metasilicic Acid (H <sub>2</sub> SiO <sub>3</sub> )	1	-	-	-	-	-	-
Others	131*	1,793*	13,550*	-	-	-	-

\* Computed Value  
 \*\* No Value Listed in Reference  
 \*\*\* Total of Listed Values Only

TABLE III-4

## IONIC COMPOSITION OF SELECTED BRACKISH WATER SOURCES

<u>Constituent</u>	<u>Roswell, New Mexico Operation(13)</u>	<u>Webster, South Dakota Well No. 4(14)</u>	<u>Buckeye, Arizona Well No. 8(15)</u>	<u>Gettysburg Air Force Base, South Dakota(16)</u>	<u>Bahrein, Arabian Gulf(17)</u>	<u>Dalpra Well No. 1 Denver, Colorado(18)</u>
Total Dissolved Solids	15,467*	1,451*	2,140	2,433*	2,196	3,647*
Chloride (Cl <sup>-</sup> )	8,040	7	1,100	440	1,020	131
Sulfate (SO <sub>4</sub> <sup>--</sup> )	1,490	765	169	436	192	1,943
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	205	298	71	765	242	473
Fluoride (F <sup>-</sup> )	-	0.68	-	0.12	-	-
Nitrate (NO <sub>3</sub> <sup>-</sup> )	-	-	-	0.2	-	6
Carbonate (CO <sub>3</sub> <sup>--</sup> )	0	-	-	0	-	0
Sodium (Na <sup>+</sup> )	4,970	102	598	765	458	886
Magnesium (Mg <sup>++</sup> )	161	74	7	4	67	72
Calcium (Ca <sup>++</sup> )	588	193	100	11	217	118
Potassium (K <sup>+</sup> )	-	9	-	9	-	16
Iron (Fe <sup>+++</sup> )	-	1.4	0.4	0.25	-	2.0
Manganese (Mn <sup>++</sup> )	-	0.92	-	0.005	-	-
Silica (SiO <sub>2</sub> )	13	-	5	3.	-	-
Other	-	-	90	-	-	-
Hardness (equiv CaCO <sub>3</sub> )	-	788.2	279	43	815	-
pH	-	7.62	7.6	7.9	7.5	7.6

\* Total of Listed Values Only

As with surface water supplies, underground aquifers may be subject to contamination by industrial, agricultural and domestic wastes. Although experience with groundwaters generally has been good, some monitoring system should be established to guard against contamination. Some of the contaminants which may find their way into underground sources are oil-well wastes, fertilizers, insecticides and detergents.

Another factor to be considered in developing brackish water wells is selection of corrosion resistant materials. Steel well casings have deteriorated rapidly in some cases, due to galvanic corrosion. Electrolytic cells can be created by variations of salinity and oxygen content with depth in the well. Transite and reinforced epoxy pipe have proved satisfactory in handling corrosive brackish water.

In general, saline groundwaters fall into four classifications:

1. Groundwater Which Has Dissolved Minerals From Surrounding Rocks

As water seeps into the ground and percolates through rock layers it becomes more saline as it dissolves minerals from materials in and adjacent to the aquifers. The nature of the impurities is determined by the materials which the water encounters. The amounts of various impurities depend on their relative solubilities, and on the intimacy and duration of contact. The plains areas of Texas and New Mexico are underlaid with rock salt, gypsum and anhydrite beds contained in Permian formations(19). These permeable formations contain enormous quantities of highly mineralized groundwater(19).

2. Groundwater Which Has Become Brackish Through the Intrusion of Seawater

Many coastal areas contain highly permeable aquifers which can provide abundant quantities of saline groundwater. Inland areas also contain salt water which entered in times of high ocean levels during interglacial periods(19). In these inland areas, it is possible to find individual aquifers containing both fresh and saline water at different depths. This is caused by differential flushing of salt water from the formations by fresh water flowing in from recharge areas(19).

Where fresh water and salt water are present in the same permeable formation, the fresh water tends to float on top of the salt water. The density of seawater is approximately 1.025 times that of fresh water. This means that for each meter of fresh water above sea

level, the fresh water will extend approximately 40 meters below sea level. Figure III-2 shows a cross sectional view of an idealized permeable island surrounded by the sea. The fresh water tends to collect in a "lens" which depresses the more dense seawater. A zone of contact exists between the fresh water and seawater. This zone of contact is usually quite narrow, 20 to 30 meters, unless affected by heavy pumping. View A represents the undisturbed freshwater lens. As water is pumped, a "cone of depression" (or drawdown) is produced in the water table level around the well. In a sand island any drawdown due to pumping has a greatly amplified effect on the line of contact between salt and fresh water. View B shows brackish water being pumped at the well. The above discussion is simplified, but illustrates the effect of saltwater intrusion into groundwater.

### 3. Connate Water(19)

Connate groundwater is water which was trapped in the surrounding formation when the formation was deposited. Some dilution of these connate waters occurs as a result of flushing by fresh groundwater. Generally, the salinity of connate water retained in limestone and sandstone increases with depth. With respect to both area and depth, however, these formations contain a widespread variation of water, ranging from slightly saline or marginal, to moderately saline, to brine. There also is considerable variation in the pumping rate which can be achieved from wells.

### 4. Water Contained in Closed Basins(19)

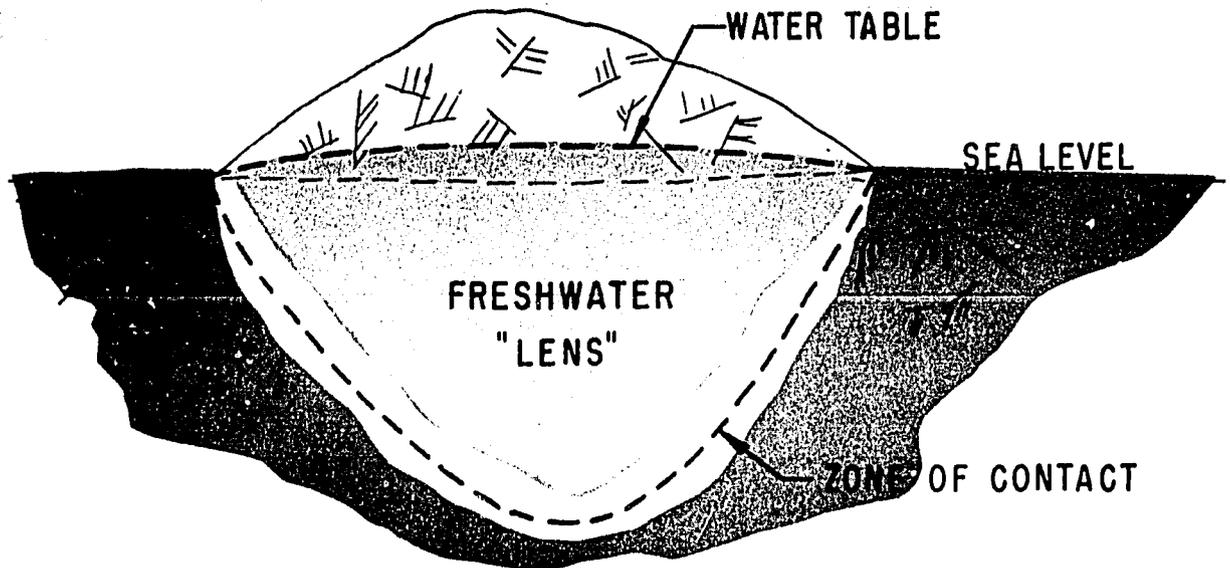
Saline water accumulates in closed basins which have no significant outflow either on the surface or subsurface. The water which drains into these basins has a high salinity due to evaporation and transpiration. Typically, these closed basins, or valleys, are filled with alluvial deposits varying in depth from a hundred to a thousand meters. Groundwater is recharged by precipitation and lost through evaporation from the low central portion of the basin. Usually a dry lake containing highly saline soils is formed, with the water level located near the land surface. This brackish groundwater may contain several thousand parts per million of dissolved solids.

## D. Salinity Terminology

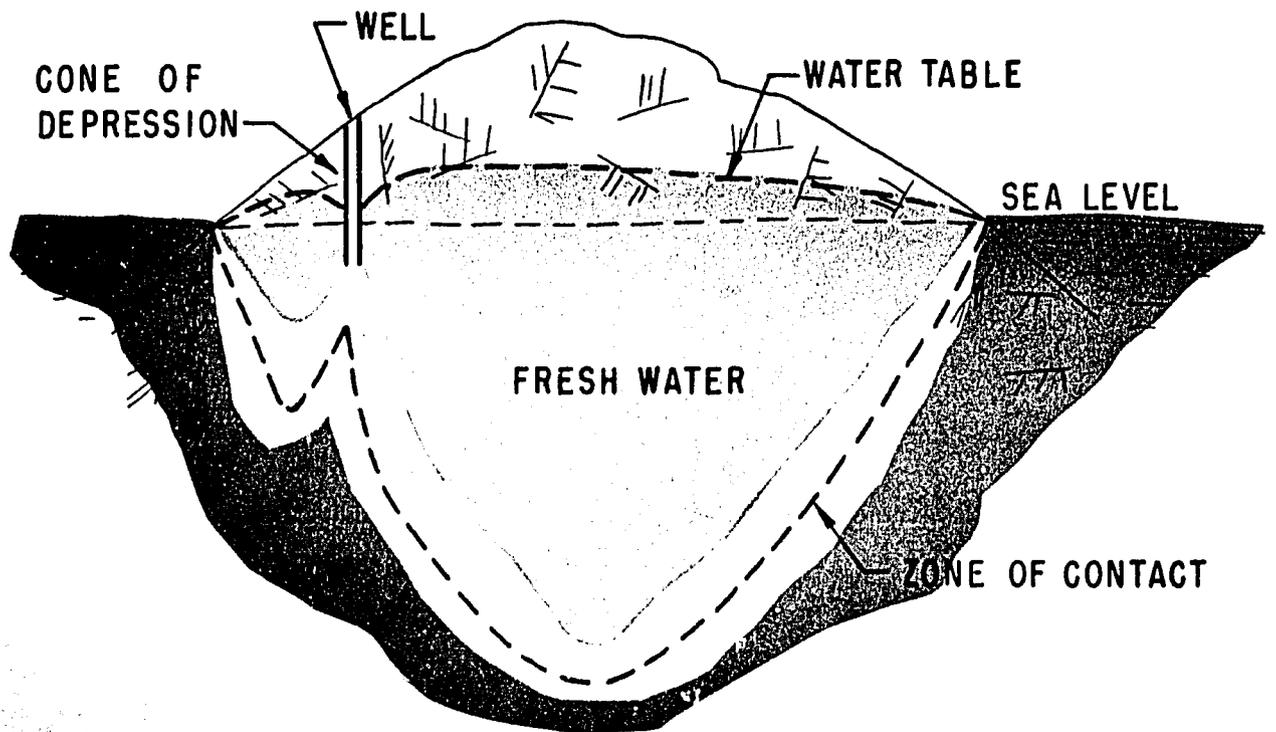
Various nomenclature and terminology have been used in the technical and trade literature dealing with desalination and water treatment. This subsection defines terms dealing with the saline properties of seawater and brackish water.

FIGURE III-2

INTRUSION OF SALT WATER INTO FRESH WATER



A-UNDISTURBED



B-DISTURBED BY PUMPING

### Bicarbonate Alkalinity

The bicarbonate ion concentration expressed in parts per million (ppm) as equivalent calcium carbonate ( $\text{CaCO}_3$ ). To convert ppm of bicarbonate to ppm expressed as calcium carbonate multiply by 1.64.

### Brackish Water

Water in which the dissolved solids content falls between that of drinking water and that of seawater. The term does not have a precise meaning with respect to dissolved solids content. Generally, water having a dissolved solids content of 1,000 to 10,000 ppm is referred to as brackish.

### Brine

A saline solution with a concentration of dissolved solids exceeding that of seawater (35,000 ppm). The effluent or reject stream from a seawater or brackish water desalting plant may be considered as brine, even though brackish water desalting plant reject streams are frequently less saline than seawater. Other brines are pumped from subsurface sedimentary deposits and are fossil waters of marine origin(11).

### Calcium Carbonate Equivalents

The impurities in naturally occurring waters frequently are expressed as calcium carbonate equivalents. This is the number of parts of the ion, element or compound per one million parts of water by weight, expressed as equivalent calcium carbonate. To convert the ppm of a given constituent to ppm expressed as calcium carbonate, multiply by the ratio of the molecular weight of calcium carbonate to that of the constituent. The molecular weight of calcium carbonate ( $\text{CaCO}_3$ ) is 100.

### Carbonate Alkalinity

The carbonate ion concentration expressed in parts per million (ppm) as calcium carbonate ( $\text{CaCO}_3$ ) equivalents. To convert ppm of carbonate to ppm calcium equivalents, multiply by 1.67.

Carbonate Hardness

The term "carbonate hardness" is synonymous with "bicarbonate hardness" and "temporary hardness," although carbonate hardness is the preferred terminology. Carbonate hardness is that hardness attributable to the bicarbonates of calcium and/or magnesium. If the "total alkalinity" (defined below) exceeds or equals the sum of the calcium and magnesium concentration expressed as ppm equivalent  $\text{CaCO}_3$ , all hardness is present as carbonate hardness. If total alkalinity is less than the sum of the calcium and magnesium concentration, the carbonate hardness equals the alkalinity. Carbonate hardness is expressed as ppm equivalent  $\text{CaCO}_3$ (12).

Chlorinity

The total amount of chlorine (in grams) contained in one kilogram of seawater, after all the bromide and iodide have been replaced by chloride(6). For seawater an empirical relationship between salinity and chlorinity is given by(2):

$$\text{Salinity} = 0.03 + 1.805 \times \text{chlorinity}$$

This definition of chlorinity is applicable only to seawater (normal, concentrated or diluted), not to other types of salt water.

Chlorosity

The total amount of chlorine (in grams) contained in one liter of seawater at a temperature of 20C (68 F), after all the bromide and iodide have been replaced by chloride(6). This definition of chlorosity is applicable only to seawater (normal, concentrated or diluted), not to other types of salt water.

Color

Color in water is caused by dissolved or finely divided organic matter extracted from decaying vegetation. Only the true color of water, due to substances in solution, is of interest in making a color determination; the suspended matter must be removed by centrifuging. The method of measuring color is by comparison with a standard solution(12).

Equivalents per Million

This is the parts per million (ppm) of the substance present divided by the equivalent weight of the substance (9). The equivalent weight of a substance is its atomic or formula weight divided by its valence.

Hardness

The characteristic of water which prevents the lathering of soap. This is principally due to the divalent cations of calcium and magnesium. In water treatment, hardness is the sum of the calcium and magnesium concentration, expressed as  $\text{CaCO}_3$ .

Hydroxide Alkalinity

The hydroxide ion concentration expressed in parts per million (ppm) of equivalent calcium carbonate ( $\text{CaCO}_3$ ). To convert ppm of hydroxide to ppm equivalent calcium carbonate, multiply by 5.88.

Milli-Equivalents per Liter (Abbreviated meq/l)

The number of milli-equivalents of a substance contained in a liter of solution. Milli-equivalents per liter is numerically equal to the number of equivalents per million (epm). The number of equivalents of a substance is obtained by dividing its mass in grams by the equivalent weight. The equivalent weight of a substance is its gram atomic weight divided by its valence.

Noncarbonate Hardness

"Noncarbonate hardness" is synonymous with "permanent hardness" or "sulfate hardness." Noncarbonate hardness, however, is the preferred terminology. It is the hardness due to the sulfates, chlorides and/or nitrates of calcium and/or magnesium. Noncarbonate hardness exists only if the total hardness exceeds the methyl orange alkalinity. It is equal to total hardness less the methyl orange alkalinity expressed as  $\text{CaCO}_3$  equivalents (12).

Parts per Million (Abbreviated ppm)

The number of parts of the substance (element, ion or chemical compound) per one million parts of water, by weight. It is numerically equal to the concentration in milligrams of the substance per kilogram of solution (mg/kg).

### Permanent Hardness

See "noncarbonate hardness."

### pH

The negative logarithm, to the base 10, of the hydrogen ion concentration in gram-equivalents per liter.

### Salinity

The total amount of solids (in grams) contained in one kilogram of seawater when all carbonate has been converted to oxide, all bromide and iodide replaced by chloride and all organic matter completely oxidized(6).

### Saturation pH (Abbreviated pHs)

The pH at which a given sample of water is saturated in a particular scale-forming constituent. At a pH value higher than pHs, the scale compound will tend to precipitate(6).

### Saturation Index

The difference between the actual pH and the saturation pH. If (pH-pHs) is positive, the water sample is supersaturated in the scale-forming compound. If the saturation index is negative, it is undersaturated. The saturation index is a measure of the departure from equilibrium and does not predict the time which may be required to reach equilibrium(6).

### Stability Diagrams

Charts showing the solubility of scale-forming compounds at a given temperature as a function of pH and alkalinity(6).

### Temporary Hardness

See "carbonate hardness."

Total Alkalinity

The sum of the carbonate, bicarbonate and hydroxide concentrations, all expressed in parts per million (ppm) as equivalent calcium carbonate ( $\text{CaCO}_3$ )(6). When a water analysis is known, one may convert ppm of carbonate, bicarbonate and hydroxide to equivalent ppm  $\text{CaCO}_3$  by multiplying the concentrations by the following conversion factors:

<u>Ion</u>	<u>Conversion Factor</u>
Carbonate ( $\text{CO}_3^{--}$ )	1.67
Bicarbonate ( $\text{HCO}_3^-$ )	1.64
Hydroxide ( $\text{OH}^-$ )	5.88

Total alkalinity is determined by titration with a standard acid solution. If the titration end point is obtained using a methyl orange indicator, the alkalinity is known as methyl orange alkalinity(12).

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- (17) Barnhill, K. G. and Sparks, J., "Electrodialysis - A Method for Treating Highly Mineralized Waters," The American Soft Drink Journal, March 16, 1964.
- (18) 1964 Saline Water Conversion Report, U. S. Department of the Interior, Office of Saline Water, p. 167.
- (19) Poole, J. L., "Saline Ground Water - A Little Used and Unmapped Resource," presented at National Water Well Exposition, Cincinnati, Ohio, Oct 22, 1962.
- (20) Critical Review of Literature on Formation and Prevention of Scale, prepared by W. L. Badger and Associates, Inc., Office of Saline Water Report No. 25, p. 34, July 1959.
- (21) Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., The Oceans, p. 173, Prentice-Hall, Inc., New York, N. Y. (1946).

## IV. DESALINATION PROCESS STATE OF THE ART

### A. Distillation

#### 1. Distillation Phenomena

##### a. Introduction

For centuries man has used simple distillation methods to produce fresh water from brackish water or seawater. Presently, the various distillation processes are the most highly developed and widely used desalting processes.

The two basic phenomena involved in distillation are evaporation and condensation. Heat is added to the saline water to cause evaporation or boiling. When saline water evaporates, the vapor formed is essentially pure water, except for droplets of saline water which may be entrained into the gas phase. The reason for this is that the dissolved inorganic salts, which constitute most of the impurities in saline water, have extremely low vapor pressures compared with that of water. The water vapor or steam produced by evaporation is contacted with a cooled surface. The water vapor condenses on the cooled surface and is collected as fresh product water.

The two basic distillation phenomena, evaporation and condensation, are discussed in detail below.

#### (1) Evaporation and Condensation

##### (a) Evaporation or Boiling

To effect a change of phase from liquid to gas at the same temperature, it is necessary that heat be supplied to the liquid. This heat is known as the latent heat of vaporization. In some distillation processes, heat is transferred to the liquid concurrently with the boiling process. In other processes, the saline water is maintained at a pressure high enough to prevent boiling from occurring at the heat exchange surface. The heated saline water is conveyed to a separate vessel where the pressure is

suddenly reduced. This pressure reduction allows a fraction of the saline water to evaporate suddenly, or "flash." This process is known as flash distillation.

Usually, heat is supplied to the saline water by steam which condenses and gives up its latent heat. Heat may also be supplied by solar radiation (solar distillation processes) or by an immiscible liquid used to transfer heat from the heat source to the saline water.

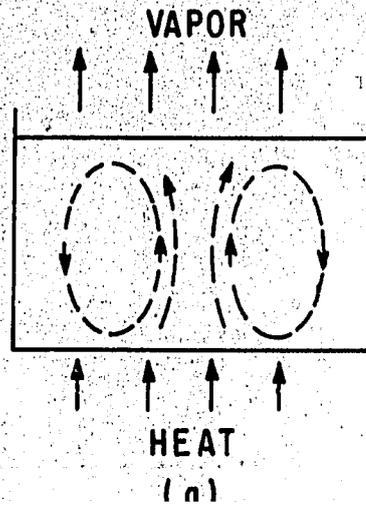
As a liquid is heated, the energies of its molecules increase. Some of these molecules attain high enough energies to leave the liquid and enter the gaseous space above the liquid surface. If the gaseous space above the liquid is enclosed and the liquid is maintained at a constant temperature, eventually a condition of equilibrium, or steady state, will be reached wherein the number of molecules leaving the liquid surface will just equal the number reentering (or condensing in) the liquid. The pressure which the molecules of a given substance exert on the walls of the container when the gaseous phase is in equilibrium with the liquid phase at a given temperature is known as the saturation pressure of that substance. If the gaseous space above the liquid contains several gases, the pressure exerted by each gas is known as its partial pressure.

If the partial pressure of the substance in the gaseous phase is less than the saturation pressure at the temperature of the liquid, evaporation will occur from the liquid phase into the gaseous phase. Provided that enough liquid surface is available, all of the vaporization can occur at the liquid surface. This process is usually called "surface evaporation." In the process of surface evaporation, hot liquid is carried to the surface by convection currents. Vapor and energy leave the liquid mass at the evaporating surface, and cooled liquid returns to the bulk of the liquid, which serves as a heat reservoir. Figure IV-1 shows the

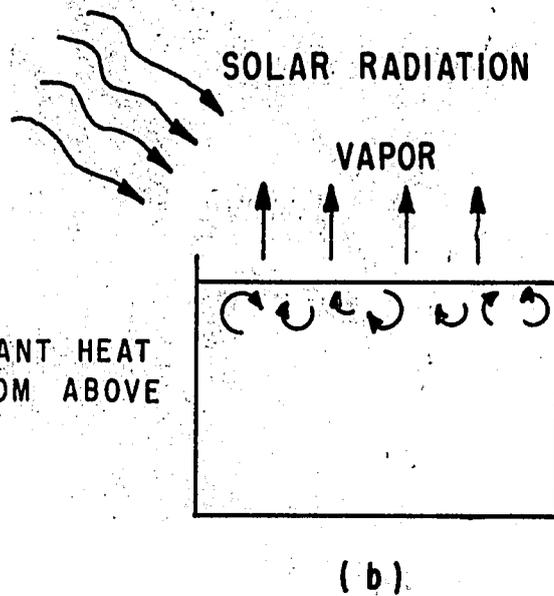
FIGURE IV-

EVAPORATION CONVECTION PATTERNS

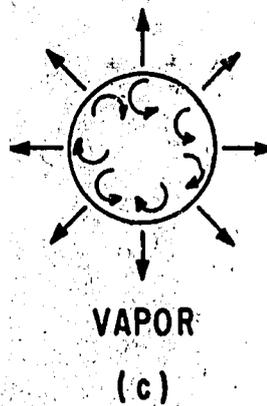
(a) VESSEL, HEAT APPLIED UNDERNEATH



(b) VESSEL, RADIANT HEAT APPLIED FROM ABOVE



(c) EVAPORATION FROM LIQUID DROP



SOURCE: HICKMAN, K., "EVAPORATION COEFFICIENTS OF LIQUIDS", FIRST INTERNATIONAL SYMPOSIUM ON WATER DESALINATION, PAPER SWD/27 OCT 3 TO 9, 1965, WASHINGTON, D. C.

convection patterns or "turnover" for three different geometries: a vessel heated from below, a liquid heated by solar radiation and an evaporating liquid drop. In theory, there is always a thin laminar layer on the surface, which remains undisturbed regardless of how vigorously the liquid is stirred by these convection currents (1). This laminar layer is from a micron to a millimeter thick (1). Hickman (1) has concluded that the principal limitation on evaporation coefficients is the resistance to the diffusion of heat and material to the liquid surface. The photographs in Figure IV-2 show convection patterns for heptane evaporating with various heat inputs.

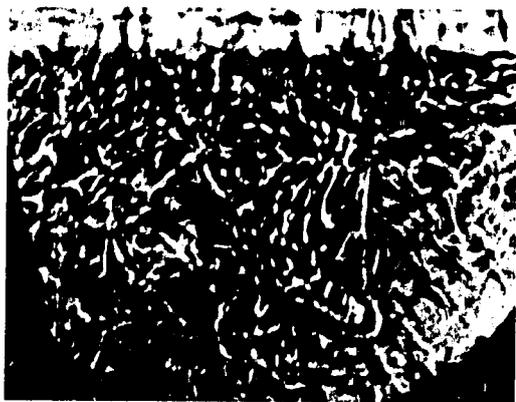
If heat is added to a body of liquid faster than it can be carried away by surface evaporation, the bulk temperature of the liquid will rise. When the liquid reaches a condition in which the saturation pressure corresponding to its temperature is greater than the total pressure in the gaseous phase above the liquid, vapor bubbles are generated within the liquid. This condition is known as "boiling." If the body of the liquid is below the boiling point, vapor bubbles may form at the heating surface and collapse as they condense in the surrounding cooler liquid. This condition is known as "subcooled" or "local boiling." When the entire liquid mass has been raised to the boiling point, a net generation of vapor can occur. Bubbles of steam form at the heat transfer surface, break away and rise to the surface. This condition is variously called "bulk boiling," "saturated boiling," "pool boiling" and "net steam generation."

Another term associated with boiling phenomena is "nucleate boiling." Nucleate boiling derives its name from the fact that there are certain discrete points on the boiling surface where vapor bubbles form repeatedly. These surface nuclei, which promote boiling, may be particles on the surface; surface ridges or imperfections which allow bubbles to form more easily; or miniscule holes in the surface, containing adsorbed gases. Various means have been employed to enhance the heat flux or heat-transfer coefficient obtainable from plain surfaces. Some of these methods are the use of sharp parallel scratches on the heat-transfer surface; treatment of the

FIGURE IV-2

CONVECTION PATTERNS IN HEPTANE

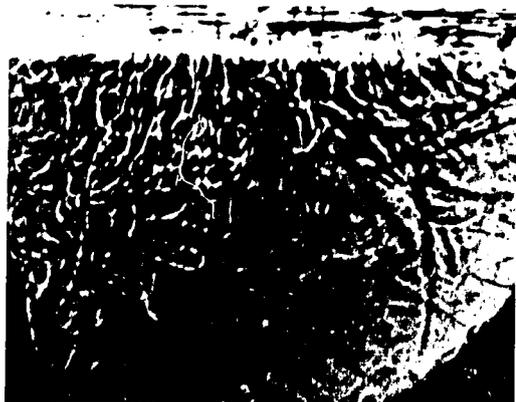
60  
Watts



1-1/2  
Min.



30  
Watts



4-1/4  
Min.



10  
Watts



11 Min.



Photographs at left show patterns with increasing application of heat energy. At right are changes of patterns as the liquid cools. Position of photographs indicates virtual wattage input during cooling.

Source: U. S. Department of the Interior,  
Office of Saline Water

heat-transfer surface with TEFLON\* to obtain a multiplicity of poorly wetted spots; and the use of a fluted tube surface with the boiling liquid flowing downward in a thin-film (2). Figure IV-3 shows nucleate boiling occurring in the thin liquid film on the crests and in the grooves of a fluted tube surface.

Dukler (3) discusses heat transfer from a vertical falling film process. While the mechanism of vapor generation is not yet fully understood, either of two extreme mechanisms of vapor generation can be postulated: 1 bubble nucleation at the wall or 2 evaporation at the film surface. Although both mechanisms could be occurring simultaneously, experimental results from a long-tube-vertical (LTV) evaporator agree very well with those which can be obtained using the surface evaporation model.

For nucleate boiling, both the heat flux and the heat-transfer coefficient increase as the temperature difference between the wall and the bulk liquid increases. If this temperature difference is made large enough, the entire heat transfer surface may become blanketed with steam. When this occurs, the heat-transfer rate drops off markedly. This transition from nucleate boiling to "film boiling" has been variously called "critical heat flux," "maximum heat flux for nucleate boiling" and "burnout heat flux." This steam blanketing does not occur until a high temperature difference (30 to 40 F) is reached between the wall and the liquid. Normally, in a high gain-ratio desalination plant the design temperature differences would be much smaller than those at which film boiling might be encountered.

In flash distillation processes, the saline water enters the flash chamber at a temperature higher than the saturation temperature corresponding to the pressure in the chamber. As the saline water flows through the entrance restriction or orifice, it undergoes a sudden pressure reduction. Almost instantly, steam bubbles begin to form in the throat of the restriction (see Figure IV-4). In flashing, the steam bubbles form in

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\* E. I. duPont de Nemours & Co, registered trade name for Tetrafluorethylene Resin.

FIGURE IV -3

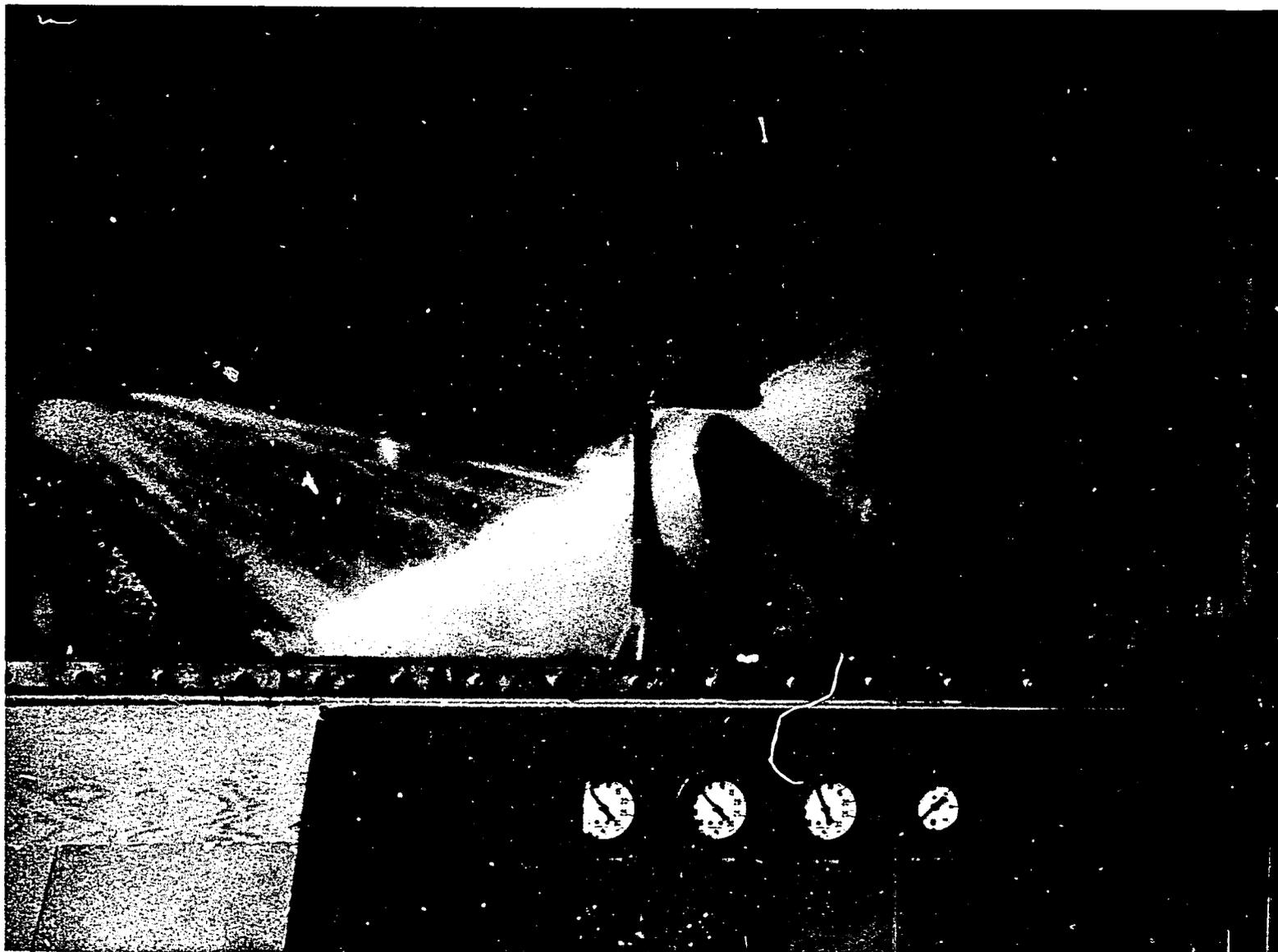
NUCLEATE BOILING IN THIN-FILM OF FLUTED TUBE



Courtesy: General Electric Company

FIGURE IV-4

FLASHING PROCESS AS SALINE WATER ENTERS FLASH CHAMBER



Courtesy: Cuno Engineering Corporation  
and OSW

the bulk liquid; the latent heat is given up by the remaining saline water which, therefore, cools as the flashing process continues. In contrast to those distillation processes in which steam bubble nucleation takes place at the heating surface, nucleation in flash distillation occurs within the bulk of the liquid.

(b) Condensation

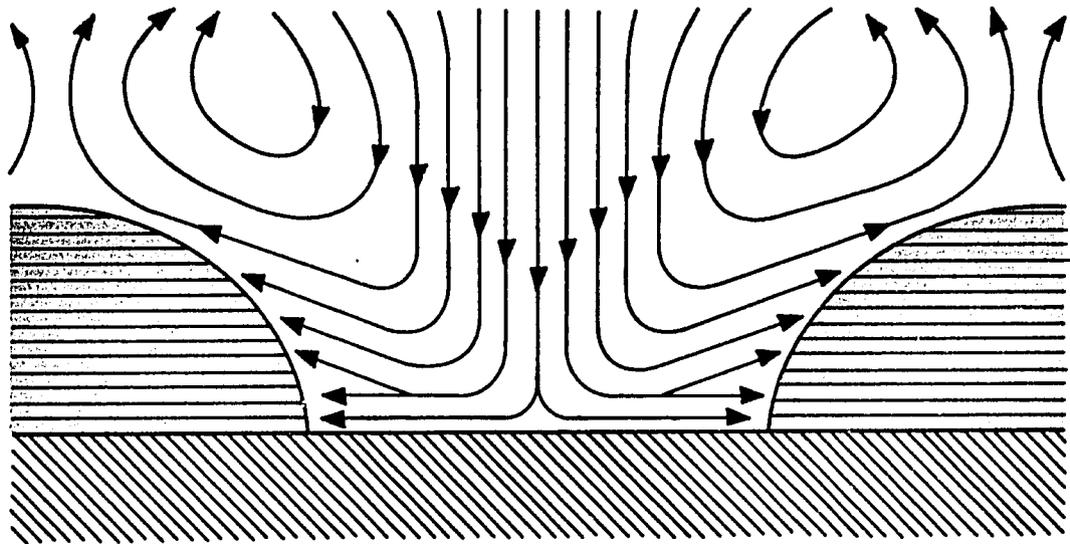
Condensation is the process by which a substance is changed from the gaseous phase into the liquid phase. To accomplish this transformation, it is necessary to remove the latent heat of vaporization. Usually this is accomplished by allowing the condensation to occur on a metallic surface which is cooled by passing a removal medium over the opposite side of the condensing surface. The heat removed from the condensing gas must be transferred through the condensing film region, through the wall of the condensing surface and into the coolant.

Basically there are two modes in which the condensation phenomenon can occur. The first mode is known as filmwise condensation. In filmwise condensation a film of the condensed liquid forms a continuous layer over the entire surface. This presents a relatively low conductivity barrier to heat transfer, since all the heat must be transferred through this liquid film.

The second mode of condensation is dropwise condensation. Generally, dropwise condensation occurs on a hydrophobic surface, i. e., a surface which is not wetted by the liquid being condensed. The condensation commences with the formation of primary drops, which grow in size and eventually merge and run off the surface. The generally accepted mechanism for dropwise condensation is that primary drops nucleate continually at specific sites on the surface (4). The condensing steam (or vapor) is cooled directly on the bare metal surface between the primary drops. The high heat-transfer coefficients obtained with dropwise condensation can be explained by postulating a rapid circulation of vapor across the surface between drops. Figure IV -5 shows the flow pattern of water vapor circulating over the heat-transfer surface to a drop and back into the main

FIGURE IV - 5

SECTIONAL DIAGRAM OF FLOW PATTERN OF  
WATER VAPOR DURING DROP - GROWTH  
PHASE OF DROPWISE CONDENSATION



SOURCE: ERB, R. A. AND THELEN E.  
"DROPWISE CONDENSATION,"  
FIRST INTERNATIONAL SYMPOSIUM  
ON WATER DESALINATION, PAPER SWD/81  
OCT 3 TO 9, 1965 WASHINGTON, D.C.

vapor stream. The vapor becomes supersaturated with moisture as it passes over the cooled plate. Some of the moisture condenses on the growing drop, and part of the heat released by condensation is given up to warm the circulating vapor stream (4).

With filmwise condensation, the condensing film heat-transfer coefficient varies from 1,000 to 4,000 Btu per hr, sq ft, F; whereas, with dropwise condensation the values range from 4,000 to 25,000 Btu per hr, sq ft, F (2). It is apparent that the dropwise condensation yields a much higher heat-transfer coefficient for given conditions than does filmwise condensation. Unfortunately, in all commercial heat-transfer apparatus, filmwise condensation is the dominant mechanism by which condensation occurs. Dropwise condensation generally has been a phenomenon which may occur intermittently or for brief periods with smooth, fresh surfaces. Until recently, anything approaching a permanent condition of dropwise condensation could not be achieved and, therefore, not be designed on the basis of higher heat-transfer rates.

Early efforts to achieve dropwise condensation included treatment of the metallic condenser tube surfaces with organic materials which formed a hydrophobic surface by being chemically linked to the surface material. However, the duration for which dropwise condensation could be achieved was very limited, being on the order of a few hours or days. Also, it has been suggested that such organic materials could be injected into the steam periodically, to renew the hydrophobic character of the condensing surface. Other efforts to achieve permanent dropwise condensation have included the use of polymer film coatings (silicone resins and fluorocarbons). These coatings must be extremely thin because of the low thermal conductivity of most of these polymers.

Franklin Institute (4) has investigated vapor-deposited films of parylene-N on bare and chromium-plated 90-10 copper-nickel tubes. This system was deemed worthy of further investigations. Also at Franklin Institute (4), experiments have been conducted of dropwise condensation on noble metals such as gold, rhodium, palladium

and platinum. Using these noble metal surfaces, dropwise condensation has been achieved for periods in excess of 11,000 hours of continuous exposure. Figure IV-6 shows dropwise condensation occurring on noble metal samples. The explanation for dropwise condensation on noble metals is the absence of a surface oxide. Water is not bonded so strongly to the metal as it is to a surface oxide.

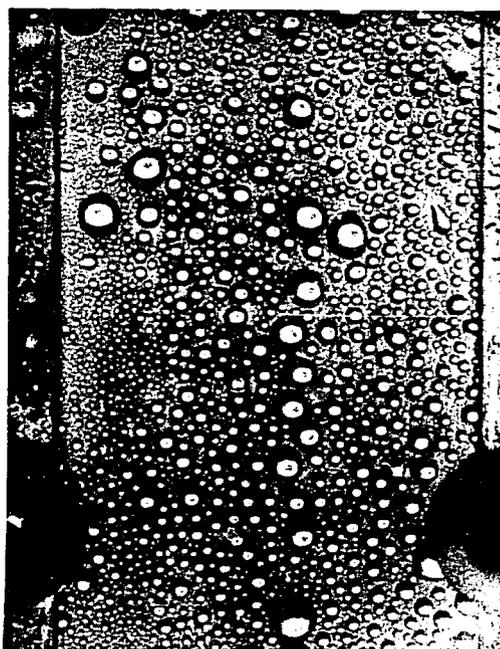
Heat-transfer measurements have been conducted on various tube samples using thin coatings of noble metals. Significant improvements in overall heat-transfer coefficients have been achieved using these noble metal coatings. It should be noted that silver coatings are not satisfactory, since the surface becomes roughened by steam generated from seawater.

It is felt the use of organic drop promoters or noble metals offer promise for achieving permanent dropwise condensation in distillation plants.

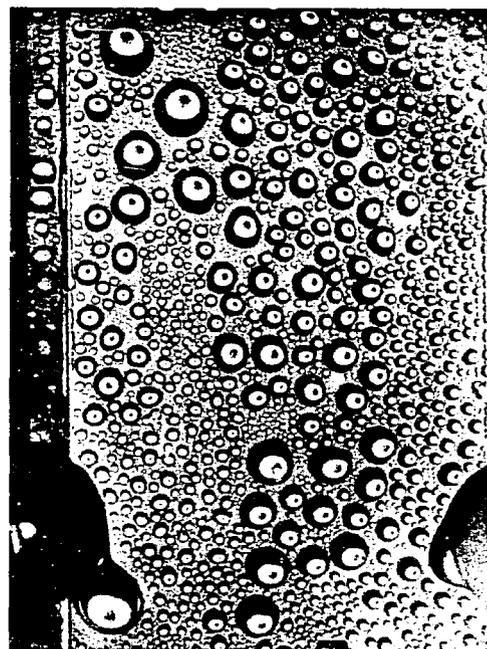
Another approach to improving condensing film coefficients has been the use of double-fluted tubes (2). Although condensation on the fluted surface is filmwise, the water is drawn into the groove by surface tension as it condenses, thereby maintaining a thin film of liquid in the crest area. Using the fluted tubes, condensing film coefficients have been achieved which are 4.5 to 7 times those obtained from plain tubes. These condensing film coefficients with fluted surfaces are approximately equal to the dropwise condensation coefficients.

FIGURE IV-6

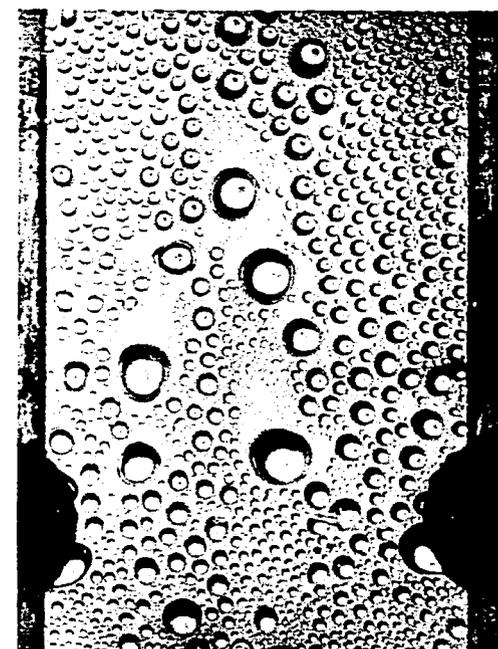
DROPSWISE CONDENSATION ON NOBLE METALS



(a) Gold



(b) Palladium



(c) Rhodium

Source: Dropwise Condensation Characteristics of Permanent Hydrophobic Systems, Office of Saline Water, R & D Progress Report No. 184

## (2) Distillation Terminology

### Backward Feed

The feed enters the last or coldest effect and flows counter-currently to the vapor (5).

### Blowdown

The concentrated solution removed from each effect (5).

### Boiling

Evaporation from inside a liquid body under the formation of vapor bubbles is known as boiling (5).

### Boiling Point Rise (BPR)

The amount by which the solution temperature is elevated above the saturation temperature corresponding to pure water at the same pressure when the solution and vapor are in equilibrium (5).

### Brine Blowdown Concentration

The concentration of the solution discharged to waste from the evaporator (5).

### Concentration Ratio

The ratio of the concentration of dissolved solids in the discharge brine to the concentration in the saline water feed to a plant. (Sometimes the concentration ratio refers to the ratio of the brine discharge concentration to the oceanwide average concentration of approximately 35,000 ppm.)

### Critical Temperature-Difference

The temperature-difference between the tube wall and the vapor on the vaporizing side, at which vapor blanketing occurs (5).

### Economy Ratio

The ratio of the pounds of water extracted to the pounds of heating steam supplied to the first effect, or to the pounds of extracted water vapor from the previous effect (5).

$$e. r. (1) = \frac{\text{lb water extracted in the first effect}}{\text{lb saturated steam fed to the first effect}}$$

$$e. r. (n) = \frac{\text{lb water extracted in the nth effect}}{\text{lb vapor produced in the (n-1)th effect}}$$

$$E. R. (N) = \frac{\text{lb water extracted from a plant comprising N effects}}{\text{lb saturated steam fed to the first effect}}$$

### Effect

A body of liquid into which a saline feed stream and steam are introduced and a brine stream is rejected. Steam from a higher pressure effect is used as the heat input to the next lower pressure effect. It may consist of a number of stages operating at successively lower pressures, but with no new saline stream introduced.

### Evaporation

The conversion of a liquid to a vapor (5).

### Extraction Ratio

The ratio of pounds of water extracted to pounds of solution fed to the effect (x. r.), or to pounds of seawater fed to the plant (X. R.) (5).

$$x. r. (n) = \frac{\text{lb vapor produced in effect n}}{\text{lb solution fed to effect n}}$$

$$X. R. (N) = \frac{\text{lb total water extracted from the plant}}{\text{lb seawater feed to the plant}}$$

### Flashing Range

The temperature range over which flashing occurs in a flash distillation plant: the maximum brine temperature minus the final brine temperature.

### Forced Circulation

Circulation induced by some form of pumping (5).

### Film Boiling

Vaporization taking place through a blanketing film of gas (as in vapor blanketing) (5).

### Forward Feed

The feed enters the highest temperature effect (the first) and flows parallel with the vapor to the last effect (5).

### Gain Ratio

(see Economy Ratio)

### Natural Circulation

Circulation that occurs as a consequence of changes in specific gravity resulting from entrainment or formation of vapor (5).

### Performance Ratio

The pounds of fresh water produced per 1,000 Btu of heat input.

### Recycle Ratio

The pounds of brine recycled through a plant to the pounds of fresh water produced.

### Scale

A deposit formed by precipitation from solution of a substance.

### Stage

This normally refers to a section of a flash distillation plant. A certain fraction of the entering brine stream flashes to vapor and is condensed as product within that stage. The heat given up by condensation is used to preheat the feed stream.

### Steam to Feed Ratio (SFR)

The ratio of the pounds of steam fed to the first evaporator to the pounds of seawater fed to the plant (5).

### Vapor Flashing

The spontaneous formation of vapor resulting from introducing a liquid at a given temperature into a space whose pressure is such that the liquid is superheated (5).

## Application to Saline Waters

### (1) Solution Properties

Seawater and brackish water are primarily aqueous solutions of inorganic salts. These dissolved salts bring about a number of differences between the properties of saline waters and pure water. One of the more important changes, from the standpoint of distillation processes, is the lowering of vapor pressure. At a given temperature, the saturation pressure of water vapor over a saline solution is less than that over pure water at the same temperature. This can be attributed to the fact that there are fewer water molecules in a given surface area of a saline solution than there are in the same surface area of pure water. Thus, the number of molecules leaving and returning to the surface is smaller, with a correspondingly reduced vapor pressure.

Another manifestation of reduction in vapor pressure is boiling point rise. At a given pressure, the temperature to which a saline solution must be heated for boiling to occur is higher than that for pure water at the same pressure. This is a direct result of the lower vapor pressure for the saline water.

These effects, of lower vapor pressure and boiling point rise, are approximately proportional to the amount of salts dissolved in the water. For normal seawater at 212 F, the boiling point rise is 1.1 F, whereas for brine with twice the concentration of seawater the boiling point rise is 2.3 F. The boiling point rise as a function of temperature and concentration is given by a graph included in the Appendix. Boiling point rise corresponds to the theoretical work which must be done to separate salt from water.

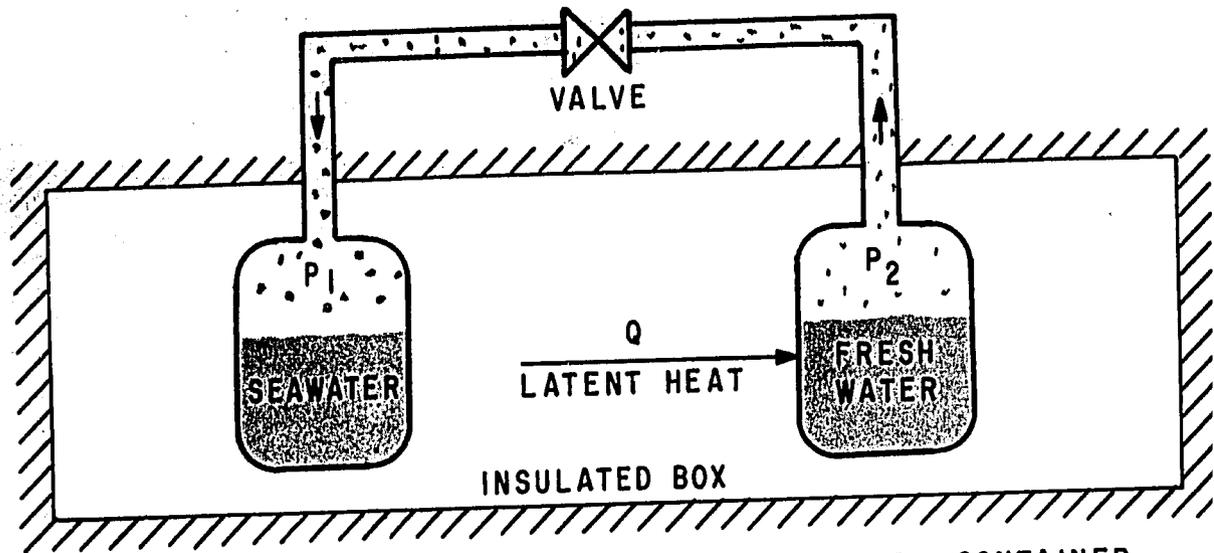
## (2) Theoretical Work - Latent Heat

To separate fresh water from a saline solution, a certain minimum theoretical energy must be expended. For seawater, this theoretical energy requirement is approximately 2.7 kilowatt-hours per 1,000 gallons. This theoretical minimum is dependent only on the temperature and salinity of the saline water and product water involved -- not on the process employed.

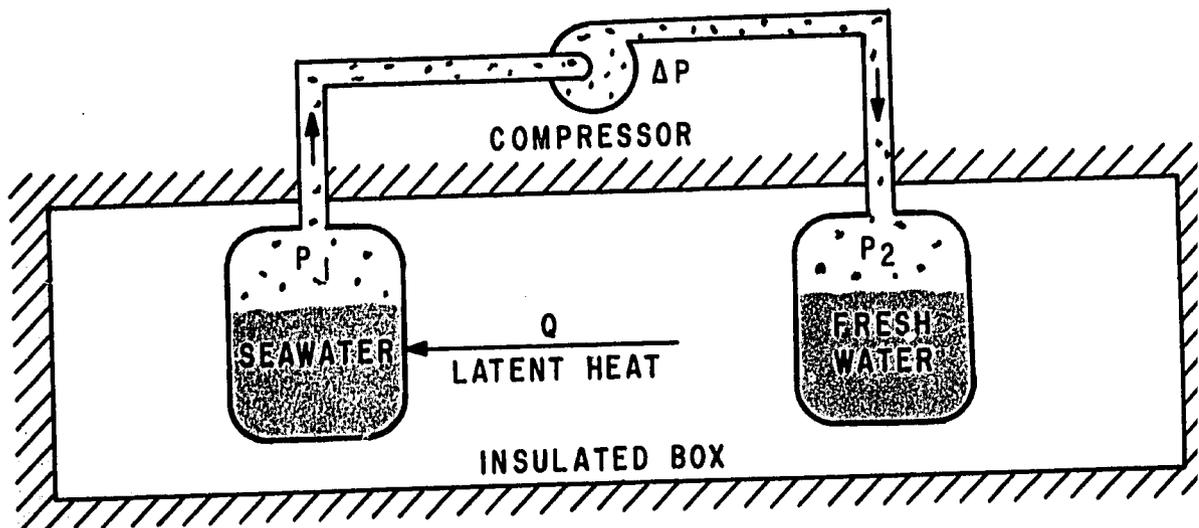
This theoretical energy requirement can be illustrated rather simply. Figure IV-7 shows two containers, one containing seawater and the other containing fresh water. The two containers are located inside an insulated box filled with a heat-transfer medium so that the two containers are maintained at the same temperature. As discussed under solution properties, the vapor pressure over the seawater is less than that over the fresh water. If the valve in the conduit connecting the two containers is opened (View A), freshwater vapor passes from the freshwater container into the seawater container. This distilling of freshwater vapor from the freshwater container into the seawater container is precisely the opposite effect to that which must be brought about if fresh water is to be separated from the seawater. By placing a compressor in the line connecting the two containers (View B), a pressure differential can be developed opposing the natural pressure differential due to the differences in vapor pressure above the two solutions (6). If this compressor-imposed differential is infinitesimally larger than the amount by which the freshwater vapor pressure exceeds that of seawater, freshwater vapor from the seawater container will be pumped into the freshwater container. The theoretical energy supplied by the hypothetical compressor is essentially equal to the energy which must be

FIGURE IV-7

FLOW OF WATER VAPOR FROM  
FRESH WATER AND SEAWATER



A. FRESHWATER VAPOR DISTILLING FROM FRESHWATER CONTAINER INTO SEAWATER CONTAINER ( $P_2 > P_1$ ).



B. COMPRESSOR EFFECTING FRESHWATER VAPOR TRANSFER FROM SEAWATER TO FRESH WATER ( $\Delta P > P_2 - P_1$ ).

supplied to separate fresh water from seawater. Note that in this case the latent heat of vaporization must be supplied to evaporate water from the seawater container. This latent heat is supplied by the heat released when the freshwater vapor condenses in the freshwater container. The heat-transfer medium in this insulated, idealized box effects this latent heat transfer between the two containers, so that no additional outside energy need be supplied other than that furnished by the compressor.

The above-described separation of fresh water from seawater is an idealized, reversible process. As soon as any appreciable amount of fresh water is removed from the seawater, the latter becomes a more concentrated solution and the energy requirements to bring about the separation are increased. Thus, only a fraction of the fresh water contained in the seawater can be economically recovered. A continual feed stream of saline water must be supplied to, and a stream of concentrated brine rejected from any actual process. This introduces additional energy losses not only in pumping these streams, but also in the temperature differentials between the supply and reject (brine) streams. In an actual process, there are heat losses from the system and additional energy inputs are required due to the inefficiencies of pumps and compressors. All actual desalting processes require from 5 to 90 times the theoretical minimum energy because of these energy losses and inefficiencies.

It is important to note, in comparing the energy requirements of various processes, that heat input requirements are not directly comparable to mechanical and electrical requirements. Heat energy is a "lower-grade" energy source and cannot be converted completely into mechanical or electrical energy. For example, where the input to a particular process is electrical, the heat requirements for generating the electricity are perhaps three or four times the electrical energy required because of the thermodynamic cycle efficiency in the power plant.

## 2. Distillation Process Descriptions

### a. Submerged-Tube Distillation

To understand properly the principles on which other distillation processes operate, it is desirable to discuss first the principles

involved in the single and multiple-effect submerged-tube distillation processes.

(1) Single-Effect Submerged-Tube Distillation

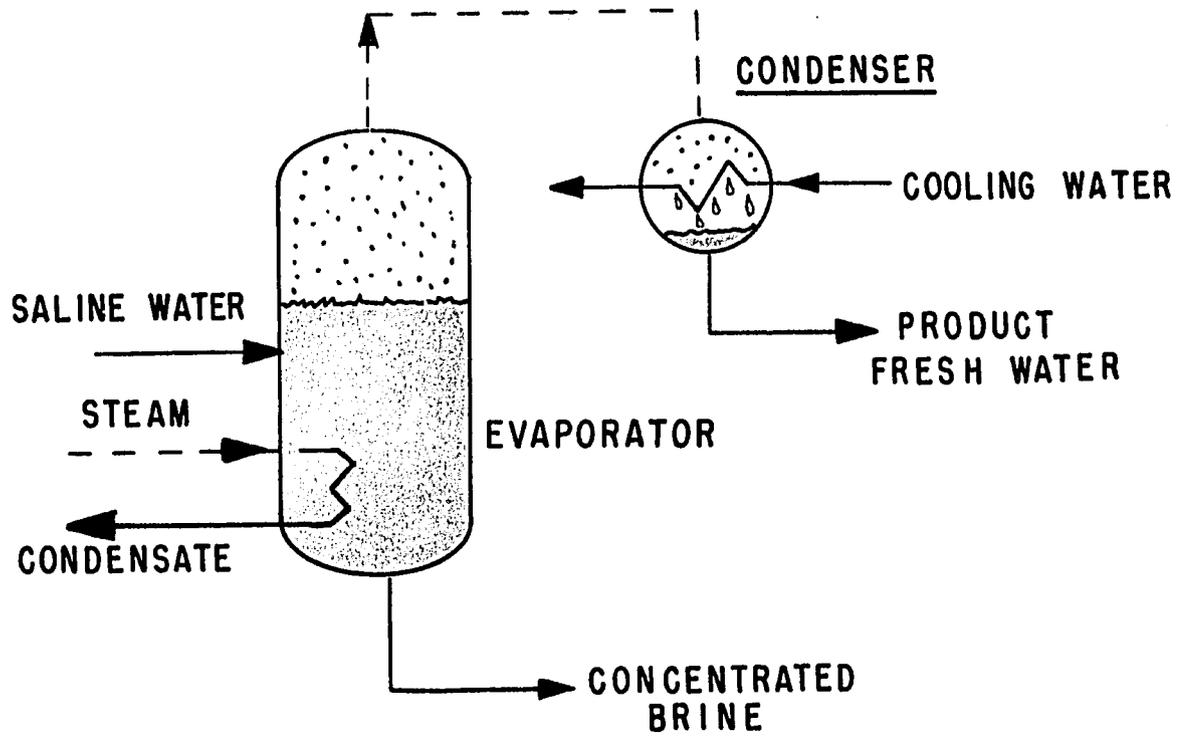
The schematic flow diagram for the single-effect submerged-tube distillation process is shown in Figure IV-8. Saline water enters the evaporator vessel and is heated by steam condensing in tubes submerged in the saline water. As a result of the heat supplied by the condensing steam, water is evaporated from the saline solution. The resulting vapor is condensed as product fresh water, and concentrated brine is discharged from the vessel. Thus, in ordinary single-effect submerged-tube distillation the water is evaporated and condensed only once. However, this is obviously quite inefficient since the latent heat given up by the condensing steam is used only once. Even in areas with low-cost fuel, this would make the cost of water prohibitively high except in special situations where only a small amount of water might be required.

(2) Multiple-Effect Submerged-Tube Distillation

It is possible to reuse the heat from the initial steam a number of times and greatly improve the economy. A number of evaporator bodies (called "effects") are arranged in series, and each successive effect operates at a lower pressure than the preceding one. This stepwise reduction in operating pressure causes a corresponding decrease in the boiling temperature required in each successive effect. Initial steam enters and is condensed in the first effect. The vapor distilled from the first effect is passed to and condenses in the tubes submerged in the second effect brine. As the vapor condenses in these tubes it releases its latent heat to the brine of the second effect. The resulting condensate is collected from the second effect tubes and comprises a portion of the product water. The vapor distilled from the second effect brine is passed to and condenses in the third effect submerged tubes, thereby heating the brine of the third effect before being collected as product water. This process is continued through each succeeding effect to the nth effect. Thus, multiple-effect distillation multiplies the amount of product water produced from a given amount of initial steam

FIGURE IV - 8

SINGLE - EFFECT SUBMERGED - TUBE DISTILLATION



- BRINE
- FRESH WATER
- STEAM, OR HEAT SOURCE

by the number of distillation steps used -- as shown in Figure IV-9, a schematic flow diagram for a multiple-effect submerged-tube distillation process.

There is a practical economic limit to the number of effects which can be used; it is necessary to maintain some difference between the temperature of the steam supplied to each effect and the temperature at which boiling occurs in that effect. There is a certain overall temperature difference available between the temperature of the steam supplied to the first effect and the temperature of cooling water used in the condenser for the last effect. Thus, since each effect requires its own finite temperature difference, the number of effects is limited.

Considerable operating experience has been accumulated with multiple-effect distillation units of the "submerged-tube" type in Kuwait and on the islands of Aruba and Curacao in the Netherlands Antilles. However, this submerged-tube type of evaporator can be considered as outdated by the improved distillation processes which are described below.

#### b. Vertical Falling and Rising Films

The vertical falling and rising film processes are essentially advanced types of multiple-effect distillation processes.

##### (1) Long-Tube-Vertical (LTV)

In the long-tube-vertical (LTV) process, the boiling takes place on the inside of long vertical tubes. In the usual arrangement, the evaporating brine flows downward, forming a thin-film on the inside surfaces of the tubes. Heat required to evaporate a portion of the brine is supplied by steam introduced into the space surrounding the outside of the tubes. Heated brine and vapor emerge from the bottom of the tubes and are separated in the bottom of the evaporator vessel. The brine is pumped to the top of the next effect and it falls through the vertical tubes in that effect. The vapor generated by evaporation from the falling film in one effect flows to the effect which is operating at the next lower pressure. Figure IV-10 schematically illustrates the flow diagram for the LTV multiple-effect distillation process.

FIGURE IV-9  
MULTIPLE - EFFECT SUBMERGED - TUBE DISTILLATION

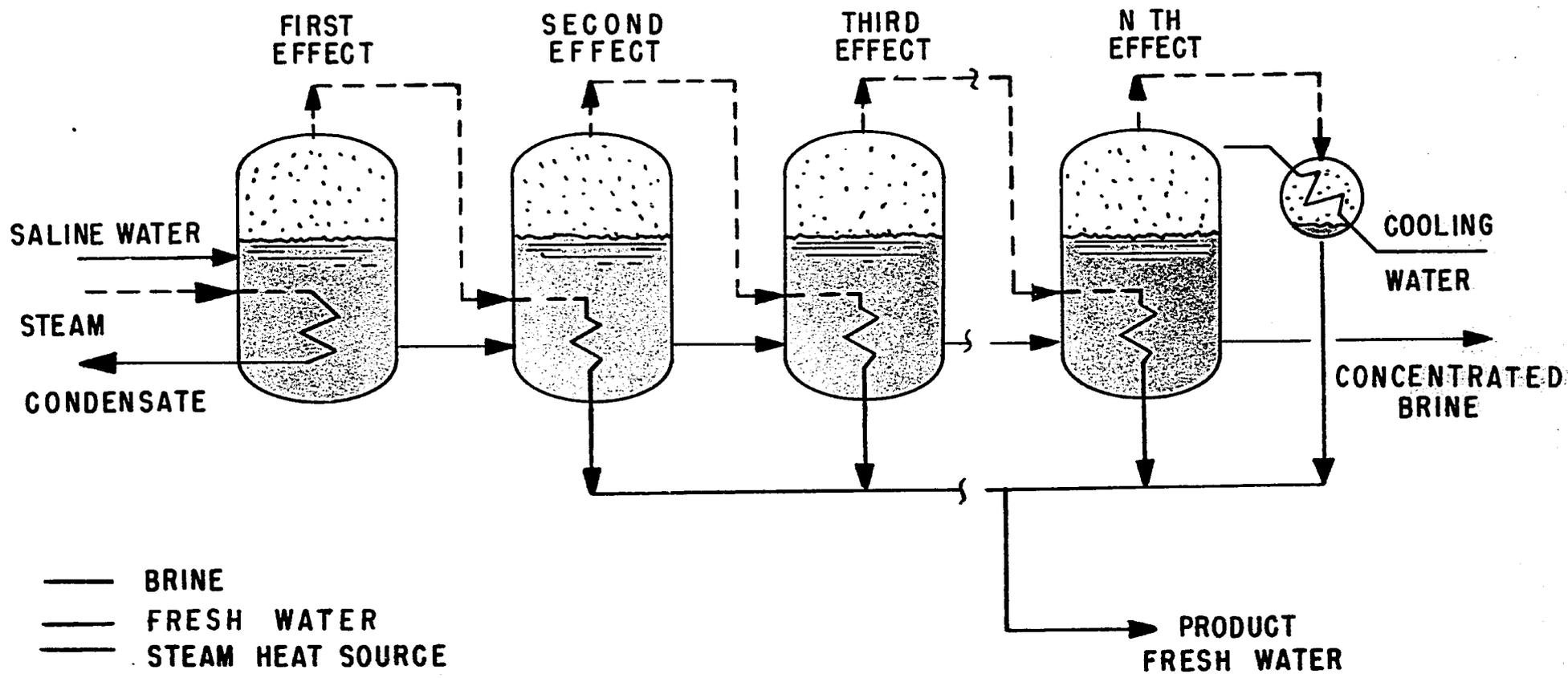
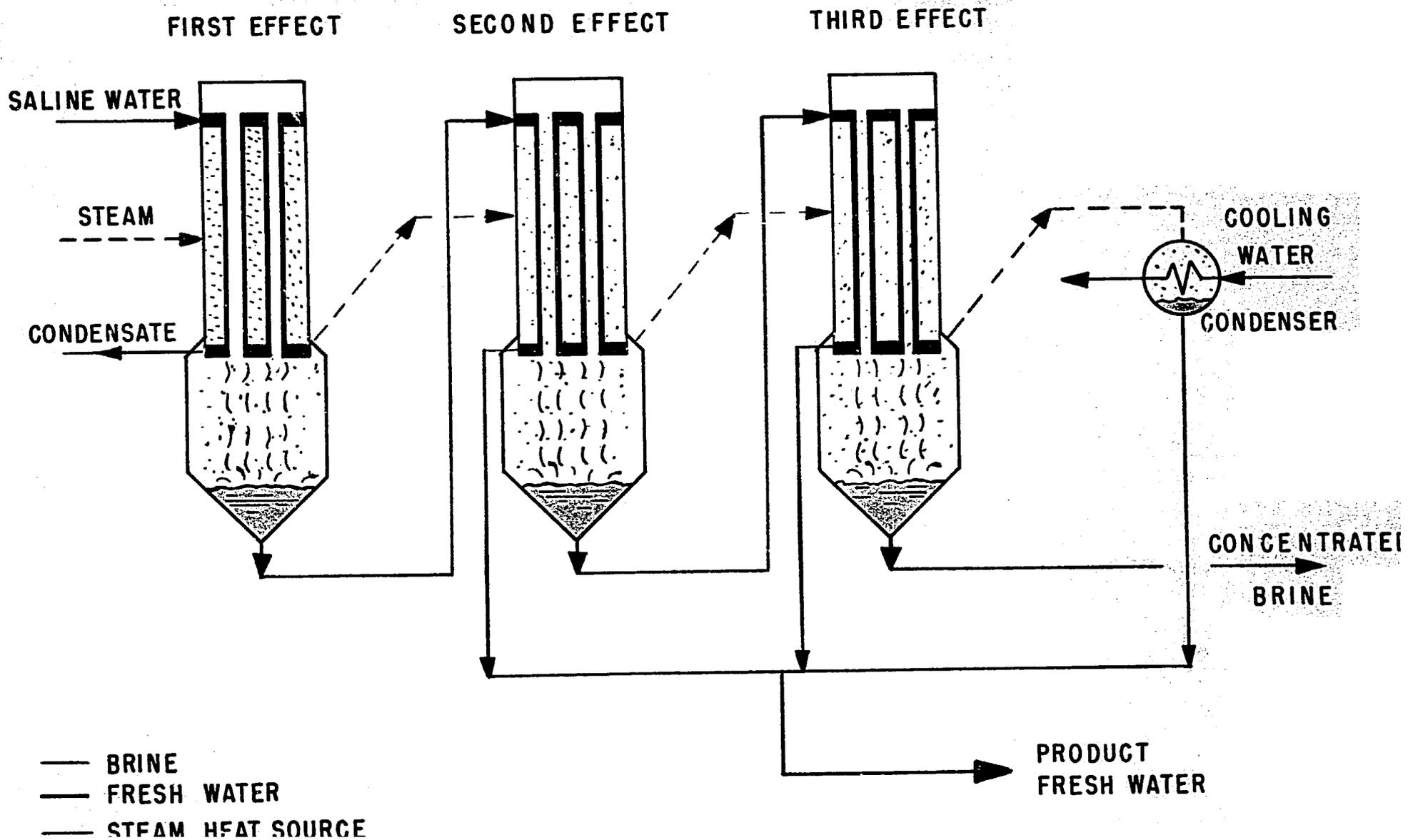


FIGURE IV-10

LONG-TUBE-VERTICAL (LTV) MULTIPLE EFFECT DISTILLATION



The LTV multiple-effect distillation process is inherently capable of operating with lower brine flow per pound of product water and higher brine concentration than other distillation processes, such as the multistage flash (MSF) process described later. This can be an important advantage when a desalination plant is located at an inland site where brine disposal poses a problem, or when it is desired to recover chemicals from the effluent brine. The lower brine flow also results in a lower acid consumption for alkaline scale control, and in approximately one-half of the electrical power requirements of that for an MSF plant. The LTV process also has the advantage of being able to adjust rapidly to different steam flows and production rates.

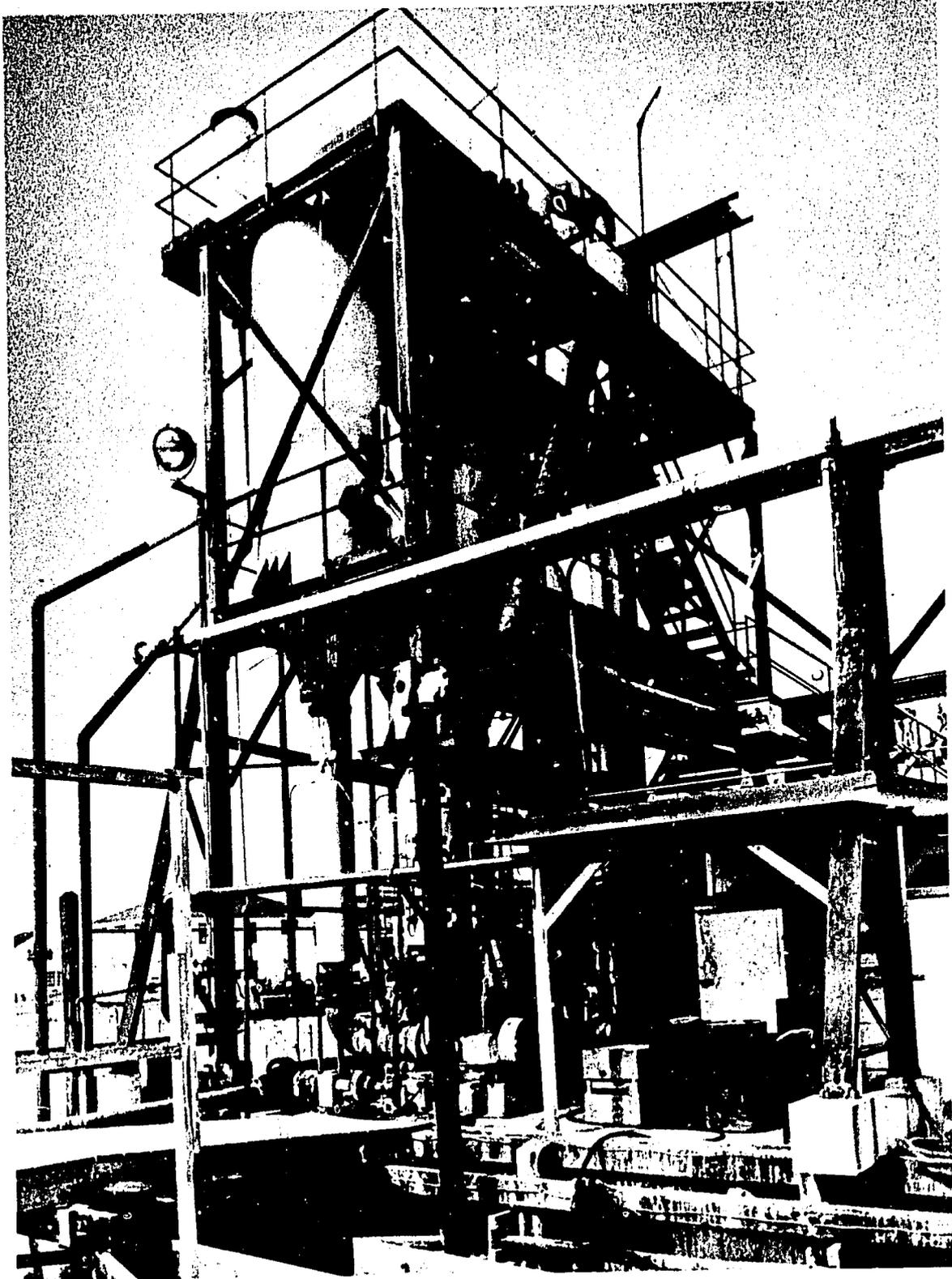
If a leak develops, the steam leaks from the steam side of the tube into the brine, because the steam side of a tube is at a higher pressure than the brine inside the tubes. This has the effect of degrading thermal performance, but it does not result in contamination of product water. By contrast, in an MSF plant a tubing leak is from the higher-pressure brine side into the lower-pressure product water side, so that the leak tends to increase the salinity of the product water.

Work on the LTV process was initiated in 1955 by W. L. Badger Associates under an Office of Saline Water (OSW) contract. The results of these studies (7), which were based on a water production capacity of 17.5 million gallons per day (mgd) - an optimistically high heat-transfer coefficient, and the use of carbon steel tubes projected a water cost of 25¢ to 40¢ per 1,000 gallons. Subsequent to this early study, W. L. Badger Associates designed and operated an LTV pilot plant at Wrightsville Beach, N. C. This pilot plant, shown in Figure IV-11, used seven 2-inch OD by 24 foot long tubes in one LTV effect. It was designed to test heat-transfer and scale prevention techniques under different operating conditions of pressure and temperature.

Results from the LTV pilot plant were used as the basis for the design of the Freeport, Texas LTV demonstration plant, which began operation in 1961. This plant, which is a part of the OSW demonstration plant program, uses 12 effects and initially had a rated water production of 1 mgd, though its capacity has since been increased. Figure IV-12 shows the LTV evaporators at the Freeport demonstration plant. An on-site

FIGURE IV-11

LONG-TUBE-VERTICAL PILOT PLANT  
WRIGHTSVILLE BEACH, N. C.



Source: W. L. Badger Company

FIGURE IV-12

LONG-TUBE-VERTICAL DISTILLATION PROCESS DEMONSTRATION PLANT  
FREEPORT, TEXAS



evaluation in 1965-1966 by Kaiser Engineers of the operation of this plant resulted in recommendations that significant effort should be exerted towards the development of the pre-treatment of seawater feed so that significantly higher first effect brine temperatures could be achieved without scaling. Among the distillation processes, the LTV process uses the least amount of seawater feed per pound of product; therefore, more sophisticated methods of pretreatment may be justified and higher brine temperatures thereby achieved (8).

Operating experience at the Freeport LTV demonstration plant has shown that treated and deaerated seawater can be heated to a temperature of approximately 265 F and a final concentration ratio of 3 to 1. These limits are set by the necessity of avoiding supersaturation of calcium sulfate anhydrite in the high temperature evaporator, and scaling by gypsum-type calcium sulfate in the low temperature evaporators (refer to Subsection IV. A. 3). If 75% of the calcium ions in the incoming seawater were removed, the seawater temperature in the first effect could be increased to its design temperature of 300 F with a concentration ratio of 5 to 1 (9). Another possibility of achieving a 300 F maximum brine temperature without scaling, is to preheat the incoming seawater stream to 300 F or higher and use calcium sulfate seeding to soften the seawater.

The carbon steel tubes originally installed in the Freeport demonstration plant lasted approximately one year. The evaporators have been retubed with admiralty-metal and aluminum-brass tubing. Both the admiralty-metal and aluminum-brass tubing have lasted approximately five years with the corrosion resistance of the aluminum-brass tubing being somewhat better than that of admiralty-metal. The highest-temperature effect now has a number of different tube materials installed, including stainless steel and copper-nickel alloy.

It is planned to modify the Freeport plant to add five effects and to install a "piggy-back" unit on the high-temperature effect. This "piggy-back" unit will utilize tubes with enhanced heat-transfer surfaces. A so-called "piggy-back" unit is a highly instrumented pilot-size effect which can be used in parallel or series with the existing effects, to

determine heat-transfer, scaling and other data for various diameters and configurations of evaporator tubes (8).

One of the limiting economic factors with the LTV process is the cost of heat exchange surfaces. This factor applies equally to most other distillation processes. At present, no specific effort is being devoted to reducing the fabrication cost of tubing. Most of the research and development effort is being directed toward improving heat-transfer performance per unit area. Franklin Institute and Union Carbide Corporation are doing work toward the attainment of permanent dropwise condensation by applying thin-films of noble metal or plastics to the condensing surface. Oak Ridge National Laboratory is developing tubes with enhanced heat-transfer surfaces, such as fluted tubes and tubes with spiral tapes on the inside wall surface. The Houston Research Institute has programs under way to determine heat-transfer and pressure drop characteristics of tubes with enhanced heat-transfer surfaces.

Another technical and economic limitation on the LTV process is that of scaling, which is discussed in detail in Subsection IV. A. 3. To some extent, the work being done by Baldwin-Lima-Hamilton Corp on scale control in high-temperature flash distillation plants is also applicable to the LTV process. However, there are some differences in the residence time characteristics, brine concentrations and temperature-concentration flow paths through the plant which introduce differences in the scaling characteristics of the two processes. For instance, in the LTV process the vapor velocities may become quite high in the low-temperature effect. This can lead to the entrainment of brine droplets into the vapor stream. Entrained drops are ineffective in contributing to vaporization and this results in a higher brine concentration in the falling liquid film than would be measured in the brine sump at the bottom of the evaporator effect. The primary effect of scaling is to limit the maximum brine temperature and concentration. This, in turn, has a direct effect on the water plant performance ratio (pounds of water per 1,000 Btu heat input). When scaling occurs, water production capacity drops off but the performance ratio stays the same.

The LTV multiple-effect distillation process has not yet been applied to commercial desalting plants, and the process presently is less advanced than the MSF distillation process.

## (2) Thin-Film and Spray-Film

The "thin-film" process, which has been developed by the General Electric Co., is another variation of the multiple-effect distillation process. The tubes are disposed vertically, and the brine flows downward in a thin-film on the inside tube surface. The "thin-film" process differs from the LTV process in that it uses shorter tubes which have fluted surfaces to achieve the thin-film. Earlier versions of the process had used a mechanical wiper blade to achieve the thin-film, but this has been superseded by a static double-fluted tube system.

The saline feedwater is distributed from a plain cone nozzle consisting of a hole approximately 1/8 inch in diameter drilled into the top distributor plate. The saline water is sprayed onto the inside surface near the top of the double-fluted tube (see Figure IV-13). The water flowing down the inside of the tube is drawn into the tube groove by surface tension. As the water evaporates some of it is splashed onto the raised portion of the flute, thereby providing a thin film of water on that portion. Similarly, on the outside surface of the tube the condensing pure product water is drawn into the groove to maintain a thin-film on the raised portion of the outer tube flute. Also, the grooves organize the falling film to provide a more uniform distribution of liquid.

Figure IV-14 shows the configuration of a double-fluted tube. The manufacturing process starts with a plain 3 inch diameter tube and the flutes are formed hydraulically. The tube is sealed to the tube sheets by O-rings retained in grooved rings which protrude beyond the grooves. The seal of the bottom tube sheet is slightly smaller than the seal of the upper tube sheet so that it will clear the upper tube sheet when the tube is installed.

FIGURE IV - 13  
TWO - EFFECT MARINE THIN - FILM  
EVAPORATOR SCHEMATIC

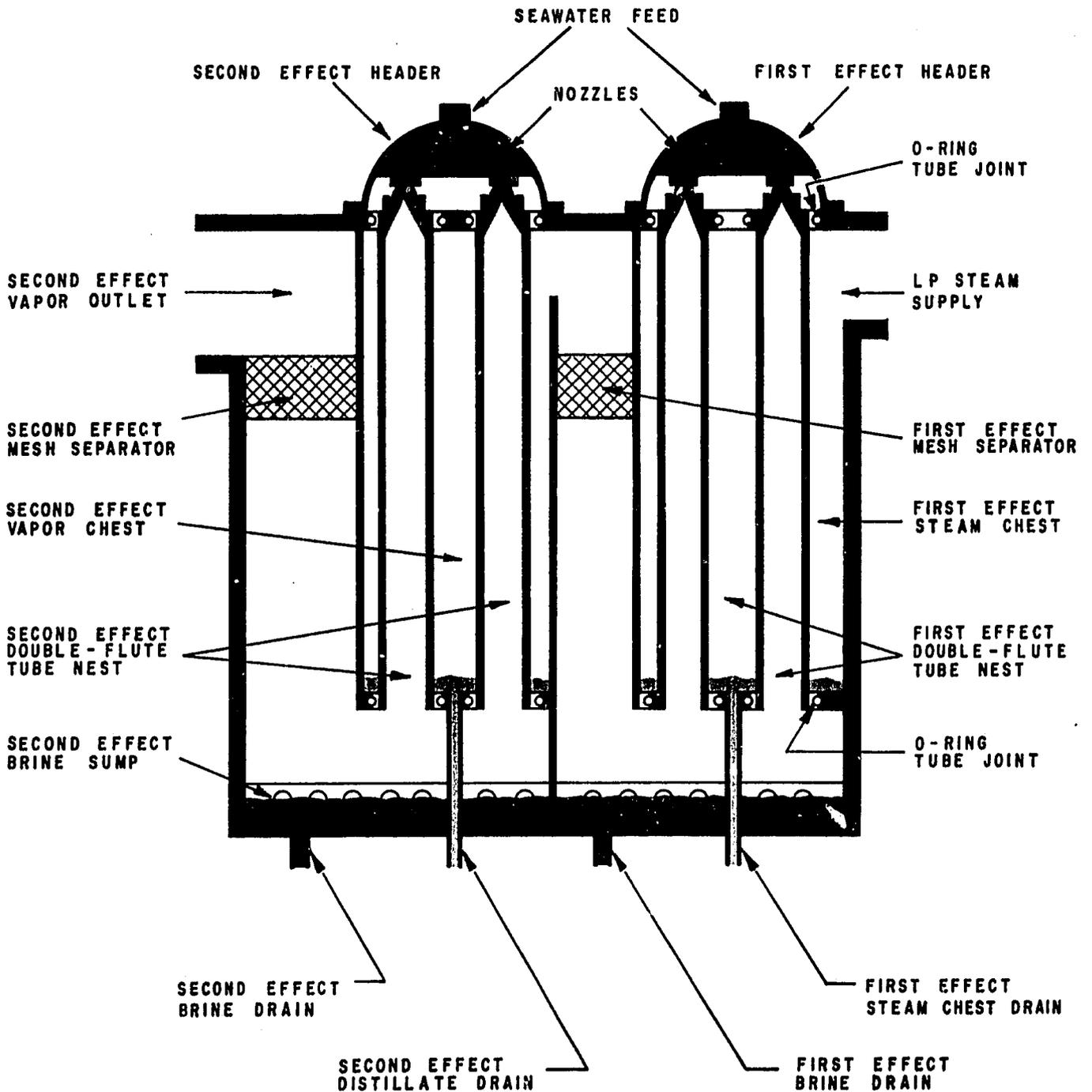
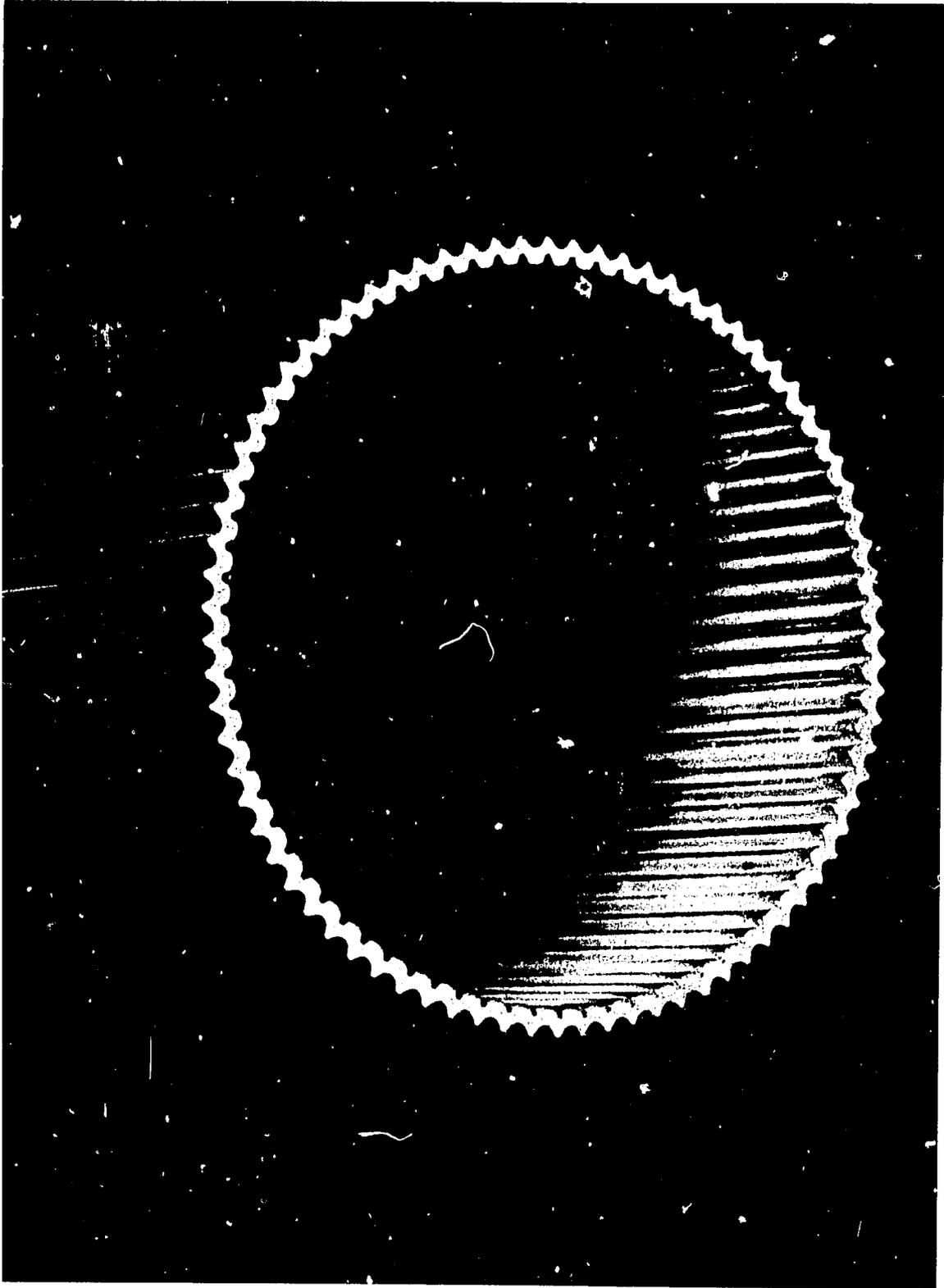


FIGURE IV-14

DOUBLE-FLUTED TUBE CONFIGURATION



Courtesy: General Electric Company

The principal advantage of the thin-film process is the achievement of higher heat-transfer coefficients in the condensing and evaporating films. This leads to the possibility of achieving a higher overall heat-transfer coefficient with commensurate reductions in heat-transfer area and evaporator size.

The largest thin-film evaporator installation built to date has been the 37,000-gpd pilot plant which was designed, built and operated by General Electric Co under OSW contract at Wrightsville Beach, N. C. This thin-film pilot plant, shown in Figure IV-15, had two effects. The first effect used 10 foot long mechanically wiped tubes and the second effect used 5 foot long double-fluted tubes. Using pH control, the plant was operated at brine temperatures up to 275 F without calcium sulfate scaling(10). An average overall heat-transfer coefficient of 1,765 Btu per hr, sq ft, F, based on the developed tube surface, was achieved using the 5 foot long double-fluted tubes.

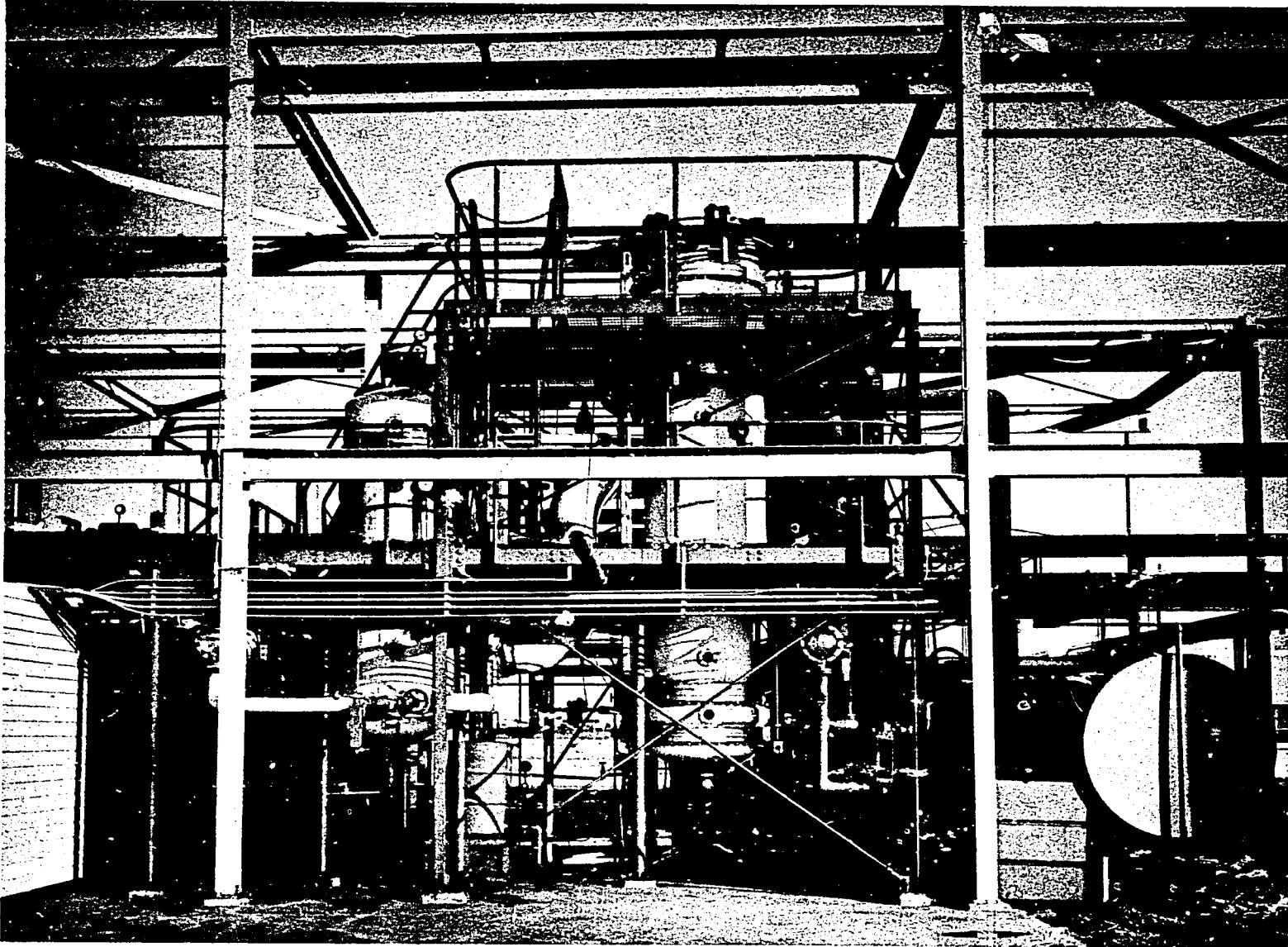
General Electric Co recently completed a study of a 50-mgd plant for OSW. The 50-mgd conceptual design used double-fluted tubes 10 feet long for the high-temperature effects and 5 feet long for the low-temperature effects.

As with other distillation processes, scale formation (refer to Subsection IV. A. 3) is a technical limitation for the thin-film process. Alkaline scale formation is controlled by pH regulation similar to that used in other falling film evaporators. It is possible that the double-fluted tubes might not be as easy to descale, once scaling occurred, as plain tubes would be. The writers know of no experimental indications to this effect, however.

Use of the double-fluted tube has made the tube wall itself the major resistance to heat transfer. From a heat-transfer standpoint it would be desirable to use copper as the material of construction. However, in the area near the top of the tube, where saline water is sprayed, the higher liquid velocity tends to erode the oxide film from copper and to promote corrosion. Aluminum-brass is the tube material which was selected as the basis for the 50-mgd design in which a plastic insert is used near the top of the tube to reduce tube wall erosion.

FIGURE IV-15

THIN-FILM PILOT PLANT AT  
WRIGHTSVILLE BEACH, N. C. - 37,000 GPD



Courtesy: General Electric Company

The "spray-film" evaporator usually employs horizontal tubes, with the brine being sprayed over the outside surface and the vapor condensed on the inside tube surface. The process may be used either in a multiple-effect distillation or in a vapor compression system described below. A small spray-film evaporator pilot plant, which was designed and built by Aqua-Chem Inc., began operation at the Wrightsville Beach, North Carolina Test Station in 1964.

The thin-film process and the spray-film process have been utilized in small commercial units but have not been developed as yet for large-scale commercial application.

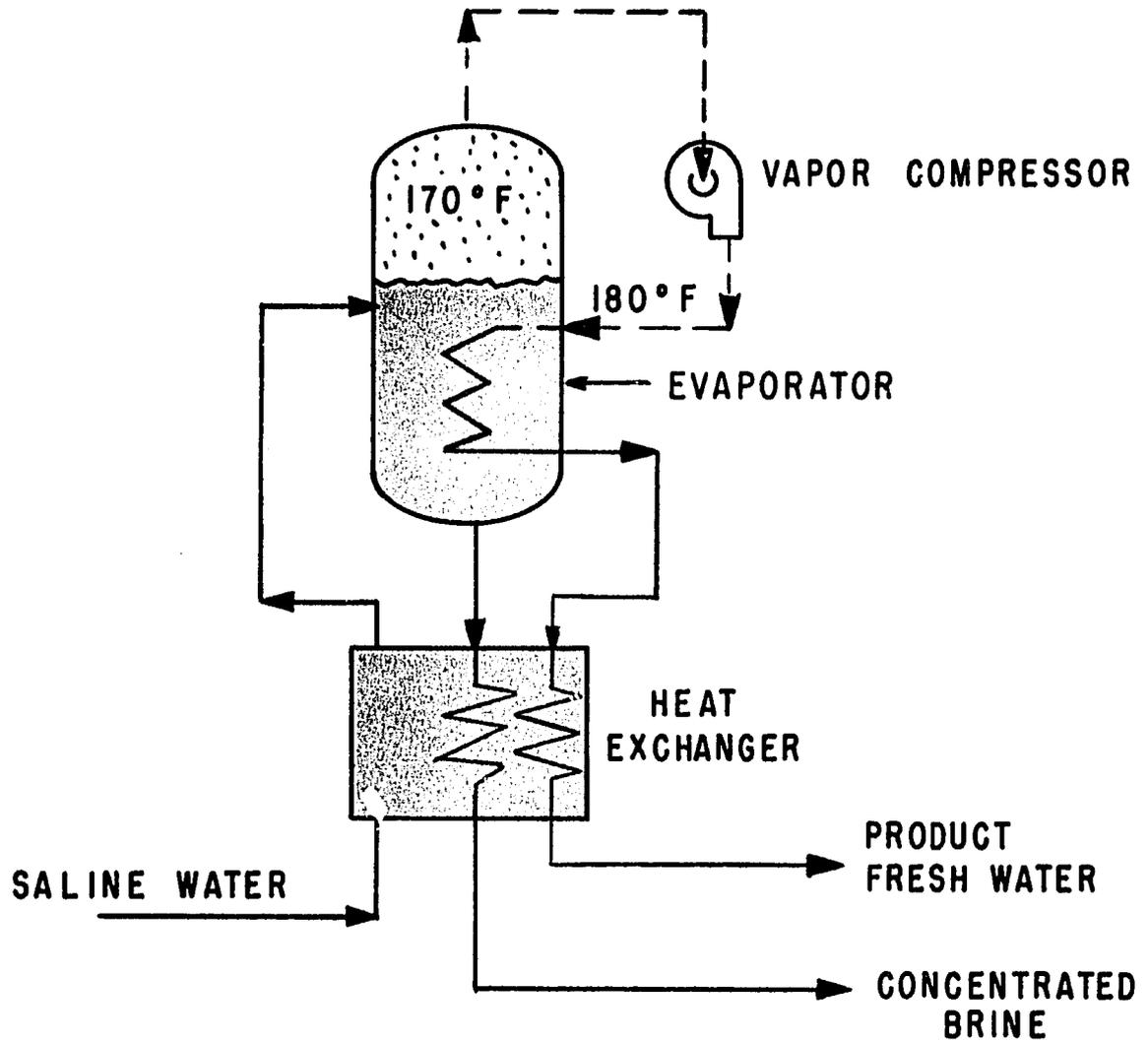
### c. Vapor Compression Distillation

The single-effect submerged-tube distillation process shown in Figure IV-8 is thermally inefficient since the heat required to evaporate the freshwater vapor (known as "latent heat") is rejected to cooling water in the condenser after being used only once. The multiple-effect distillation process, discussed above, is one way of economizing on the heat input. Another way of re-using the heat is the vapor compression distillation process.

Figure IV-16 is a schematic flow diagram for the vapor compression distillation process. The steam from the evaporator is compressed by the vapor compressor. This compression increases the pressure and condensation temperature of the product water vapor. The compressed vapor supplies the heat necessary to boil the saline water to generate freshwater vapor in the evaporator. Thus the latent heat of vaporization is recovered. The mechanical energy which must be added is that which is necessary to compress the product vapor and raise its temperature so that the latent heat can be transferred to the saline water. Most plants using the vapor compression distillation process require relatively less energy than other distillation techniques. Usually, the energy to drive the vapor compressor is supplied as electrical power, or as mechanical energy by a diesel engine. It might also be furnished as steam to drive a steam-turbine-driven compressor. Residual heat in the concentrated brine and freshwater condensate is partially recovered by heat exchange with the incoming saline water stream.

FIGURE IV - 16

VAPOR COMPRESSION DISTILLATION



— BRINE  
- - - FRESH WATER

Vapor compression plants require much less cooling water than other types of distillation plants. They are, therefore, particularly well suited to inland brackish water areas where cooling water may be in short supply.

The disadvantages of the process are the high cost of developing the large vapor compressors required for large-scale water desalination plants and the relative unattractiveness of the process where low cost heat is available, such as in dual-purpose plant applications. Plants using the vapor compression process encounter the same tube-scaling problems as those using other distillation processes which employ heat transfer surfaces immersed in the saline water. It also should be noted that an auxiliary steam source is required for plant startup.

Other than the Roswell demonstration plant operation, there is no OSW-funded research and development work directed towards the vapor compression distillation process at the present time.

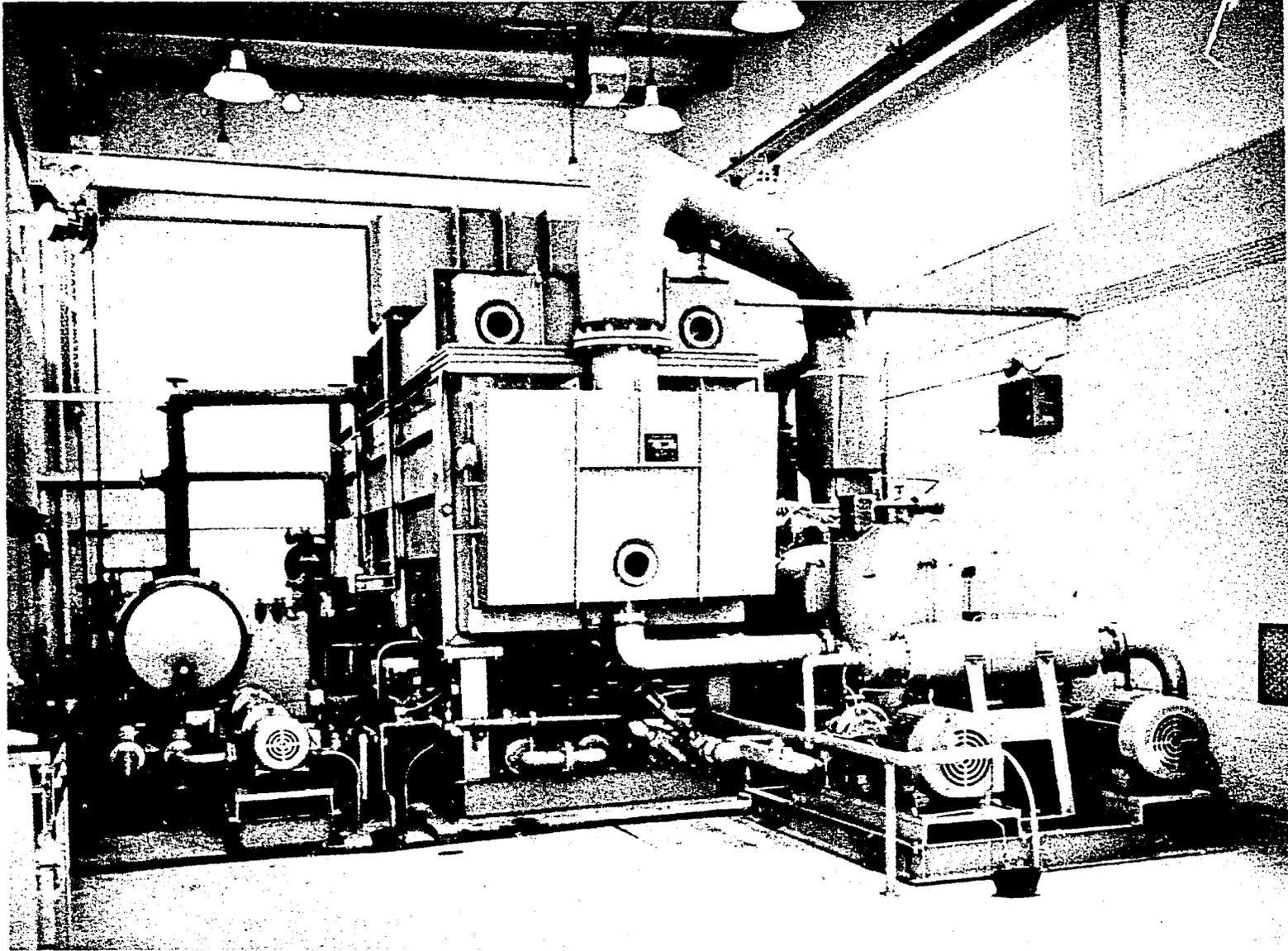
Generally, vapor compression has found application in relatively small plants with capacities less than 200,000 gpd and where fuel is relatively expensive or difficult to obtain(11). Many small water production units using the vapor compression principle have been used for shipboard and military installations.

Figure IV-17 shows a 40,000-gpd electric-motor-driven vapor compression unit which furnishes water for a U.S. Air Force base in Utah.

The OSW's 1-mgd demonstration plant at Roswell, New Mexico is the largest operating plant using the vapor compression distillation process. This plant, which started operation in 1963, is described in Section V, Description of Typical Plants. An on-site evaluation in 1965-1966 by Kaiser Engineers of the Roswell operations(12) indicated that the principal problems causing poor plant performance were:

FIGURE IV-17

VAPOR COMPRESSION DISTILLATION UNIT FOR BRACKISH WATER  
HILL AIR FORCE BASE, UTAH - 40,000 GPD



Courtesy: Aqua-Chem, Inc

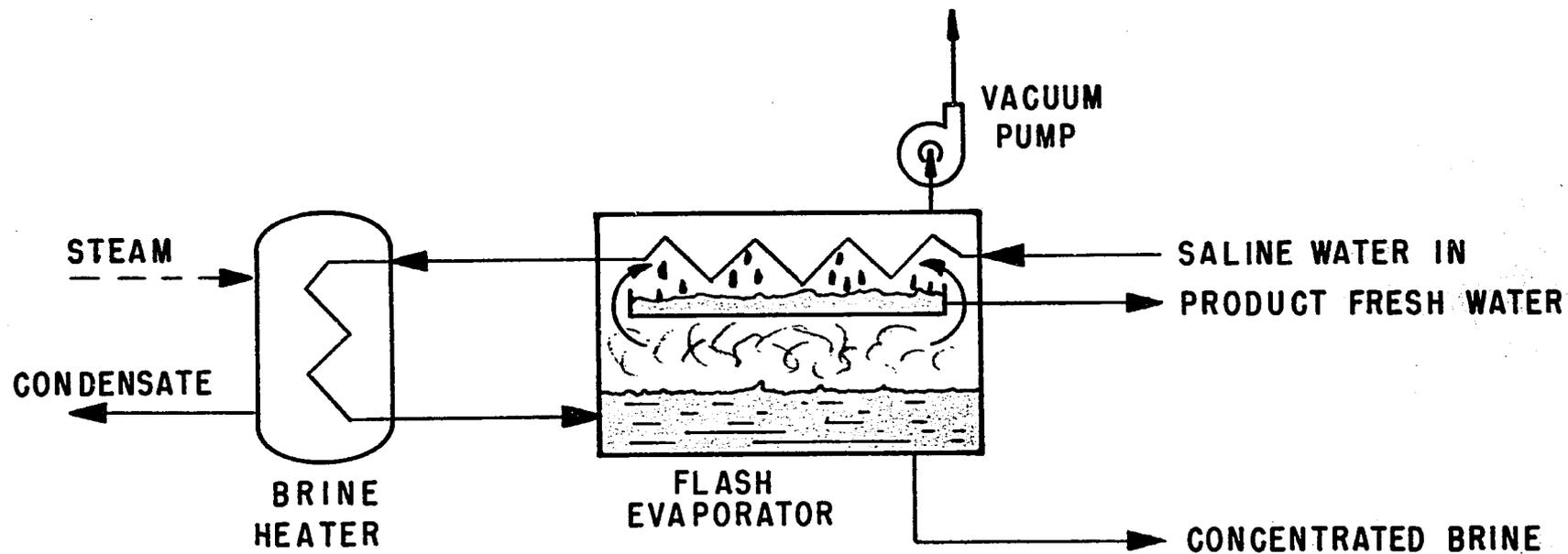
- (1) Silica, calcium sulfate and small amounts of calcium carbonate scale formation resulting from inadequate pretreatment of the feedwater.
- (2) Presence of noncondensable gases in the first and second effect heat exchangers.
- (3) Inadequate brine level control in the first and second effect flash chambers.

d. Multistage Flash (MSF) Distillation

In the flash distillation process, the incoming saline water stream is preheated by using it to condense the product freshwater vapor. The final temperature increase is provided by steam supplied to a brine heater. The saline water stream is maintained at a pressure sufficiently high to ensure that no boiling occurs in the preheater or brine heater. Hot saline water from the brine heater is introduced into a flash chamber maintained at a pressure lower than the vapor pressure of the heated saline water. As this sudden pressure reduction occurs, a portion of the heated saline water stream flashes into vapor. This freshwater vapor is condensed, and collected in a trough as the product. A vacuum pump or ejector is used to remove noncondensable gases from the flash chamber. Figure IV-18 is a schematic flow diagram for a single-stage flash distillation process.

Figure IV-19 is a schematic flow diagram of a single-effect multistage flash (MSF) distillation process. Multiple stages are employed to provide countercurrent heat transfer for good heat recovery. Each successive stage operates at a lower pressure and temperature than the preceding one. The latent heat from each increment of flashed vapor is recovered and used to preheat the brine feed stream. Sufficient tube surface is provided in each stage to condense all the flashed vapor, and this maintains the pressure in each stage. The steam, which must be supplied to the brine heater, is only that necessary to provide the final temperature boost to the brine feed before it enters the first flash stage. Orifices or weirs are introduced into the flashing brine stream to regulate the brine flow and maintain the pressure differential between stages. The condensed distillate is collected in a trough below the condenser and it

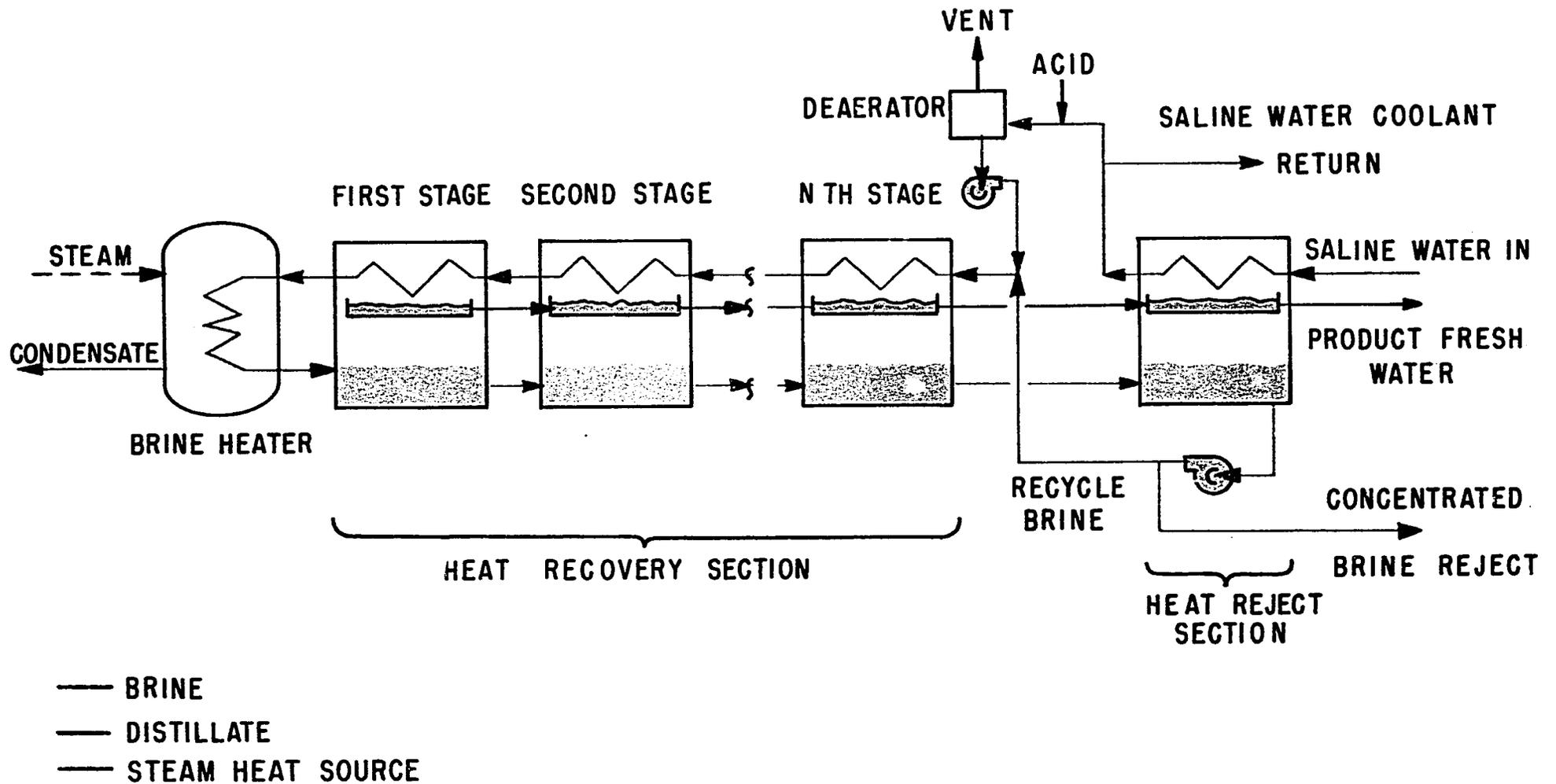
FIGURE IV-18  
SINGLE-STAGE FLASH DISTILLATION



—— BRINE  
—— FRESH WATER  
—— STEAM HEAT SOURCE

FIGURE IV-19

MULTISTAGE FLASH (MSF) DISTILLATION WITH RECYCLE



cascades from stage to stage. The distillate flow between stages also is controlled by orifices or weirs. The schematic flow diagram shown in Figure IV-19 includes the feature of brine recycle. Recirculation of brine usually is employed to increase the concentration of the brine rejected from the process. This in turn reduces the saline water makeup and the saline water pretreatment cost. The recycle brine stream has a flow seven to ten times the production rate of fresh water and a salt concentration about twice that of seawater.

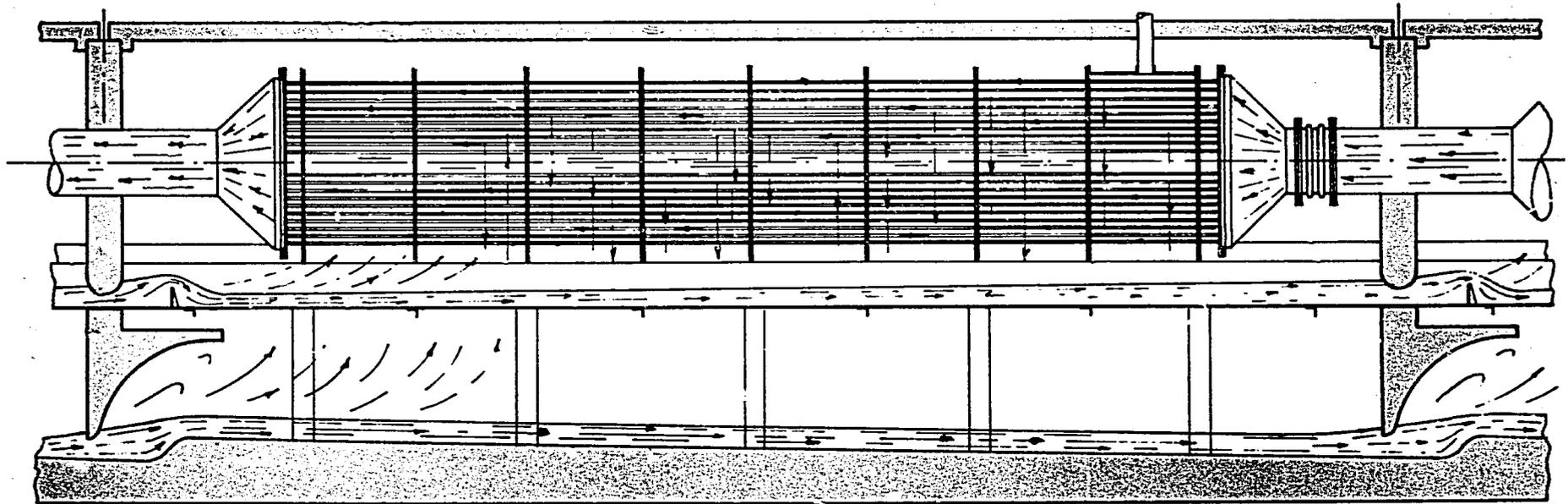
Aqua-Chem Inc holds basic patents on the long-tube flash evaporator and on the use of brine recirculation. Most of the MSF plants now being built or planned utilize these two features. The validity of these patents has not yet been tested in the courts. Before proceeding with the construction of a plant employing these features, the plant owner should obtain a "hold harmless" clause from equipment suppliers, indemnifying the owner for any liability for patent infringements.

The MSF plants built to date have used steel evaporating chambers. However, current development work indicates the feasibility of using concrete with a protective lining, e. g., steel or plastic. Figure IV-20 is a cross-sectional view of an MSF evaporator stage utilizing a concrete evaporator structure.

The MSF process also may be employed with once-through brine circulation. This arrangement has the advantage that the salt concentration of the saline water being heated in the recovery stage and brine heater is the same as that of the saline water feed to the plant. Also, the residence time of the brine in the high-temperature flash stages and in the brine heater is shorter in the once-through arrangement than in the recirculating arrangement, so that scale-forming compounds have less chance to precipitate from solution. Thus, using once-through brine circulation, the combination of lower salt concentration and shorter residence time should permit the attainment of higher temperatures in the brine heater without initiating scaling. In comparison, the brine recirculation arrangement shown in Figure IV-19 has the advantage that the amount of feedwater which must be acidified and deaerated for alkaline scale prevention is approximately one-third of that for a once-through arrangement. For a particular installation, an economic study is necessary to determine which

FIGURE IV-20

MULTISTAGE FLASH (MSF) STAGE



system will be more advantageous. It should be noted that the once-through brine circulation generally will not be as attractive in a dual-purpose power generation-water desalination plant as in a single-purpose plant, since the economic brine-heater temperature will usually be less than the upper limit imposed by scale prevention considerations.

Presently, the MSF distillation process is the desalting process in the most advanced state of development. There are more than 15 MSF plants with capacities of 1 mgd or more in operation at the present time. Nearly all of the recent and proposed commercial plants are of the MSF type. Operating experience with MSF type plants has been accumulated at Guantanamo Bay, Cuba; Kuwait and Qatar on the Persian Gulf; the Virgin Islands; Curacao, Netherlands West Indies; Cardon, Venezuela; Nassau in the Bahamas; Eilat, Israel; Spanish Morocco; and many other places.

As a part of the OSW demonstration plant program, an MSF distillation plant was constructed at San Diego, California. That plant, known as Pt Loma-I, used 36 stages and initially was rated at 1 mgd. Based on successful operating experience, the plant was rerated at 1.25 mgd. The Pt Loma-I plant (shown in Figure IV-21) operated from 1962 until 1964, at which time it was disassembled and moved to Guantanamo Bay, Cuba.

In March 1966, the Florida Keys Aqueduct Commission awarded a contract for a desalting plant at Key West, Florida. This oil-fired MSF plant will have a capacity of 2.62 mgd.

The OSW has outlined a 5-year engineering development program leading to the construction of large-scale distillation plants (13). The program, depicted chronologically on Figure IV-22, includes the following steps:

- An advanced technology plant of 1 to 2 mgd
- A 17-mgd test module
- A 50-mgd prototype
- A 150-mgd dual-purpose plant

FIGURE IV-21

MULTISTAGE FLASH (MSF) DISTILLATION DEMONSTRATION PLANT  
SAN DIEGO, CALIFORNIA

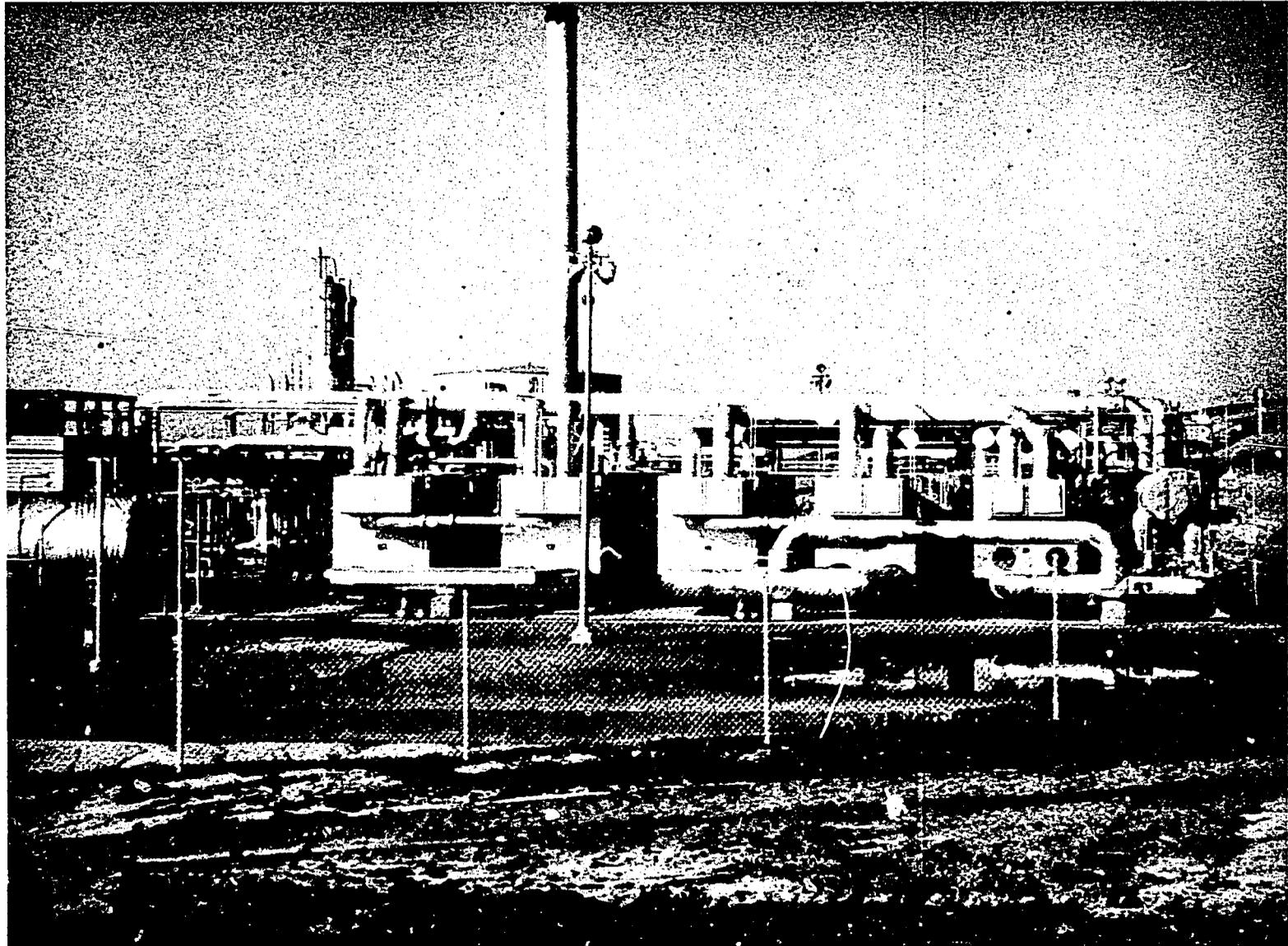
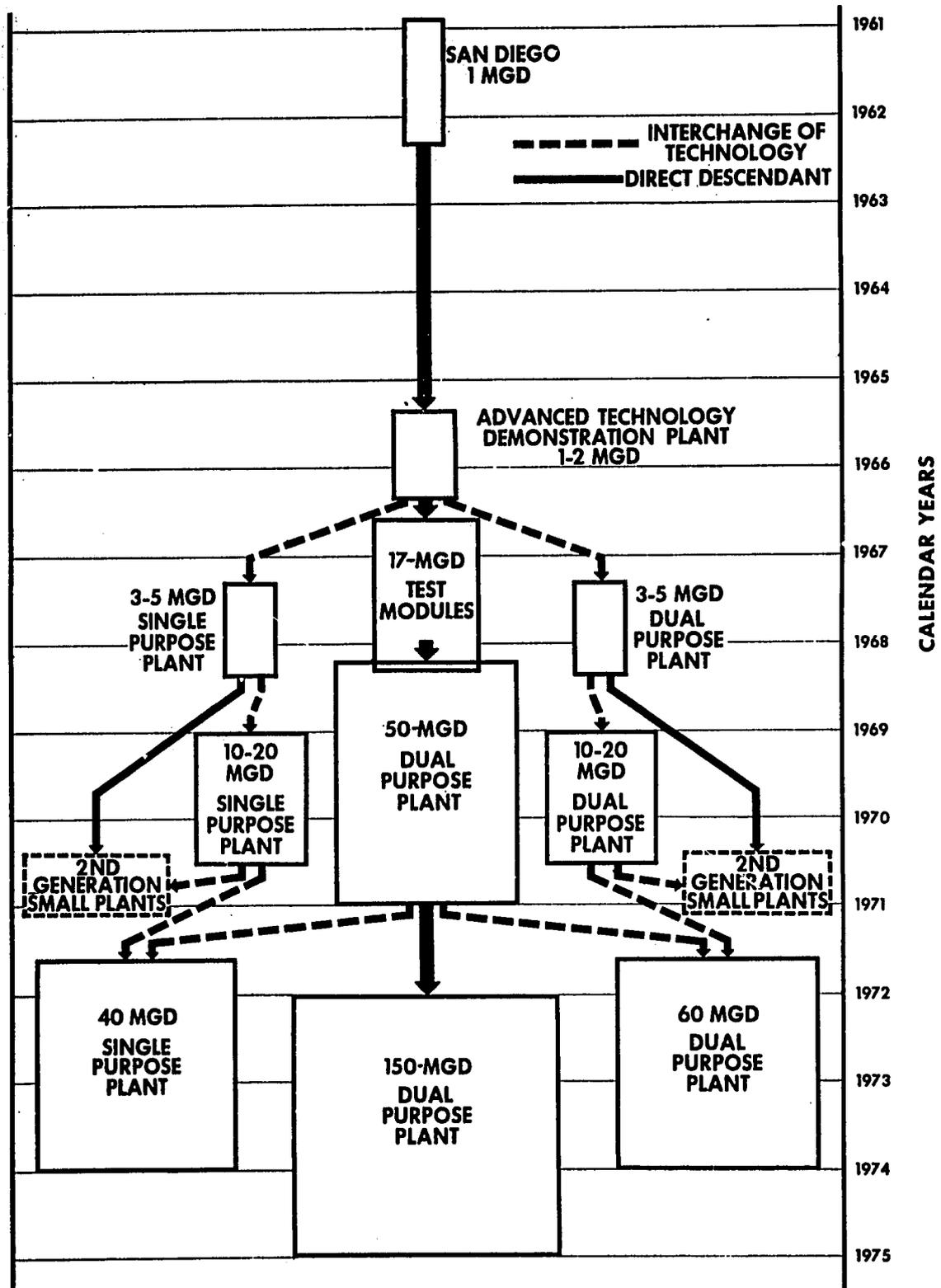


FIGURE IV -22

CHRONOLOGICAL DEVELOPMENT AND CONSTRUCTION  
OF LARGE DISTILLATION PLANTS



Source: U. S. Department of the Interior,  
Office of Saline Water

The advanced technology plant is the 1-mgd Clair Engle Desalting Plant which will be constructed in San Diego, California. The plant will utilize the multieffect multistage (MEMS) flash distillation process; it is discussed in the following subsection and in Section V, Description of Typical Plants.

The module is a section of the prototype plant which can simulate the operation of a complete plant and confirm essential design parameters(13). The "17-mgd" test module represents a cross-section of a 17-mgd unit of the 50-mgd prototype, and this section will have a production capacity of 2.5 mgd. Figure IV-23 illustrates the 17-mgd test module which will be built at OSW's San Diego Saline Water Test Facility. An isometric of the 50-mgd prototype desalination plant is shown on the left. The shaded area is the test module; it is shown enlarged at the upper right.

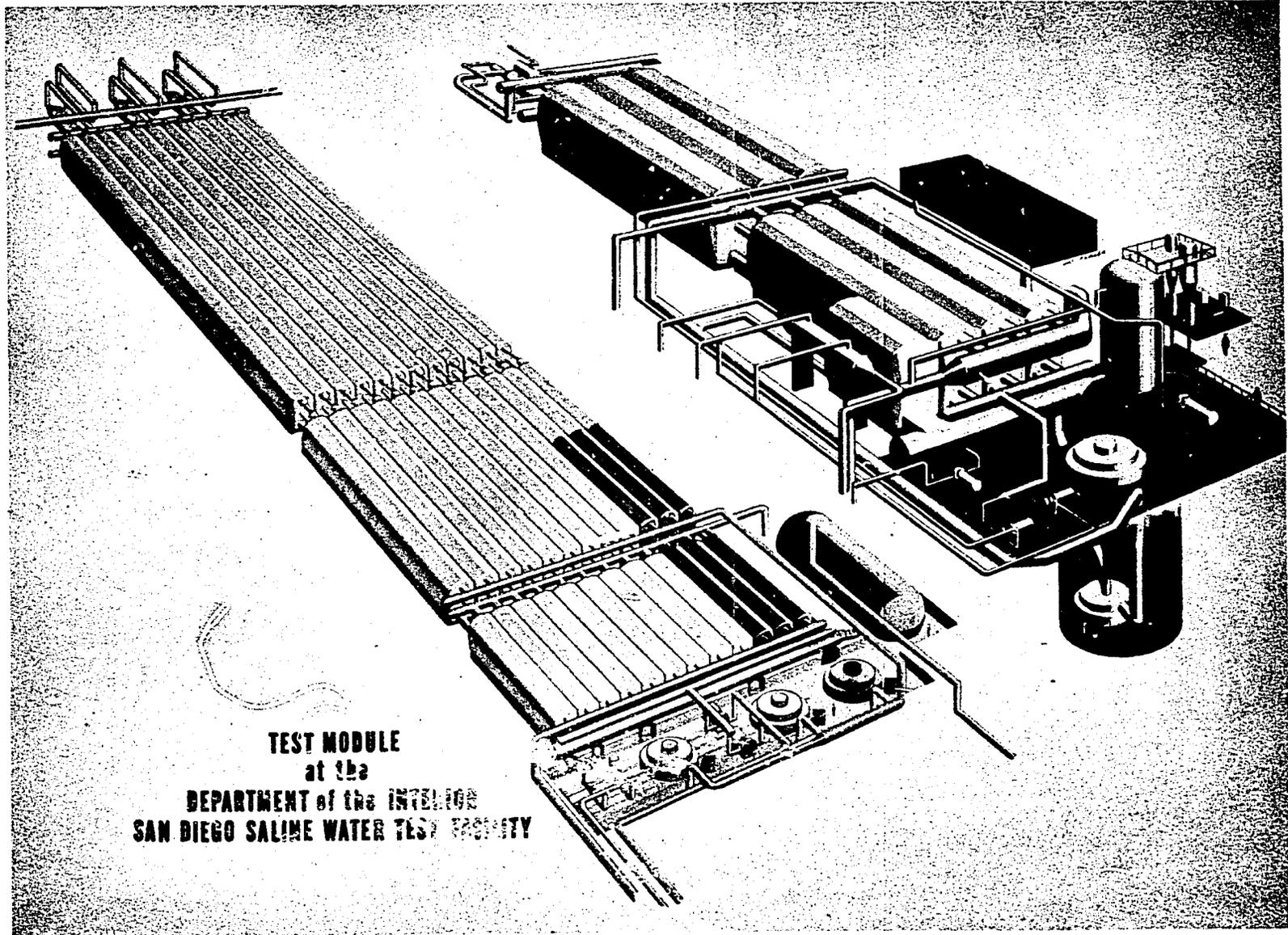
The 150-mgd Metropolitan Water District project in Southern California also will utilize the MSF distillation process. This dual-purpose plant will be constructed in two phases. The first phase is a 50-mgd evaporator train. Five years later, two additional 50-mgd trains will be built, to bring the plant to its total capacity of 150 mgd. Experience gained through the construction and testing of the experimental modules, representing sections of a 50-mgd plant, at the San Diego Saline Water Test Facility will be factored into the design of the initial 50-mgd evaporator train for the Metropolitan Water District dual-purpose plant.

The limitations imposed on the MSF process due to scale formation are discussed in Subsection IV. A. 3. Research and development work being done at Wrightsville Beach, N. C. is described in that subsection.

One technical limitation of the MSF process is the failure of flashing brine to reach equilibrium with the vapor in a stage.

FIGURE IV -23

TEST MODULE AT THE DEPARTMENT OF THE INTERIOR  
SAN DIEGO SALINE WATER TEST FACILITY



Courtesy: Fluor Corporation, Ltd

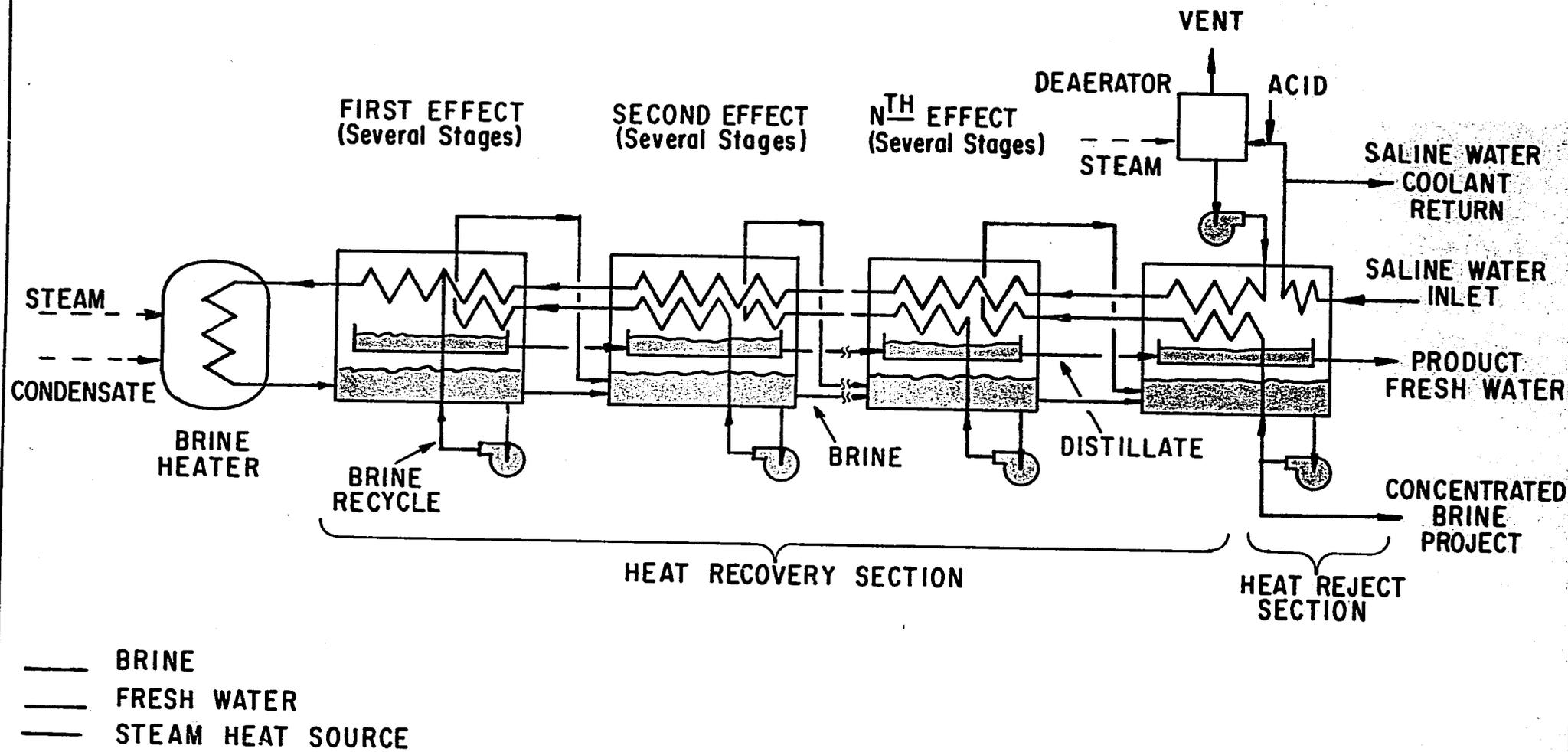
The warmest brine tends to stay along the bottom of the flash chamber. The average temperature of the brine leaving the stage may exceed the vapor temperature plus the boiling point elevation by from 1 to 3 F. This effect can be overcome by introducing baffles, or a "kickplate," or a streamlined flow obstacle into the flow stream. If this is done, however, the brine flow per unit width of the flash chamber is reduced. This effect is more pronounced at temperatures lower than 150 F. Research and development work to determine the dynamics of the flashing process and the proper design of flow-regulating orifices is being conducted by American Machine & Foundry, Cuno Engineering Corporation under OSW sponsorship. Baldwin Lima-Hamilton also has an OSW contract to investigate flashing phenomena.

e. Multieffect Multistage (MEMS) Flash Distillation

A variation of the MSF process is the multieffect multistage (MEMS) flash distillation process. The schematic flow diagram for the MEMS process is shown in Figure IV-24. In the single-effect MSF process described previously, only a single brine recirculation loop (or effect) is employed. The MEMS process uses several brine recirculation loops (or effects), and each effect in the MEMS process consists of a number of stages. The MEMS process offers a number of potential advantages in comparison with the usual MSF process:

- (1) In the single-effect MSF process the high-temperature stages of the evaporator train are exposed to brine which is almost as concentrated as that being discharged from the plant. Because of the multiple recirculation loops employed in the MEMS process, a lower brine concentration can be used in the high-temperature stages. Thus, the MEMS process will be able to operate at higher temperatures in the high-pressure stages before being limited by calcium sulfate scale formation (refer to Subsection IV. A. 3). Whereas the single-effect MSF process has been limited to an upper temperature of approximately 250 F, it is expected that temperatures 15 to 20 F higher than this may be used with the MEMS process.
- (2) Heat recovery (known as regeneration) from the flashing brine stream becomes more efficient as the number of

FIGURE IV-24  
MULTIEFFECT MULTISTAGE (MEMS)  
FLASH DISTILLATION PROCESS



stages is increased. In the single-effect MSF process, however, there is a practical limitation to the number of stages which may be used. This limitation is imposed by the available pressure difference required to maintain the flow of brine between stages. The pressure difference available at the low-temperature end of the cycle is the limiting factor. This is because the pressure difference corresponding to a given temperature increment increases rapidly above 180 F. By using a number of recirculation loops (or effects), it is possible to use more stages per temperature interval and to increase the recirculation rate at the high-temperature end of the cycle. This results in greater heat economy.

The primary potential advantage of the MEMS process is its ability to operate with higher brine heater temperatures than those possible in the MSF process. However, higher brine temperatures are accompanied by higher corrosion rates and by the necessity of designing the higher temperature stages for corresponding higher pressures. For brine temperatures below 250 F, the MSF process yields lower unit water costs than those of the MEMS process. The MEMS process may offer some advantage over the MSF process where the cost of steam is high enough to justify the use of higher brine temperatures for economic reasons, e. g. , in single-purpose desalting plants or in fossil-fueled dual-purpose electric power-water desalting plants.

The MEMS process has been developed by American Machine & Foundry Co (AMF), Cuno Engineering Corp at its Waterford, Connecticut research facility, under a program funded by the OSW. Operation of the MEMS process was demonstrated by a four-effect, 64-stage pilot plant which produced 7,200 gpd of fresh water. AMF is continuing development work with a larger pilot plant consisting of ten stages in one effect and operating over a temperature range of 250 to 150 F.

It has been proposed (14) that for large dual-purpose power-water desalting plants, an MEMS process plant should be interposed at the crossover between the high-pressure and low-pressure turbines. Steam would be taken from the high-pressure turbine exhaust and run through the MEMS plant

operating over a temperature range between 250 F and 150 F. Low-pressure steam at 150 F would be generated in a reboiler and conveyed to a low-pressure turbine. One advantage of this arrangement is that it would be possible to valve out the desalting plant and continue to operate the power plant independently of the water plant, whereas in an MSF plant using exhaust steam from the low-pressure turbine or large amount of extraction steam, shutting down the water plant essentially disrupts electrical generation. However, this disruption can be avoided--in the extraction steam case by proper operation, in the back pressure turbine case by equipping the brine heater with an auxiliary seawater cooling line such that the brine heater can be operated as a normal condenser.

The New York State Atomic and Space Development Authority announced in 1965 that it would proceed with the design and development of a nuclear powered desalting plant at Riverhead, Long Island(15). The plant will be a triple-purpose installation, producing 1 mgd of fresh water, 2,500 kilowatts (net) electrical power, and 400,000 curies of cobalt-60 radioisotope per year. This project is currently pending financial negotiations.

The 1-mgd Clair Engle Desalting Plant is to be built at the San Diego Saline Water Test Facility. This advanced-technology plant will utilize the MEMS process. The plant, which will be capable of operating at brine temperatures up to 350 F, has 66 stages and a performance ratio of 20 pounds of fresh water per 1,000 Btu. These improvements in performance will be accomplished with a reduction in overall plant size compared to the Pt Loma-I MSF plant(13).

Until the Clair Engle Desalting Plant has demonstrated satisfactory operation, the MEMS process must be considered as less proven than the MSF process.

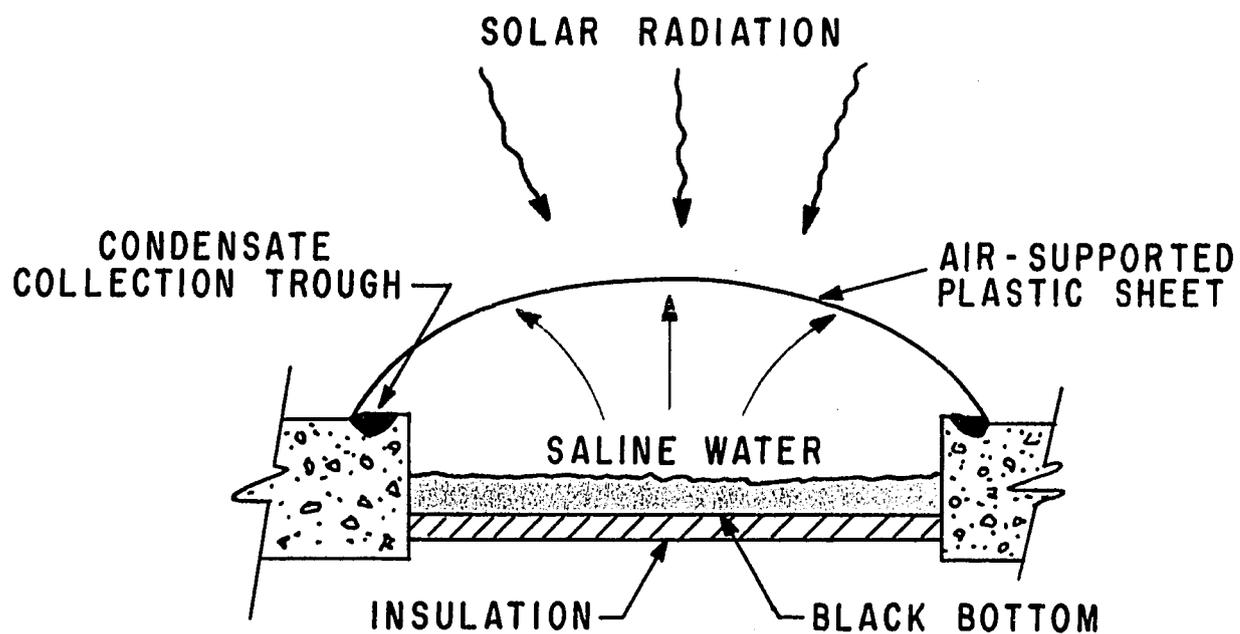
#### f. Solar Distillation

##### (1) Simple Solar Distillation

A simple solar still is shown in Figure IV-25. Sunlight enters the still through a transparent cover made of either glass or plastic. Most of the solar radiation is absorbed on the black bottom of the still. The absorbed energy is released as heat which warms the saline water contained

FIGURE IV-25

SIMPLE SOLAR STILL



—— BRINE  
- - - FRESH WATER

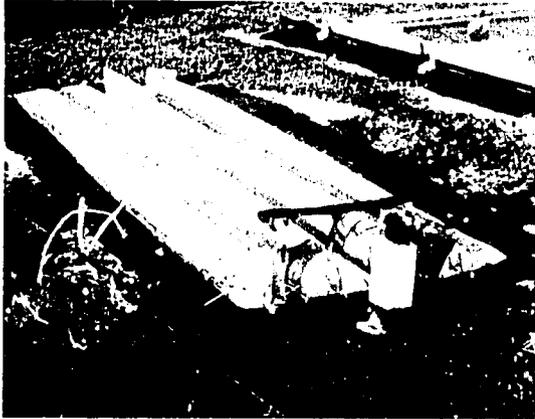
in the basin. As the temperature of the saline water increases, so does its vapor pressure. Pure water vapor saturates the air above the water. The vapor condenses on the cooler transparent surface and runs down into the condensate collection trough. Although sunlight is "free," large collection areas are necessary, and consequently the still is relatively expensive to construct and use.

A 6,000-gpd solar distillation unit was built and operated in the Chilean Andes as long ago as 1872(16). From 1958 through 1965 OSW's Solar Distillation Research Station near Daytona Beach, Florida tested a number of different types of solar stills. Figure IV-26 shows some of the various types of solar stills tested. One of these stills was a "deep-basin" still which uses a pool of water approximately 1 foot deep. This deep-basin design provides sufficient storage of heat and water so that freshwater production continues throughout the night. During December 1963, a 1,600 square foot inflated plastic still was tested. In 1964, a nominal 7,500-gpd inflated plastic solar still was put into operation on the Greek island of Symi(9).

The two principal technical and economic limitations on solar distillation processes are the construction cost of the stills and the daily water production per unit collection area. Past research work has been directed at circumventing both of these obstacles. Various plastic films have been used instead of the more permanent glass coverings. An expendable still, constructed of an inflatable single plastic tube, was developed in the hope that it would be cheap enough to be discarded if any part failed.

Of various construction materials evaluated in this program, asphaltic mat with a polyvinyl chloride core, and butyl rubber sheeting appeared to be the most promising as basin lining materials(16). The most promising transparent plastic films were DuPont's Tedlar and Weatherable Mylar films and Allied Chemicals' Aclar film(16).

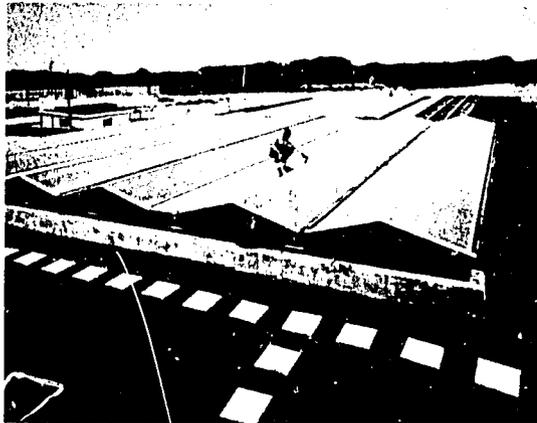
SOME SOLAR STILLS TESTED AT OSW'S  
DAYTONA BEACH TEST STATION



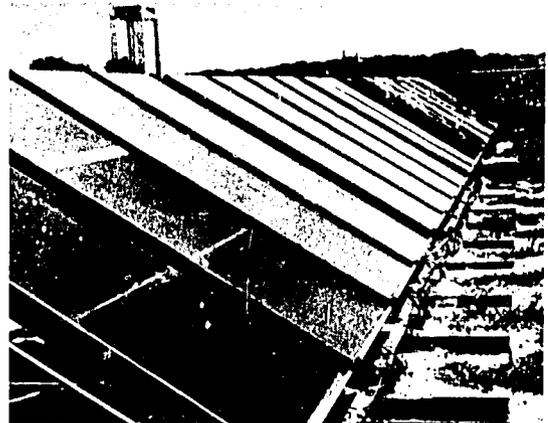
Inflated Plastic Still



Inflated Plastic Still



Glass-Covered Basin Still



Tilted-Wick Still

Source: U. S. Department of the Interior,  
Office of Saline Water

With an incident solar radiation of 2,000 Btu per sq ft day, the daily water production from the simple solar stills varies from 0.08 to 0.13 gallon per sq ft-day. The multiple-effect humidification process described in the following subsection is one approach to increasing the water production per unit collector area.

One operating problem is the formation of slime on the basin liner. Apparently, this slime consists of suspended matter in a web structure of fungi or bacteria. This problem was overcome by using a sand prefilter to remove suspended matter from the saline water feed (16).

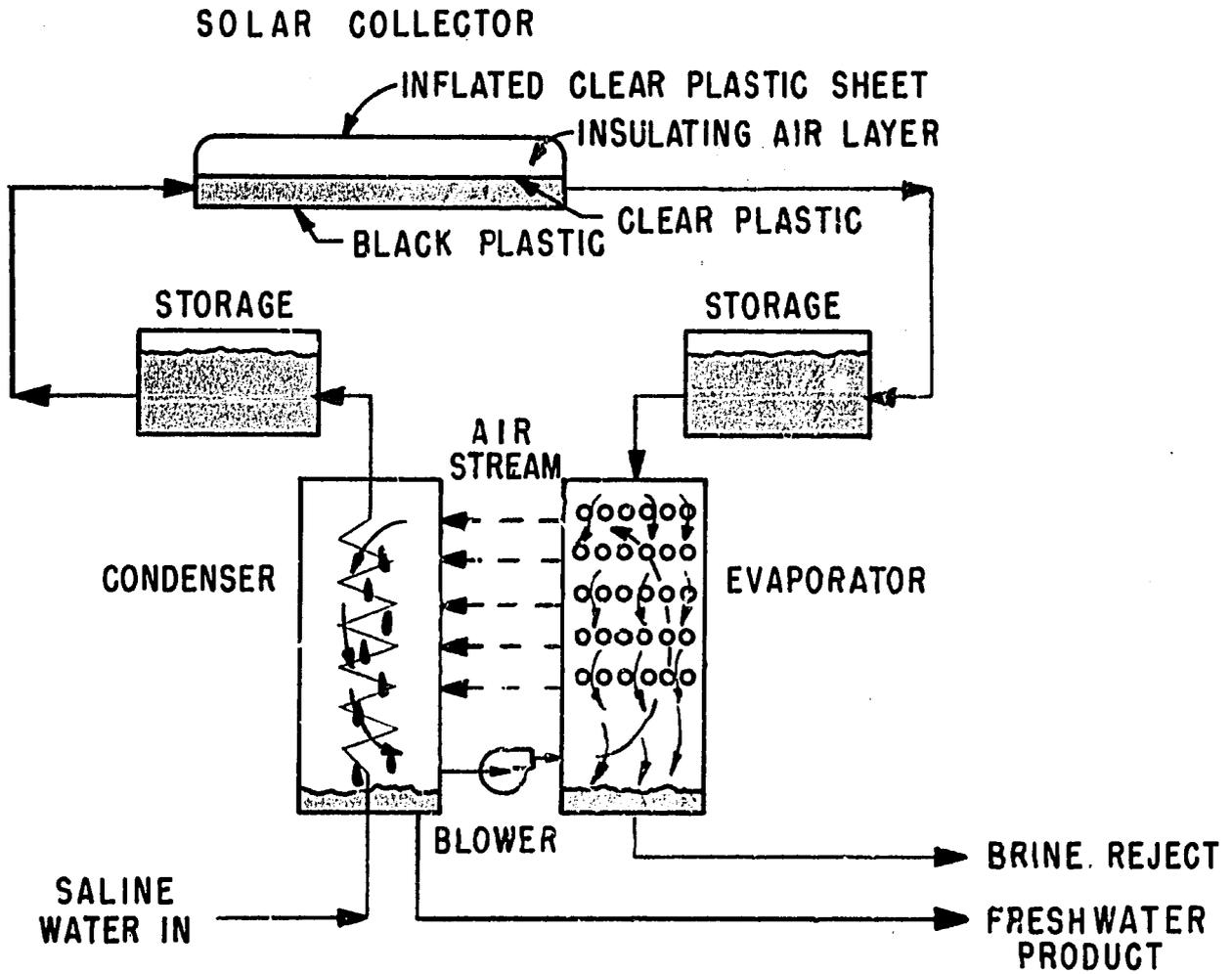
The simple solar distillation process is most likely to find application in relatively small units (less than 50,000 gpd), where solar intensity is high, fuel is expensive, labor costs are inexpensive and land area is available at nominal cost. This process is not economically attractive for large-scale water desalting plants.

## (2) Solar Heated Multiple-Effect Humidification

By separating the process of collecting solar radiation from the processes of evaporating saline water and condensing fresh water, it is possible to achieve multiple-effect distillation. This can be accomplished by the solar heated multiple-effect humidification process shown schematically in Figure IV-27. The solar collector consists of three plastic layers. The two top layers are transparent, and are separated by an insulating air gap. The saline water flows between the second clear plastic sheet and the bottom black sheet. During the period of maximum sunshine, the saline water is pumped through the solar collector and heated. This heated saline water is stored in an insulated tank so that water production can continue on a 24-hour per day basis. In the evaporator tower, heated saline water flows downward through a number of packed beds filled with polyethylene packing, where it is contacted countercurrently with dry air. As the air rises it is heated and saturated with moisture by the falling hot water. The hot, moist air is ducted to the condenser where the moisture is condensed as the product fresh water. The incoming saline water is used as the coolant inside the finned condenser tubes. The

FIGURE IV-27

SOLAR HEATER MULTIPLE-EFFECT  
HUMIDIFICATION PROCESS



— BRINE  
- - - FRESH WATER

preheated saline water feed is pumped to an insulated storage tank which serves as the supply for the solar collector.

The feasibility of using solar energy as the heat source for a multiple-effect humidification process was demonstrated in an experimental plant at the University of Arizona. A pilot plant was completed in 1964 at Puerto Peñasco, Mexico (see Figure IV-28).

The Puerto Peñasco pilot plant employs eight effects and produces 5,000 gpd of fresh water. The water production is 0.5 gallon per sq ft-day, which is approximately five times that which could be achieved with a simple solar still (single effect) (17).

Other research work on the multiple-effect humidification process has been done at Georgia Institute of Technology.

Although the process may be applicable for small-scale water production, operating experience is not sufficient to predict its economics.

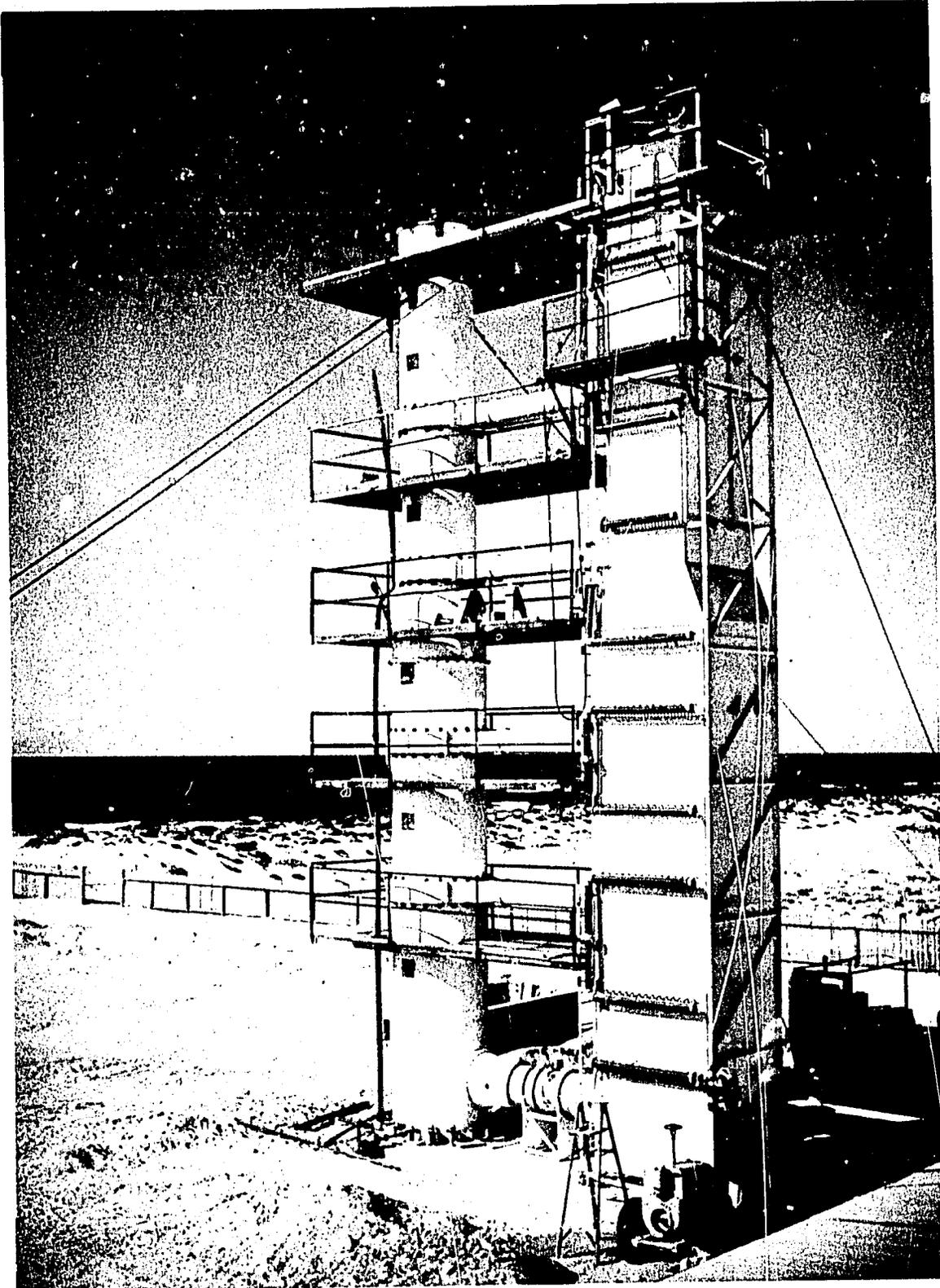
### 3. Distillation Process Limitations

#### a. Scale Formation

Distillation processes are particularly susceptible to the formation of scale deposits, which act as thermal insulators tending to reduce the water production capacity. Most saline water contains calcium, magnesium, bicarbonate and sulfate ions in addition to sodium and chloride ions. The principal scale-forming compounds are calcium carbonate, magnesium hydroxide and calcium sulfate, all of which become less soluble as the solution temperature is increased. By adding acid (or other additive which increases the hydrogen ion concentration) to the feed stream, the solubility of carbonates and hydroxides is increased. The formation of calcium sulfate scale can be prevented by maintaining the calcium sulfate concentration below its solubility limit, by reducing the calcium in the saline water feed stream or by recirculating a slurry containing calcium sulfate crystals. The latter technique allows the scale to precipitate preferentially on the "seed" crystals in the slurry, rather than on heat exchange surfaces.

FIGURE IV-28

PUERTO PEÑASCO PILOT PLANT



Source: U. S. Department of the Interior,  
Office of Saline Water

If scale is allowed to form it may have a number of detrimental effects on distillation processes. Normally, when scale forms it deposits on heat exchange surfaces, and this increases the resistance to heat transfer. Also, it may accumulate in pipelines, orifices and other flow passages, thereby impeding the flow of process fluids. Both the increased heat-transfer resistance and the fluid pressure drop increase the energy input per pound of product water. At the San Diego, California Multi-stage Flash (MSF) Demonstration Plant, scale compounds and organic sludge which formed barely-discernable scale deposits in the brine heater and condenser tubing caused a 10% increase in specific fuel consumption (18).

Once scale compounds have been formed in a process system, removal may require burdensome corrective measures, such as dissolving the solids in product water or using acid injection. Some tightly adhering scale compounds, such as calcium sulfate anhydrite, may require mechanical or thermal shock, brushing or drilling, to be removed. Any prolonged plant shutdown for descaling means lost water production; this adds to the cost of fresh water produced. In addition, overdosing with acid may cause corrosion in process equipment.

From the foregoing it can be seen that scale formation must be avoided. Fortunately, methods are available for pretreating the saline water and for controlling scale formation; these are discussed in the following subsection.

Three factors must exist before scale-forming compounds will precipitate from solution (19):

- The saline solution must be supersaturated locally in the scale compound.
- Nucleation sites must be available, on which crystals of the scale compound can form.
- There must be sufficient contact time between the supersaturated solution and the nucleation sites.

If one or more of these conditions can be eliminated, the initial formation of scale can be prevented. However, once nucleation of crystals has started, the deposition rate becomes much greater for the same conditions of supersaturation and contact time (19).

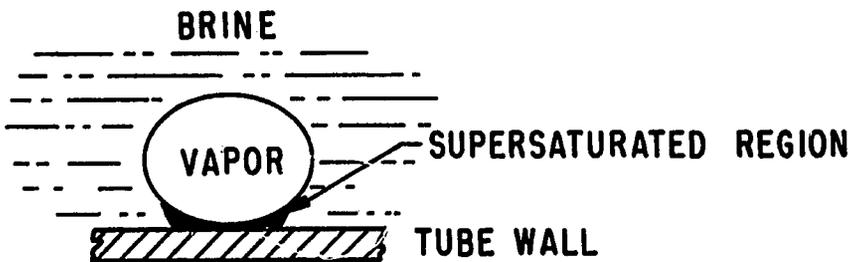
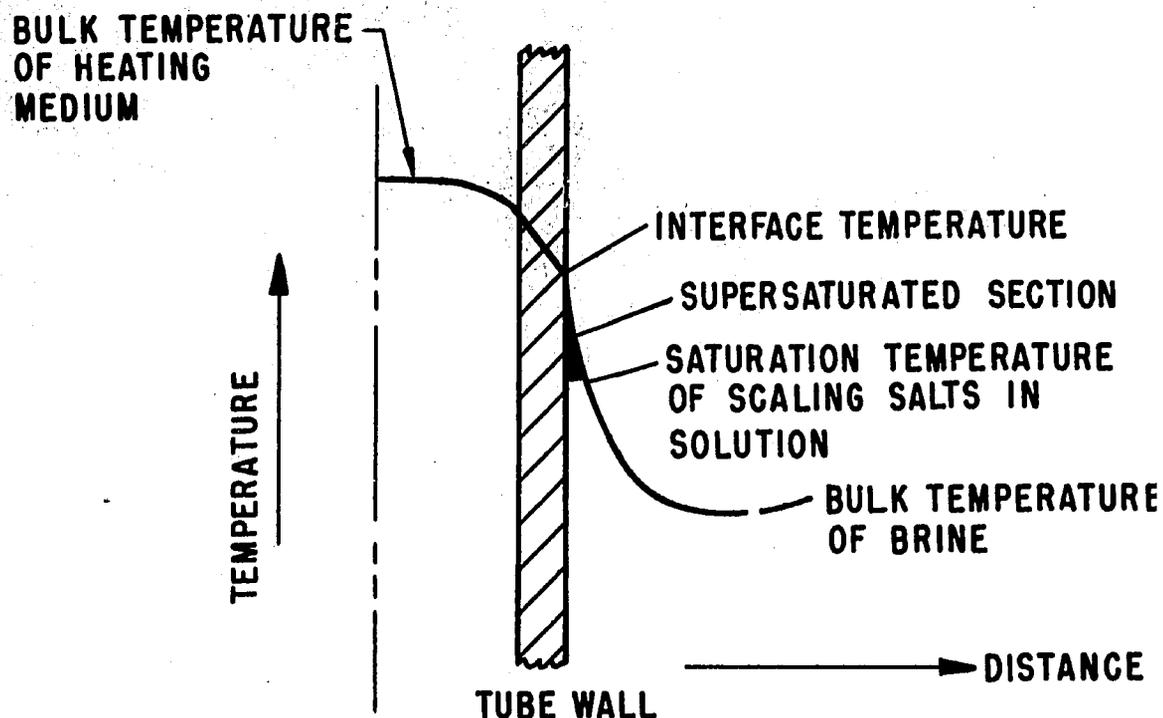
The scale-forming tendencies in a particular application depend both on the composition of the saline water used as feed to the plant, and on the path of operating conditions present in the plant. As discussed in Section III, the ionic composition of seawater and various brackish saline waters may differ markedly. Most of these saline waters contain calcium, magnesium, bicarbonate and sulfate ions. The solubility of the principal scale compounds is a function of temperature and pH, and of the concentration of other salts present.

Calcium carbonate, magnesium hydroxide and calcium sulfate all have inverted solubility characteristics, i. e., they become less soluble as the solution temperature increases. When saline water is heated, the temperature at the wall surface is higher than that in the bulk liquid (see Figure IV-29). Since the scale compounds are less soluble at higher temperatures, if the concentration of the brine is near saturation in some scale-forming constituent it will tend to precipitate on the wall. If boiling occurs at the wall, as in a submerged tube evaporator, brine near the point of bubble formation will be more concentrated than the bulk liquid.

The Appendix contains stability diagrams, which are equilibrium solubility charts for scale-forming compounds. Charts are included for calcium carbonate and magnesium hydroxide in natural waters (200 to 1,000 ppm total dissolved solids), and for calcium carbonate, magnesium hydroxide and calcium sulfate in seawater (25,000 to 100,000 mg per liter). For a given scale-forming constituent, the pH at which the water is saturated in that constituent can be determined. If the actual pH value is higher (i. e., more alkaline) than the saturation pH, that constituent will precipitate from solution. The solubility of calcium carbonate is affected by temperature, pH and alkalinity (carbonate plus bicarbonate plus hydroxide expressed as equivalent ppm  $\text{CaCO}_3$ ), whereas the solubility of  $\text{MgOH}_2$  is dependent on temperature and pH.

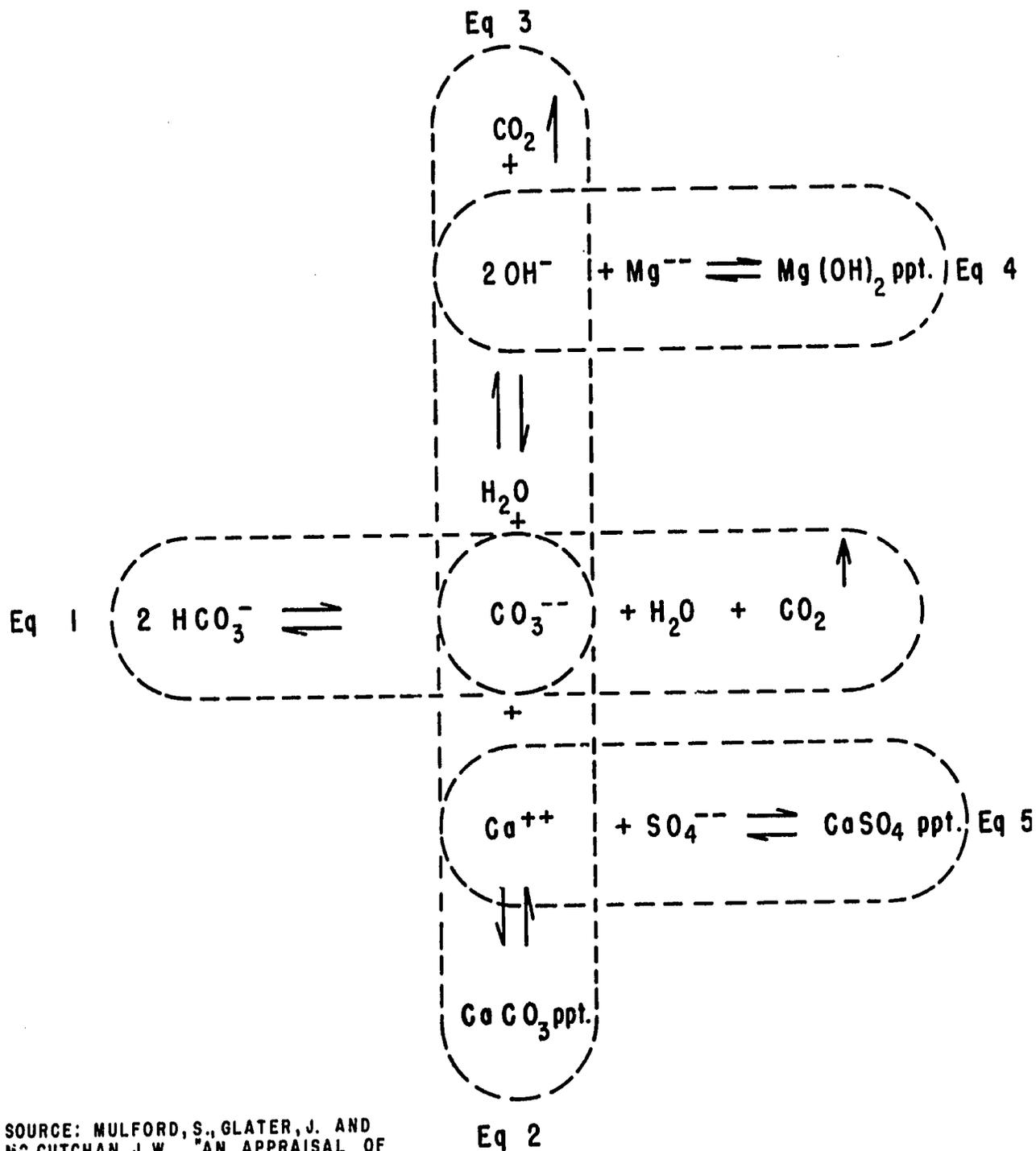
Figure IV-30 gives the principal scale-forming reactions in seawater. The alkaline scales, calcium carbonate and magnesium hydroxide, are formed due to the thermal decomposition of bicarbonate ions as seawater is heated. Practically all of the carbonate in seawater is present as bicarbonate. As the seawater is heated, bicarbonate ions decompose into carbonate ions and carbon dioxide gas (Eq 1, Figure IV-30). When

MECHANISM OF SCALE FORMATION



SOURCE: TIDBALL, R.A. AND WOODBURY, R.E.  
 "METHODS OF SCALE CONTROL IN FLASH  
 SYSTEMS", FIRST INTERNATIONAL SYMPOSIUM  
 ON WATER DESALINATION, PAPER SWD/24  
 OCT 3 TO 9, 1965, WASHINGTON, D.C.

FIGURE IV-30  
PRINCIPAL SCALE-FORMING REACTIONS  
TO FORM PRECIPITATES IN SEAWATER (16)



SOURCE: MULFORD, S., GLATER, J. AND  
 MC CUTCHAN, J.W., "AN APPRAISAL OF  
 SCALE-CONTROL METHODS AT THE OSW  
 FLASH EVAPORATOR PLANT IN SAN DIEGO,  
 CALIF," FIRST INTERNATIONAL SYMPOSIUM  
 ON WATER DESALINATION, PAPER SWD/11,  
 OCT 3 TO 9, 1965, WASHINGTON, D.C.

normal untreated seawater reaches approximately 170 F (20), the carbonate and pH reach a level where calcium carbonate begins precipitating (Eq 2, Figure IV-30). If the seawater temperature is raised still further, the carbonate ions decompose into carbon dioxide and hydroxyl ions (Eq 3, Figure IV-30). As the additional carbon dioxide is released, the solution becomes more basic and magnesium hydroxide scale starts to form. The relative rates of forming calcium carbonate and magnesium hydroxide scale depend on the temperature level and the rate of carbon dioxide evolution (18). Magnesium hydroxide forms rapidly above a temperature of 200 F at a pH of 8.3 or greater (20). It has been reported, however, that in an MSF plant fed with untreated seawater the principal scale-forming constituent up to 250 F is calcium carbonate (20).

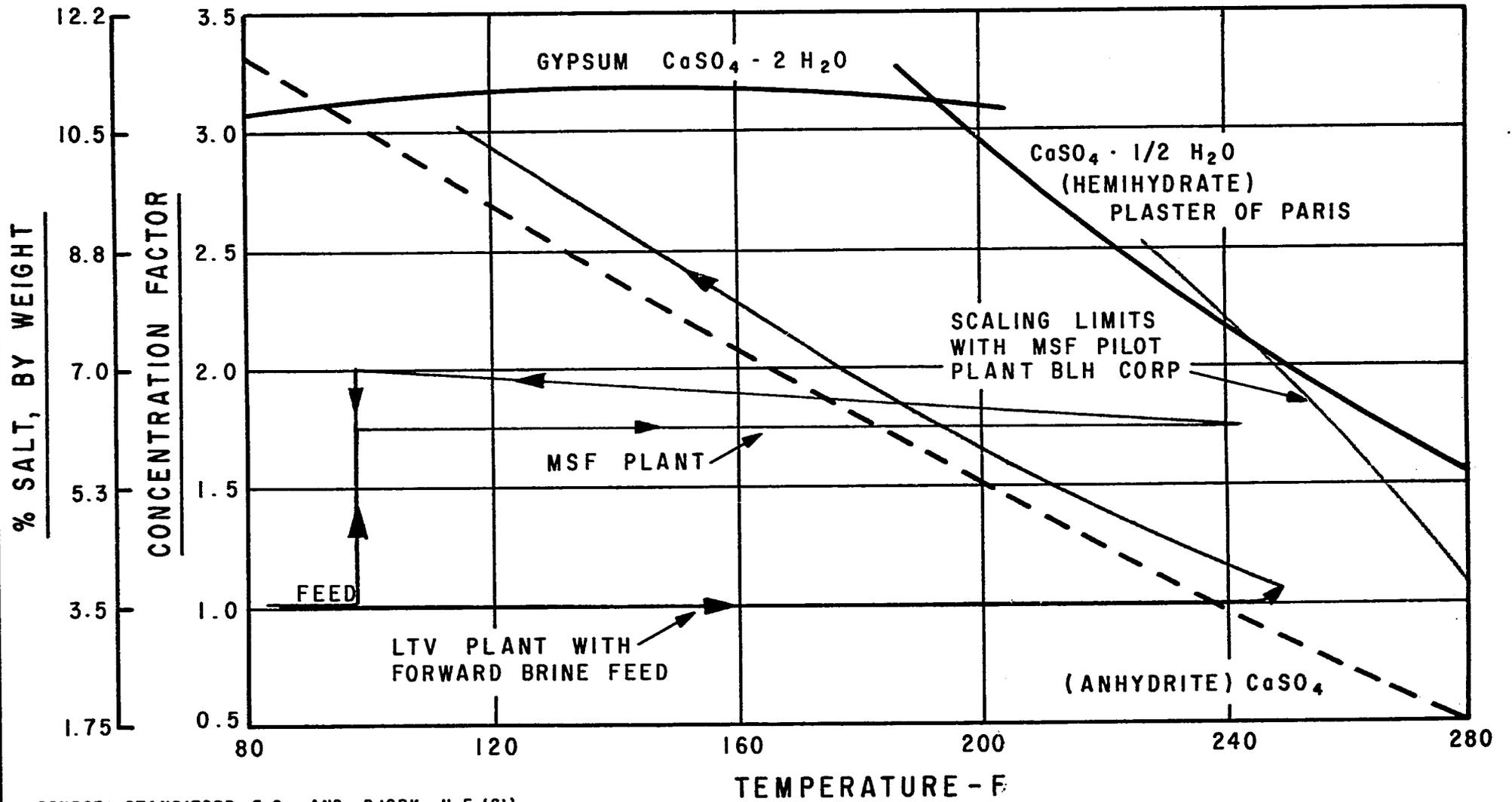
Whereas the alkaline scales can form in unconcentrated seawater with heating alone, calcium sulfate forms after some critical amount of concentration occurs. There are three different forms in which calcium sulfate may crystallize:

- Calcium sulfate anhydrite ( $\text{CaSO}_4$ )
- Calcium sulfate hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ), commonly known as "plaster of paris"
- Calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), or "gypsum"

Figure IV-31 shows the approximate solubility or scaling limits for each of these constituents as a function of temperature and concentration factor (based on seawater feed at 35,000 ppm). These solubility limits are equilibrium values and do not take into account the reaction kinetics of forming the scale compounds. Above 90 F, calcium sulfate anhydrite is the stable form of calcium sulfate. The anhydrite is an extremely adherent scale which is only slowly soluble in concentrated sodium chloride brine and is difficult to remove mechanically. The hemihydrate is a metastable form; however, it forms much more rapidly than the anhydrite, which forms so slowly that the equilibrium concentrations of anhydrite can be exceeded somewhat. That is, an actual process can operate with brine concentration somewhat supersaturated in anhydrite. At low temperatures, with concentration ratios greater than approximately 3 to 1, calcium sulfate dihydrate is the stable

FIGURE IV - 31

CaSO<sub>4</sub> SCALING LIMITS FOR SEAWATER



SOURCE: STANDIFORD, F.C. AND BJORK, H.F. (21),  
TIDBALL, R.A., AND WOODBURY, R.E. (20)

form. Figure IV-31 shows the evaporation paths for the Freeport, Texas long-tube-vertical (LTV) demonstration plant and for an MSF plant (21). Note that the evaporation paths for these two types of plants both operate into the region between the anhydrite and hemihydrate equilibrium curves.

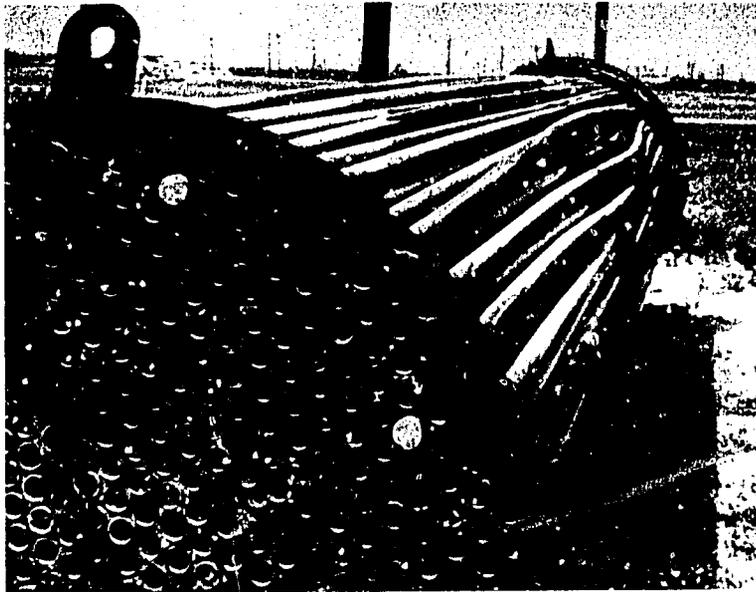
In an LTV process with forward brine feed, similar to the operating path for the Freeport, Texas demonstration plant, the scale formed in the high-temperature effects will tend to be a mixture of hemihydrate and anhydrite. In the low-temperature effects, the dihydrate gypsum scale tends to form if the concentration ratio exceeds approximately three. Figure IV-32 shows gypsum scale deposited in 2 inch diameter tubes in a tube bundle removed from the low-temperature, twelfth effect of the Freeport, Texas demonstration plant. The Freeport, Texas plant has operated at temperatures up to 275 F without scaling in the high-temperature, first effect.

From the flow path for a single-effect MSF plant, as shown on Figure IV-31, it will be seen that the MSF plant does not achieve concentration ratios much over two. Therefore, gypsum scaling is not a problem in an MSF plant (20). In an MSF plant operating with recycle, the scale compound formed in the high-temperature flash stages is calcium sulfate anhydrite. It is also possible to get calcium sulfate hemihydrate, if the temperatures are raised sufficiently to be to the right of the hemihydrate curve shown on Figure IV-31.

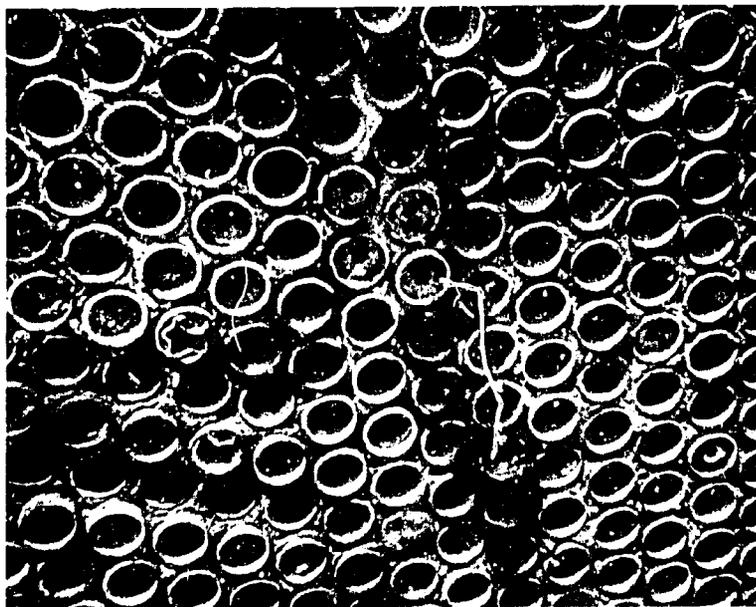
The Baldwin-Lima-Hamilton Corporation has carried out an extensive testing program (22) under OSW sponsorship, to determine the scaling limits in an MSF plant as a function of temperature, pH and brine concentration ratio. The initial was performed on a six-stage, 10,000-gpd flash distillation pilot plant at Wrightsville Beach, North Carolina. The green line shown on Figure IV-31 is the scaling limit obtained in the flash distillation plant when pH control is used to eliminate alkaline-scale,  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . The scale compound formed over most of the curve is calcium sulfate hemihydrate, although some anhydrite scale is formed at high temperatures with recycle. As a result of these tests, it was concluded that by using pH control followed by adequate carbon dioxide removal, calcium sulfate scaling could be avoided up to 280 F in an MSF plant employing brine recycle, and up to 300 F in a "once-through" system (20).

FIGURE IV -32

GYPSUM ( $\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$ ) SCALE



Tube-bundle which was removed from low-temperature effect of LTV Demonstration Plant, Freeport, Texas.  
Note thermally induced tube bowing.



Gypsum scale in low-temperature effect removed from LTV process plant, Freeport, Texas

Present tests are being conducted with a 16-stage, 25,000-gpd flash distillation pilot plant at OSW's Wrightsville Beach Test Station. This pilot plant, shown in Figure IV-33, represents one effect of a multieffect multistage (MEMS) process, and operates over a 50 F temperature range.

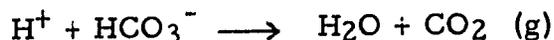
b. Scale Control and Pretreatment

The following paragraphs discuss various methods of scale control and pretreatment.

(1) Bicarbonate Removal by H<sub>2</sub>SO<sub>4</sub>

Proper bicarbonate removal makes it possible to eliminate the formation of calcium carbonate and magnesium hydroxide scales. Sulfuric acid is injected into the feed stream to neutralize the bicarbonate ions and reduce the pH to approximately 4.

Decarbonation and deaeration may be accomplished in either one step or two steps. A two-step treatment process is shown schematically in Figure IV-34. After acid injection, the makeup seawater stream is taken to an atmospheric-pressure decarbonator, where most of the carbon dioxide is removed according to the following reaction:



Air is usually used to sweep the evolved carbon dioxide out of the seawater stream (20). This is acceptable since the seawater already is saturated with air. The decarbonator may be either a packed column, spray pond or cooling tower.

The seawater stream leaving the decarbonator is taken to the vacuum deaerator where the balance of the carbon dioxide plus dissolved oxygen are stripped from solution by steam.

As the carbon dioxide is driven from solution, the pH returns to the neighborhood of 6 or 7. Most plants using acid injection are provided with a system for neutralizing the effluent with caustic if necessary. At the San Diego MSF

FIGURE IV-33

THE 16-STAGE, 25,000-GPD FLASH DISTILLATION PILOT PLANT  
BEING OPERATED TO STUDY SCALE PREVENTION AT  
WRIGHTSVILLE BEACH

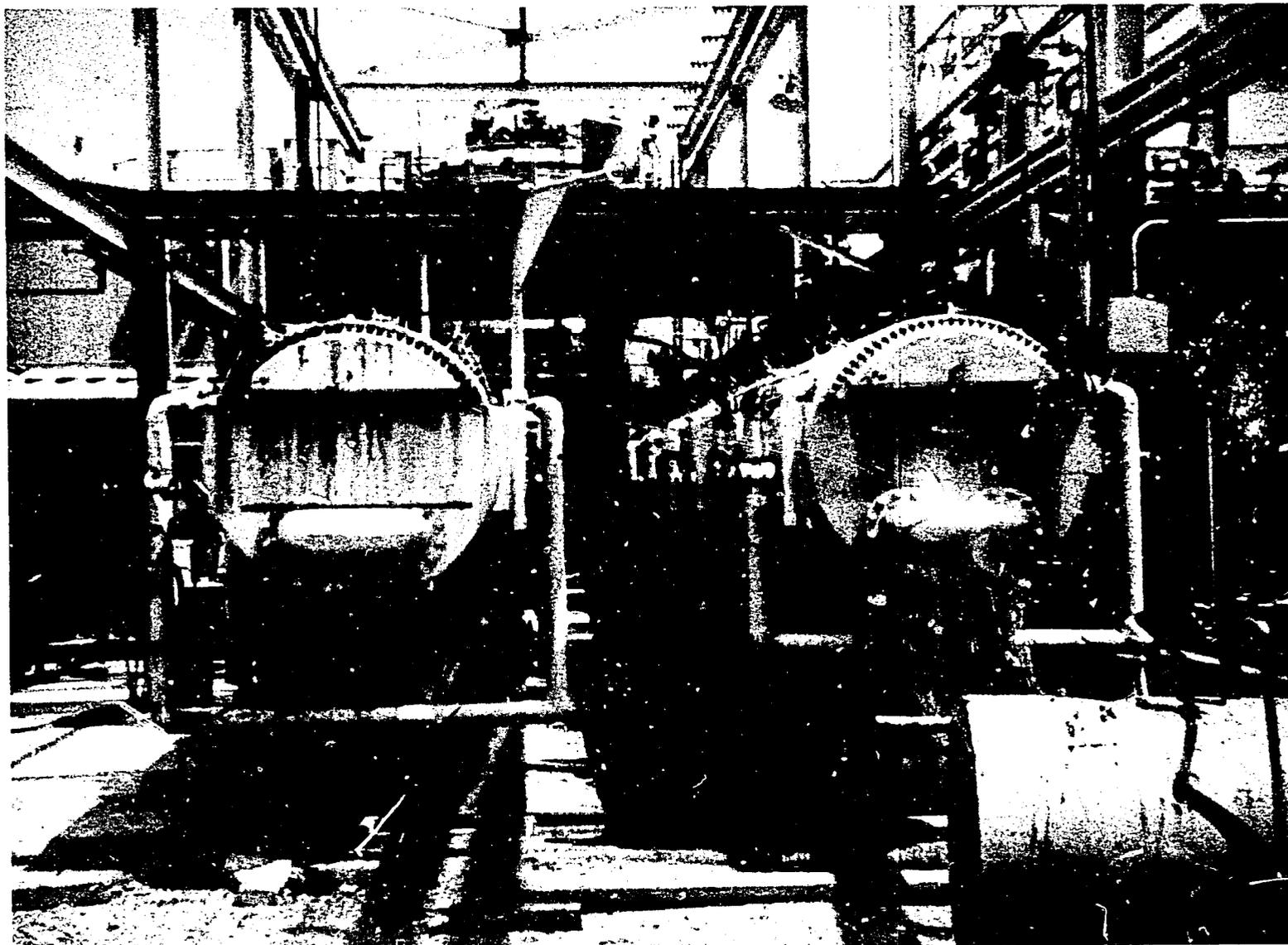
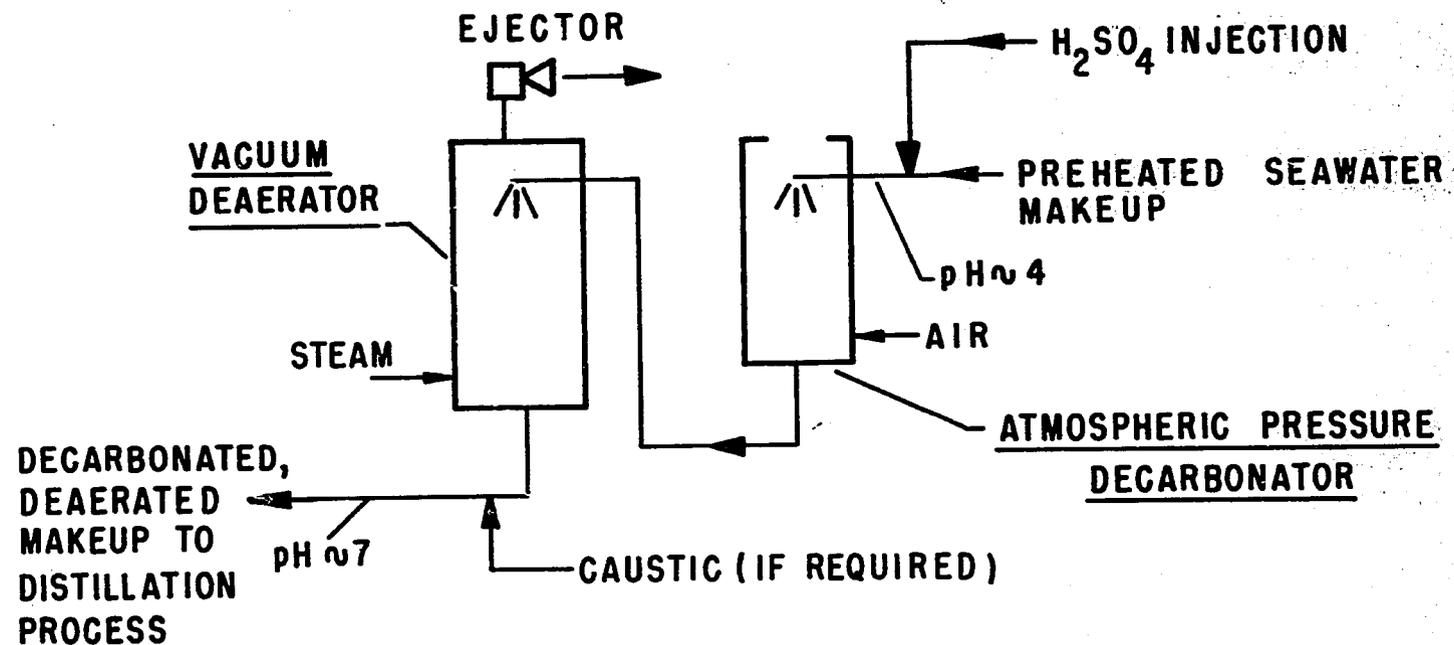


FIGURE IV-34  
TYPICAL FLOW SHEET SHOWING  
DECARBONATION AND DEAERATION FOR SCALE CONTROL



demonstration plant, it was found possible to add acid stoichiometrically equal to the bicarbonate concentration. The rapid recovery of pH to nearly neutral made it unnecessary to neutralize with caustic (18).

Also it is possible to accomplish the decarbonation and deaeration in one step. However, this places an added non-condensable load on the ejector removing gases from the deaerator.

With proper degassing, oxygen can be reduced to approximately five parts per billion and alkalinity to one part per million (23).

It is important to achieve good acid mixing with the seawater makeup stream. At the Freeport, Texas Demonstration Plant this is accomplished by using mixing orifices. Another technique which can be utilized to enhance mixing is to pre-dilute the acid stream. However, this technique makes the acid stream more corrosive. Following acid injection, the pH should be measured after good mixing has been accomplished.

If acid injection is accomplished after some preheating of the seawater stream to 130 to 145 F, the steam and power requirements for deaeration are reduced appreciably over what would be necessary at lower temperatures (20).

## (2) pH Control

The formation of calcium carbonate and magnesium hydroxide scale can be prevented by maintaining the brine pH below 7 (20). In addition to sulfuric acid, various weaker acids, such as citric acid, have been used for pH control in smaller installations (6). Also it is possible to use salts which hydrolyze to produce an acidic pH. The best known of these salts is ferric chloride. The dosage rate used is 78 grams of anhydrous ferric chloride per ton of seawater (24).

An electrolytic cell has been used to generate ferric chloride using sacrificial iron anodes. This technique permits a closer control of the dose rate by regulating the current supplied to the cells (24).

Cuno Engineering Corporation, under Navy sponsorship, has developed a method of forming hydrochloric acid in situ from seawater. This process takes a sidestream from the main seawater stream and passes it through an electro-dialysis cell wherein the hydrochloric acid is formed.

### (3) Proprietary Chemicals

A number of proprietary chemical formulations have been employed as a means of alkaline scale prevention. These compounds retard scale formation but do not completely prevent it. Among the various compounds which have been investigated are those listed in Table IV-1.

Hagevap-LP was used in concentrations of 3 to 5 ppm at the Point Loma MSF demonstration plant (18). It proved effective in retarding scale formation with brine concentration factors of 1.5 and maximum brine temperatures of 200 F. However, a gradual deterioration in plant performance of up to 5% per month was experienced on two long runs lasting four months and six months. It was found possible to use sulfuric acid injection to remove the alkaline scales formed ( $1/3 \text{ CaCO}_3$  and  $2/3 \text{ Mg(OH)}_2$ ) in situ. At temperatures above 200 F, the Hagevap-LP undergoes rapid decomposition (6). At the San Diego MSF demonstration plant, sulfuric acid injection supplanted the use of Hagevap-LP for alkaline scale prevention at temperatures above 200 F. The estimated treatment costs with either Hagevap-LP or sulfuric acid were approximately the same (3¢ per 1,000 gallons).

In addition, Hagevap-LP, along with other proprietary chemicals, was tested for effectiveness in the MSF pilot plant operated at Wrightsville Beach, N. C. (20). The other compounds tested were SP-1230, EES-VAP, and S-3435 (see Table IV-1). These tests were run at brine concentration factors of 2.0 at 200 F, and 1.7 at 215 F and 250 F. None of the compounds performed satisfactorily under these conditions; a soft sludge-like deposit formed on heat exchange surfaces within 100 hours. It was found that concentrations of between 2 ppm and 4 ppm of these materials gave the best results.

TABLE IV -1

PROPRIETARY SCALE-RETARDING CHEMICALS

<u>Name</u>	<u>Constituents</u>	<u>Source</u>	<u>References</u>
Hagevap-LP	Mixture of sodium tripolyphosphate, lignin sulfonic acid derivatives, and esters of polyalkylene glycols	The Hagen Corp, Pittsburgh, Pa.	(18), (22)
SP-1230	Starch phosphate 1230 cornstarch containing 4% phosphorus as orthophosphate U. S. Pat. 2, 884, 412	American Maize Products Co. , 250 Park Avenue New York, N. Y.	(22)
EES-VAP	Sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$ U. S. Pat. 3, 135, 670	U. S. Navy	(22)
S-3435	Reagent S-3435 modified polyacrylic acid (mol wt about 6, 000) diluents sodium and ammonium hydroxide	American Cyanamid Co. Industrial Chemicals Division Wayne, New Jersey	(22)
- -	Polyacrylic acid, mean mol wt 20, 000	Canadian Industries Ltd	(25)
- -	10% ethyl acrylate, 90% acrylic acid copolymer	Canadian Industries Ltd.	(25)

Tests have been conducted at the Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia using polymer additives as alkaline scale preventers (25). In these tests, it was found that polyacrylic acid (mean molecular weight 20,000) and a copolymer of 10% ethyl acrylate and 90% acrylic acid, were effective in preventing scales at temperatures up to 240 F. The mechanisms involved appeared to be: (a) the deflocculating action of the polymer, and (b) the formation of a thin-film on the heat exchange surface, which periodically strips off and reforms. The "regenerating film" mechanism apparently carries away a small amount of scale compound which has been deposited on the film.

#### (4) Seeding and Sludge Recycle

Crystals grow much more rapidly if nuclei or "seeds" are present on which they can grow. By introducing fine "seed" crystals into a brine stream, scale-forming compounds, which are supersaturated in solution, can precipitate preferentially on the seed crystals rather than on heat exchange surfaces. The resulting sludge remains suspended in blow-down, leaving no deposits in the evaporator. This "seeding" technique has been applied successfully in a number of process industries. Calcium sulfate scale can be prevented in salt evaporators by maintaining a suspension of calcium sulfate crystals in the salt concentrating evaporators.

It is not necessary that the seed crystals even be the same material as the precipitating scale compound, although usually either calcium carbonate or calcium sulfate crystals have been used.

A variation of the seeding technique is called "contact stabilization". In the contact stabilization process, supersaturated brine is withdrawn from the evaporator before the scale has had time to deposit. The supersaturated brine is passed through a bed of sand or limestone, where the scale compound precipitates on the granular material. The brine, after being depleted in the scale-forming compound, is returned to the evaporator.

Seeding was demonstrated as a technique of scale control in the LTV pilot plant operated for the Office of Saline Water at Wrightsville Beach, North Carolina (26)..

In these tests, calcium carbonate, magnesium hydroxide and calcium sulfate seeds were used. The use of calcium sulfate seeds was found to present operating difficulties due to the formation of calcium sulfate hemihydrate "plaster" in any area where the liquid was cooled somewhat. While calcium carbonate seeding proved successful at lower temperatures, magnesium hydroxide scale formed with a top brine temperature of 250 F, and the calcium carbonate seeds were gradually replaced by magnesium hydroxide. The use of a magnesium hydroxide slurry proved successful in preventing scale formation at 250 F, and was selected for use as the scale-control means in the Freeport, Texas demonstration plant.

The "sludge recycle" system is a modification of the seeding technique, in which a portion of the brine blowdown is recycled and fed into the makeup water. In this way, it should be possible to operate with a self-perpetuating sludge once the distillation process is under way.

As mentioned above, the Freeport, Texas LTV Demonstration Plant was designed to use a slurry of magnesium hydroxide crystals for scale control. The slurry was added to the deaerator sump, with the solids being recovered from the brine reject stream. However, calcium carbonate scale formed on a downstream control valve stem and made it inoperable. The precipitation of calcium carbonate scale has been attributed to a higher magnesium hydroxide solubility than had been expected from published solubility data. This caused an unexpectedly high pH, which converted bicarbonate to carbonate and precipitated calcium carbonate. After only two days' operation the magnesium hydroxide sludge recycle was abandoned, and sulfuric acid pH control has since been used for alkaline scale control. It has been suggested that the problem could have been circumvented by adding the magnesium hydroxide seeds after preheating to a higher temperature (21).

As part of its experimental program on scale control in distillation plants, Baldwin-Lima-Hamilton Corporation evaluated sludge recirculation (22). Both calcium carbonate and calcium sulfate sludges were employed in a six-stage

MSF distillation pilot plant. Using sludges containing from 1.5% to 3% by weight of calcium carbonate, runs of up to 920 hours were made with a brine concentration factor of 1.7. The heat-transfer rates decreased by only 30% in the condenser section of the heat recovery stages during the 920-hour run at a maximum brine temperature of 250 F. Comparable data at a maximum brine temperature of 300 F could not be obtained because of extensive formation of calcium sulfate, magnesium hydroxide and calcium carbonate scale in the brine heater tubes.

The calcium sulfate sludge recirculation tests were unsuccessful when the calcium sulfate was introduced near the cold end of the flash evaporator train. The calcium sulfate crystals dissolved into the brine at the low-temperature end of the process. If the brine concentration was increased to prevent this, heavy deposits of calcium sulfate scale were formed in the brine heater tubes.

Other tests were conducted by Baldwin-Lima-Hamilton on an LTV pilot plant, using a combination of sulfuric acid injection to control alkaline scales, and using calcium sulfate sludge recirculation at the high-temperature end of the plant. It was concluded that this process should be investigated further as a method of scale control in distillation plants operating at temperatures above 250 F (22).

#### (5) Ion-Exchange Pretreatment

If the concentration of the scale-forming constituents in saline water could be reduced economically, it would be possible to achieve higher operating temperatures and higher brine concentration factors. Calcium sulfate scaling is the area of principal concern, since calcium carbonate and magnesium hydroxide scales can be avoided by acid injection and decarbonation. In theory, the calcium sulfate scaling limits can be raised by removing either the calcium ions (cations) or the sulfate ions (anions). In seawater, there are more than twice as many chemical equivalents of sulfate ions present as there are of calcium. The selectivity ratio of available ion-exchange resins is better between sodium and calcium ions than it is between sulfate and chloride ions. Finally, cation-exchange resins are less expensive than anion-exchange resins. For these reasons, it is easier to remove the calcium ions than the sulfate ions.

A cation-exchange process has been devised to lower the calcium ion concentration in the saline water feedstream (23). This process is depicted schematically in Figure IV-35. In this process, calcium goes into the resin and displaces sodium ions, which then replace the calcium in the entering saline water stream. Brine blowdown returning from the distillation unit is concentrated with sodium ions. This brine blowdown is used to regenerate the ion-exchange resin by releasing the calcium from the resin and replacing it with sodium.

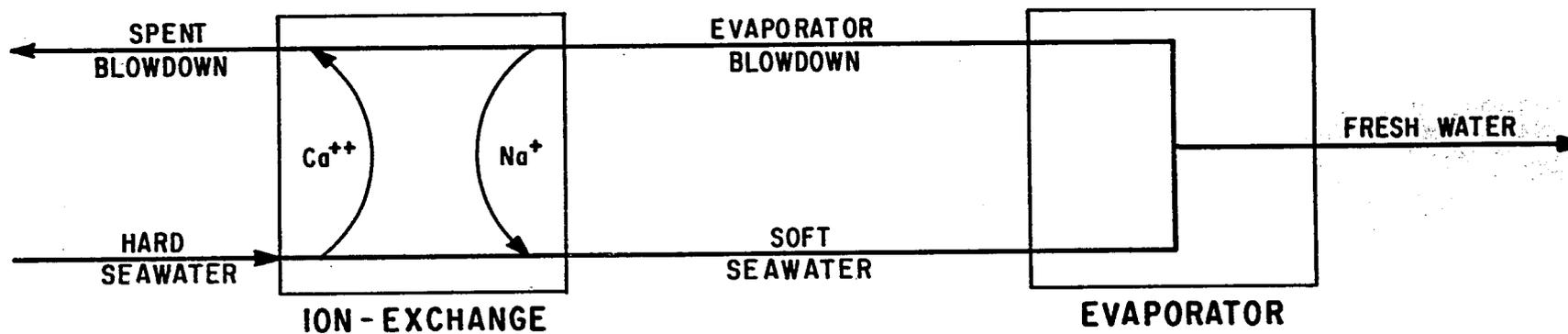
It is not necessary to remove all of the calcium from the feedstream to effect a considerable improvement in the scaling limits of seawater. Figure IV-36 shows the solubility limits of calcium sulfate dihydrate (gypsum) and calcium sulfate anhydrite for normal seawater, and for seawater with 50% and 75% of the calcium ions removed

A flowsheet for a multiple-stage ion-exchange process is shown in Figure IV-37. This process employs two softening stages (S-I and S-II) and three regeneration stages (B-I, B-II and B-III). The resin is contacted with influent seawater or brine blowdown in each column. The resin and seawater or brine flow concurrently to a cyclone separator, where the resin and liquid stream are separated. The resin is conveyed as a slurry to the next stage. This process, which removes 75% of the calcium ions from the raw seawater stream, would permit maximum brine temperatures of 435 F and brine concentration factors of 4.8 in the blowdown (23).

#### (6) Lime-Magnesium Carbonate Process

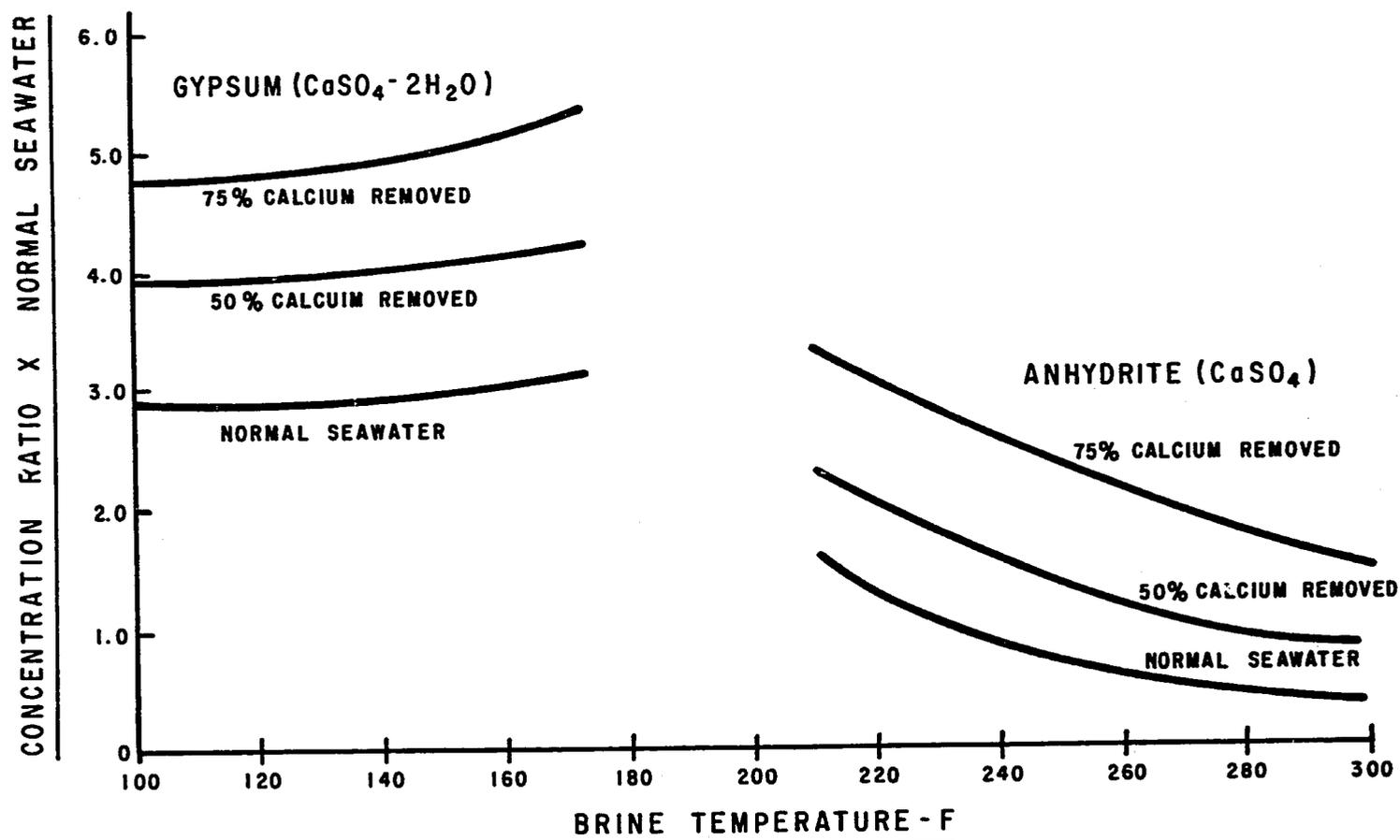
W. R. Grace & Co has devised a lime-magnesium carbonate process for removing calcium ions from seawater (27). The process involves the addition of magnesium carbonate trihydrate ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ) to seawater to precipitate the calcium from solution as calcium carbonate ( $\text{CaCO}_3$ ). The addition of lime ( $\text{CaO}$ ) to seawater converts bicarbonates ( $\text{HCO}_3^-$ ) in seawater to carbonates, and causes more calcium carbonate to be precipitated. Tests of the process, which began in 1964, have indicated that as much as 88% of the calcium present in seawater can be removed by the process.

FIGURE IV - 35  
ION-EXCHANGE SOFTENING FLOW DIAGRAM



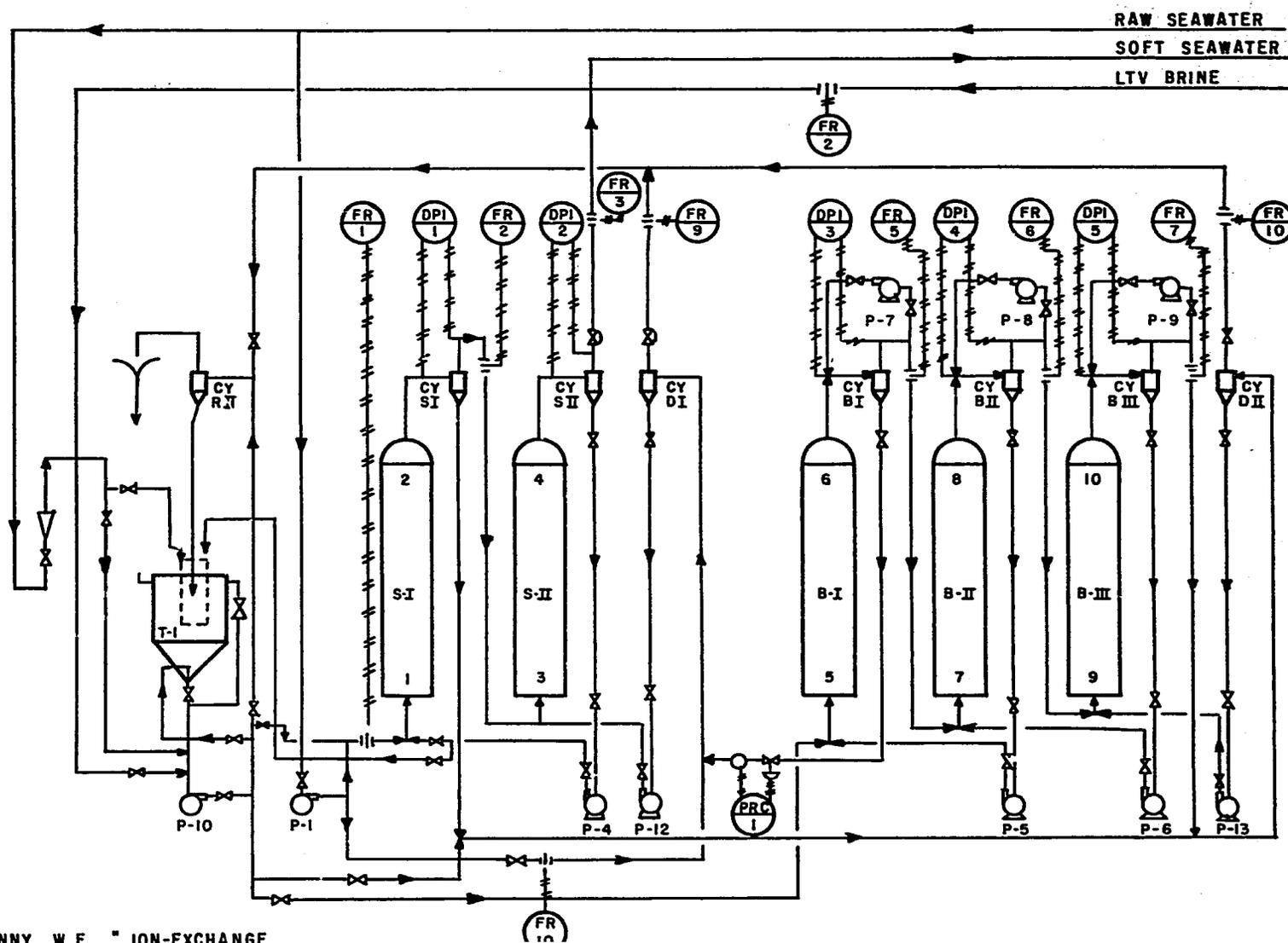
SOURCE: McILHENNY, W.F., "ION-EXCHANGE  
PRETREATMENT," FIRST INTERNATIONAL  
SYMPOSIUM ON WATER DESALINATION  
SWD/20, OCT 3 TO 9, 1965, WASHINGTON D.C.

FIGURE IV-36  
SOLUBILITY OF CALCIUM SULFATE IN CONCENTRATED  
SEAWATERS AT VARIOUS TEMPERATURES



SOURCE: MC ILHENNY, W.F., "ION-EXCHANGE  
 PRETREATMENT," FIRST INTERNATIONAL  
 SYMPOSIUM ON WATER DESALINATION  
 SWD/20, OCT 3 TO 9, 1965, WASHINGTON, D. C.

# ION-EXCHANGE FLOW SHEET CONTINUOUS STAGED OPERATION



SOURCE: MC ILHENNY, W.F., "ION-EXCHANGE PRETREATMENT," FIRST INTERNATIONAL SYMPOSIUM ON WATER DESALINATION, SWD/20, OCT 3 TO 9, 1965, WASHINGTON, D.C.

The lime required for the process is obtained by heating the precipitated calcium carbonate to produce lime (CaO) and carbon dioxide (CO<sub>2</sub>) gas. Some of the lime is used to precipitate magnesium hydroxide, Mg(OH)<sub>2</sub>. Flue gases from the calcining operation contain 12% CO<sub>2</sub> and are used to carbonate the magnesium hydroxide and thus produce the required magnesium carbonate.

The seawater treatment costs have been tentatively estimated at 5 to 7 cents per 1,000 gallons of fresh water produced, based on a 10-mgd distillation plant (27). Continuous work is being directed toward further evaluating the technical and economic potential of the process.

### c. Corrosion of Materials by Saline Water

#### (1) General

Corrosion considerations play an important part in the materials selected for, and in the cost of water produced by a saline water conversion plant. In addition to the effect of corrosion considerations on the capital cost of the plant, corrosion will affect operating and maintenance costs for replacement of components and for retubing heat exchangers and condensers, and will affect the plant availability. In a large seawater desalting plant utilizing evaporator units with a large number of tubes, the occurrence of the tube failures can have a significant effect on the plant reliability. This is because the larger the number of tubes in a given unit, the higher the probability that a given number of tube failures will occur within a given operating period.

Buildings and process equipment exposed to aerosol salt spray or mist near the ocean may be subject to serious corrosion. To the extent possible, the site location and layout should be chosen to minimize the exposure of buildings and equipment to aerosol salt spray from the marine environment.

In the MSF distillation process, the pressure of the brine circulated through the condenser sections is higher than the ambient pressure in a particular flash stage. This means that if a leak develops in a tube, the direction of

the leak is such that the salinity of the product water will increase. In the LTV process, however, the pressure in the condensing freshwater side of the unit is higher than that of the evaporating brine, so that a tube leak is not so critical from the standpoint of product water contamination. However, the thermal performance of the LTV unit is sacrificed. In an operating desalting plant, before a unit is shut down for retubing, a decision would have to be reached as to how much degradation of product water purity or plant thermal performance could be tolerated.

In a dual-purpose power-water desalting plant, shutdowns of the desalting plant for inspection and maintenance would be scheduled to coincide as nearly as possible with periodic shutdowns of the power plant for inspection and maintenance. Provision should be made in the design for pumps, piping and particularly heat exchanger tube-bundles to be accessible for inspection, repair and replacement.

The selection of materials for a desalting plant is essentially an economic trade-off between choosing lower priced, shorter-lived materials (which will result in higher maintenance and replacement expenses, and either a larger number of installed spares or a lower plant reliability factor) and higher-priced longer-lived materials (which will result in a higher plant reliability factor, decreased maintenance costs and fewer installed spares).

The material-selection criteria will differ appreciably, depending on the particular desalting process under evaluation. For instance, distillation processes generally are more susceptible to corrosion than are freezing plants, because they operate at higher temperatures.

Many metallic materials depend on the presence of a tightly adhering oxide film to reduce the corrosion rate. New condenser tubes sometimes experience a rapid corrosion attack during the initial period following installation, before the protective film has had a chance to develop fully. The resistance of aluminum and titanium to corrosion depends on the presence of a tightly adhering oxide film. In the case of aluminum, the corrosion rate in deaerated water is higher than that in aerated water. The resistance of aluminum to

corrosion depends on the presence of dissolved oxygen in the seawater to maintain its passivity. Thus, the deaerated seawater normally used in distillation plants might be detrimental to aluminum equipment. Again, in the case of titanium, an oxidizing medium must be present to maintain the passive film. Thus, the corrosion rate of titanium in aerated water should be somewhat lower than that in deaerated water.

It is the accepted theory that the corrosion of metals is electrochemical in nature, i. e. , that corrosion will tend to take place in those areas or regions (called the anodic region) in which the metallic ions can go into a solution and leave electrons behind. A corrosion cell also contains a cathodic region, where certain ions, usually hydrogen, tend to deposit from solution. Corrosion can be interrupted by any mechanism which tends to disrupt the overall operation of the corrosion cell. The electrons released in the anodic regions are conducted through the base metal to the cathodic regions. Hydrogen ions ( $H^+$ ) are neutralized (or reduced) in the cathodic regions, and form atomic hydrogen which accumulates as an invisible layer on the cathode. If the layer of atomic hydrogen builds up sufficiently, the counterelectromotive force of the hydrogen opposes cell current flow and retards the corrosion reaction (28). This phenomenon is known as polarization. If dissolved oxygen is present in the saline water, it will diffuse to the cathodic area and react with the hydrogen to form water. Thus, the presence of dissolved oxygen tends to reduce polarization and allow corrosion to continue.

Also, the properties of the saline water being processed will influence the choice of materials, since corrosion is affected by many variables, including salinity, oxygen concentration, pH, temperature, presence of living organisms and pollution. The analysis for bacteria, gas content, the ratio of ferrous to ferric ions and other properties which would change rapidly during transportation should be made near the source rather than in a distant laboratory (29).

## (2) Variables Affecting Corrosion

### (a) Oxygen

At atmospheric pressure, the solubility of oxygen in saline water and seawater is approximately 8 ppm. For most metals (excluding aluminum and titanium) the corrosion rate increases with increasing oxygen concentration. When the pH of the saline water is between 5 and 9 the corrosion of steel is controlled by the rate at which oxygen diffuses to the local cathodes. Oxygen removes the deposit of hydrogen from the cathodic areas, thus forming water. Thus, if the oxygen concentration is reduced the corrosion rate is decreased.

### (b) Salt Concentration

Generally speaking, the corrosion of most metals increases as the salt content of the water to which it is exposed increases. For steels, however, this only holds up to a salt concentration of 3% to 4% by weight. At higher salt concentrations the corrosion rate tends to decrease because of the lower solubility of oxygen in more concentrated brines.

### (c) Acidity (pH)

If the pH of the saline water is below 5 the solution can react directly with steel, liberating hydrogen without oxygen being present (29). Generally, the effect of low pH is to increase the corrosion rate of most metals. However, aluminum is more susceptible to corrosion in an alkaline environment (high pH).

### (d) Galvanic Corrosion

In evaluating the selection of materials for a saline water conversion plant it is important to keep in mind the effect of galvanic corrosion. Generally, galvanic corrosion occurs when two metals having a different electromotive potential are brought into electrical contact. The less noble metal acts as the anode, and the corrosive attack on the anodic material is accelerated. If the anodic area is small and the cathodic area is large

the corrosion rate of the anodic material can be quite large. However, if the reverse situation obtains, i. e., a large anodic area and a small cathodic area, the situation may be acceptable even though the anodic material will be corrosively attacked (30). Generally, it is preferred to use either the same material throughout or materials having close to the same electromotive potential to avoid galvanic corrosion problems (31).

(e) Differential-Aeration Cells (30)

Corrosive attack may also occur due to the formation of differential aeration corrosion cells. Crevices, areas under barnacles, other marine growths, and scale deposits will tend to be deficient in oxygen. These low-oxygen areas will act as the anode of a corrosion cell. The cathodic area is the exposed metal surface in contact with saline water having a higher oxygen concentration. The corrosive attack tends to occur under the deposits or in the crevice areas, frequently resulting in severe pitting.

(f) Anaerobic Bacteria

Certain saline waters which have a low oxygen concentration may contain anaerobic bacteria which can cause corrosive attack on various metals. Some of these anaerobic bacteria reduce sulfates to hydrogen sulfide. Alloys containing copper will be corrosively attacked and a black porous copper sulfide scale will be formed on the metal surface (32).

(g) Impingement and Cavitation

Another factor influencing corrosion is the velocity of the saline water stream in contact with the metal surface. The high-velocity impingement of liquids on a surface tends to erode or destroy the protective film, thereby exposing fresh metal to rapid corrosive attack. The inlet areas of condenser tubes are particularly susceptible to corrosion due to the turbulence introduced near the tube inlet (30).

A related phenomenon is cavitation. This occurs wherever the velocity of the liquid stream is high enough to reduce the static pressure of the liquid to less than the vapor pressure at that temperature. Bubbles will form in the area of cavitation and collapse downstream. The repeated hydraulic shock of the collapsing vapor bubbles tends to destroy the protective film and promote corrosion in the cavitation area. Pump impellers are particularly susceptible to corrosion due to cavitation (29). Resistance to erosion by flowing saline water is high for stainless steels, titanium and Hastelloy-C. The copper-nickels, aluminum and aluminum bronzes have somewhat lower resistance to erosion. Copper is particularly susceptible to erosion and cannot be used in any area where the velocity exceeds 2 feet per second.

(h) Temperature

Corrosion increases as the temperature of the saline water to which the metallic surface is exposed increases.

(i) Stress-Corrosion Cracking (31)

Another phenomenon is known as stress-corrosion cracking. This results in those areas which have high design or residual stresses. Aluminum brass and Admiralty metal are susceptible to stress-corrosion (or season) cracking, if stored in areas of high humidity where fumes are present. The copper-nickels have good resistance to stress-corrosion cracking.

(j) Pitting

Certain metals are susceptible to pitting corrosion if left in contact with stagnant seawater for prolonged periods. Aluminum-brass is more susceptible to pitting than some other copper alloys.

(3) Materials of Construction

(a) Steel

Steel is one of the most widely used materials of construction in desalination plants. This is primarily because it is less expensive than most alternative materials

which might be employed and has reasonably good corrosion properties under controlled conditions. It is used for the shells of distillation units and for pipelines. Carbon and low-alloy steels give acceptable performance in contact with deaerated saline water at temperatures up to 250 F (33). Various coatings, cement lining or cladding are sometimes applied to reduce corrosion of the carbon-steel base material (34).

Steel in contact with seawater experiences a fairly uniform rate of corrosive attack; however, it also is subject to pitting attack especially where large portions of the surface are covered with mill scale (30). Figure IV-38 illustrates the corrosion rate of carbon steel in aerated and deaerated water as a function of temperature (31).

#### (b) Aluminum

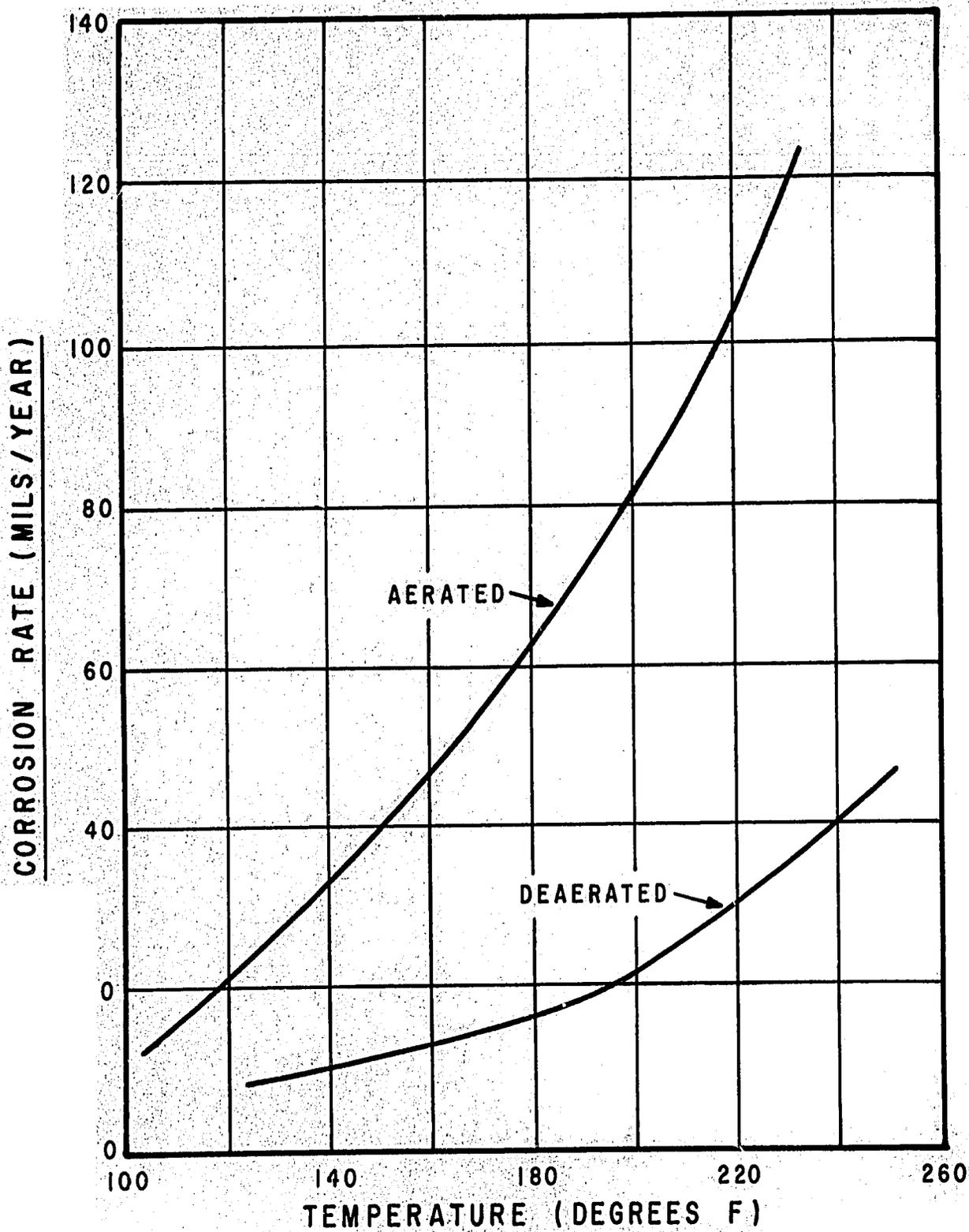
The use of aluminum is feasible in seawater processing plants if precautions are taken to reduce pitting and galvanic corrosion (33). Aluminum is particularly susceptible to pitting attack by heavy metal ions such as copper and nickel, although chloride ions also may cause pitting (33). No equipment containing copper or nickel alloys should be installed in the same process stream with aluminum equipment.

Direct electrical contact also should be avoided between aluminum and other metals. If aluminum is not insulated electrically from other metals, galvanic corrosion of the aluminum will occur, with the aluminum acting as the anode of the galvanic corrosion cell (33).

Aluminum's resistance to seawater corrosion is dependent on the maintenance of its protective oxide film. Thus, the corrosion rate of aluminum in deaerated seawater is higher than it is in seawater containing oxygen. It has been suggested (33) that the corrosion resistance of aluminum in contact with deaerated seawater may be improved by a thicker alumina coating obtained by anodizing.

Table IV-2 lists the chemical composition of some aluminum alloys which might be used in a water desalination plant (33). Type 1100, which is commercially pure

FIGURE IV-38  
CORROSION OF CARBON STEEL  
IN HOT SEAWATER



SOURCE: TUTHILL, A.H., INCO,  
"SUMMARY OF DURABILITY OF  
CONDENSER TUBE ALLOY FOR  
LARGE SALINE WATER CONVERSION  
PLANTS," MARCH 15, 1965

COURTESY: INTERNATIONAL  
NICKEL COMPANY

aluminum, exhibits a higher resistance to seawater corrosion than the wrought or cast aluminum alloys (33). The high-strength 2000 series alloys, containing copper, have the poorest corrosion resistance. However, these high-strength aluminum alloys can be protected by cladding them with either commercially pure aluminum or an aluminum-zinc alloy. This cladding is selected not only because of its better corrosion resistance but also because it is slightly anodic to the base material.

(c) Copper -Base Alloys

The high-copper alloys (brasses, bronzes and copper-nickels) are widely used for seawater service because of their corrosion resistance, erosion resistance, high thermal conductivity and resistance to fouling by marine organisms. Table IV-3 lists the chemical composition of some high copper alloys used in desalination plants (33).

Both admiralty-brass and aluminum-brass are used extensively as tubing materials for heat exchangers and condensers. Arsenic is added to inhibit dezincification and the resulting loss of strength. Because of the addition of aluminum, aluminum-brass has better resistance to erosion and impingement; however, it is more susceptible to pitting in stagnant seawater.

TABLE IV-2

CHEMICAL COMPOSITION OF SOME ALUMINUM ALLOYS  
RESISTANT TO SEAWATER CORROSION (WEIGHT PERCENT)

<u>Aluminum Alloy</u>	<u>Al</u>	<u>Fe</u>	<u>Cr</u>	<u>Cu</u>	<u>Zn</u>	<u>Mg</u>	<u>Mn</u>	<u>Si</u>	<u>Other</u>
1100	99*	-	-	0.20	0.10	-	0.05	-	-
3003	97.1	0.70	-	0.20	0.10	-	1.25	0.60	-
5056	93.0	0.40	0.70	0.10	0.10	5.00	0.10	0.60	-
6061	96.6	0.70	0.25	0.28	0.25	1.00	0.15	0.60	0.15 Ti
43 (casting)	93.2	0.80	-	0.10	0.20	0.05	0.30	5.3	-

\* Minimum

TABLE IV-3

CHEMICAL COMPOSITION OF HIGH-COPPER ALLOYS  
RESISTANT TO SEAWATER CORROSION (WEIGHT PERCENT)

<u>Copper Alloy</u>	<u>Cu</u>	<u>Zn</u>	<u>Fe</u>	<u>Ni</u>	<u>Al</u>	<u>Sn</u>	<u>Mn</u>	<u>Si</u>	<u>Other</u>
Arsenical Admiralty	71	28	-	-	-	1	-	-	0.03 As
Aluminum-Brass + As	77	21	-	-	2	-	-	-	0.03 As
Aluminum Bronze	(89.5- 94.5)	-	0.50	-	5-9.5	-	-	-	-
Silicon Bronze	94.8	-	-	-	-	-	-	3.3	-
Phosphor (Sn) Bronze	89.7	-	-	-	-	10	-	-	0.25P
90-10 Cu Ni (Fe mod)	88.3	-	1.3	10	-	-	0.4	-	-
70-30 Cu Ni (Fe mod)	68.9	-	0.5	30	(0.5- 1.5)	-	0.6	-	-

Source: Moore, R. E., "Materials for Water Desalting Plants",  
 Part 2, Chemical Engineering, October 14, 1963

The bronzes (copper-tin, copper-aluminum, and copper-silicon) are not used as extensively in seawater service as the brasses (33). Tin (or phosphor) bronze has been used in England for condenser tubes subjected to erosive or corrosive conditions (30) (33). Tin bronze has good resistance to erosion by seawater, but its higher cost has deterred more extensive usage (33). Aluminum-bronze has high resistance to cavitation erosion, and has been used for pumps, impellers and valves (33). At low flows, aluminum bronze is subject to severe pitting corrosion.

The copper-nickels give excellent resistance to corrosion by seawater both under low- and high-velocity flow

conditions. The two most commonly applied alloys are 90-10 copper-nickel and 70-30 copper-nickel. Both alloys are modified by the addition of iron which increases their resistance to impingement attack.

The most commonly used tubing alloys for seawater service are admiralty-brass, aluminum-brass, 90-10 copper-nickel, and 70-30 copper-nickel. Figure IV-39 shows the percentage of tubing failures as a function of time for these alloys, under both severe and mildly aggressive conditions. These data show that the lowest tube failure rate is experienced with the copper-nickels. However, these materials are also more expensive than the brasses. Some manufacturers recommend the use of aluminum brass tubing because of its lower cost and satisfactory corrosion resistance. The choice of tubing material for a particular application is primarily one of economics, taking into consideration first cost, interim replacements and the effect of tubing failures on plant availability. Since the precise failure rate cannot be predicted in advance, the choice will also involve a good deal of judgment on the part of the plant designers.

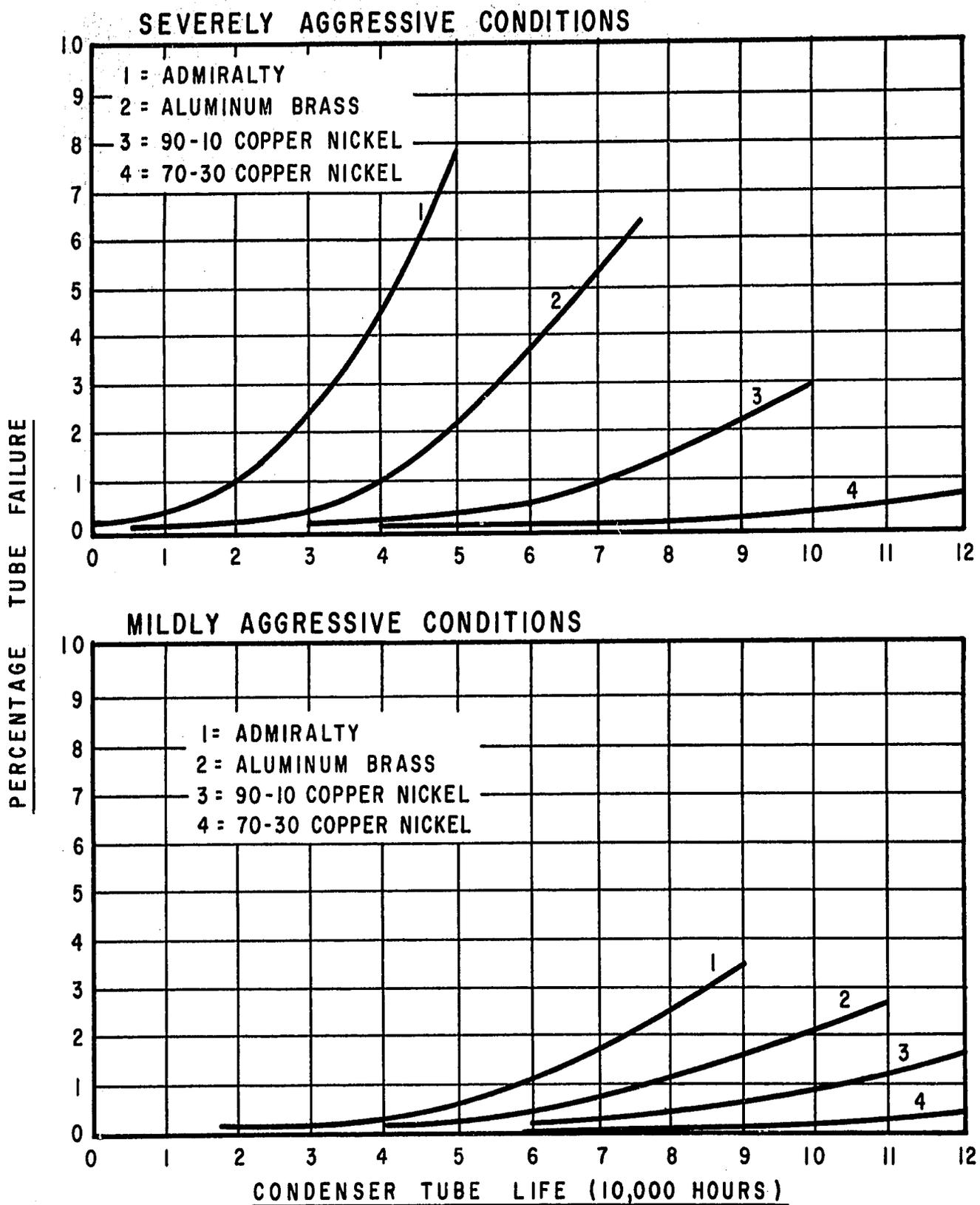
#### (d) Nickel-Base Alloys

The compositions of the high-nickel alloys, Monel, K-Monel, Inconel, Inconel-X and Hastelloy-C are given in Table IV-4.

Monel has a higher resistance to seawater corrosion at high temperatures and velocities than even the copper-nickels. It is considered one of the best alloys for seawater service in a diversity of applications such as pumps, impellers, piping, heat exchangers, valves and fittings (30). Although Monel has a high resistance to corrosion in dynamic seawater, it is subject to pitting on prolonged exposure to static seawater (33).

Inconel and the age-hardenable Inconel-X are even more resistant to corrosion by high-temperature seawater at high velocity than either Monel or the copper-nickels. Inconel is not subject to chloride stress-corrosion cracking as are the austenitic stainless steels (33). Like

FIGURE IV-39 (a)  
RELATIVE PERFORMANCE OF  
COPPER ALLOY TUBES IN SEAWATER

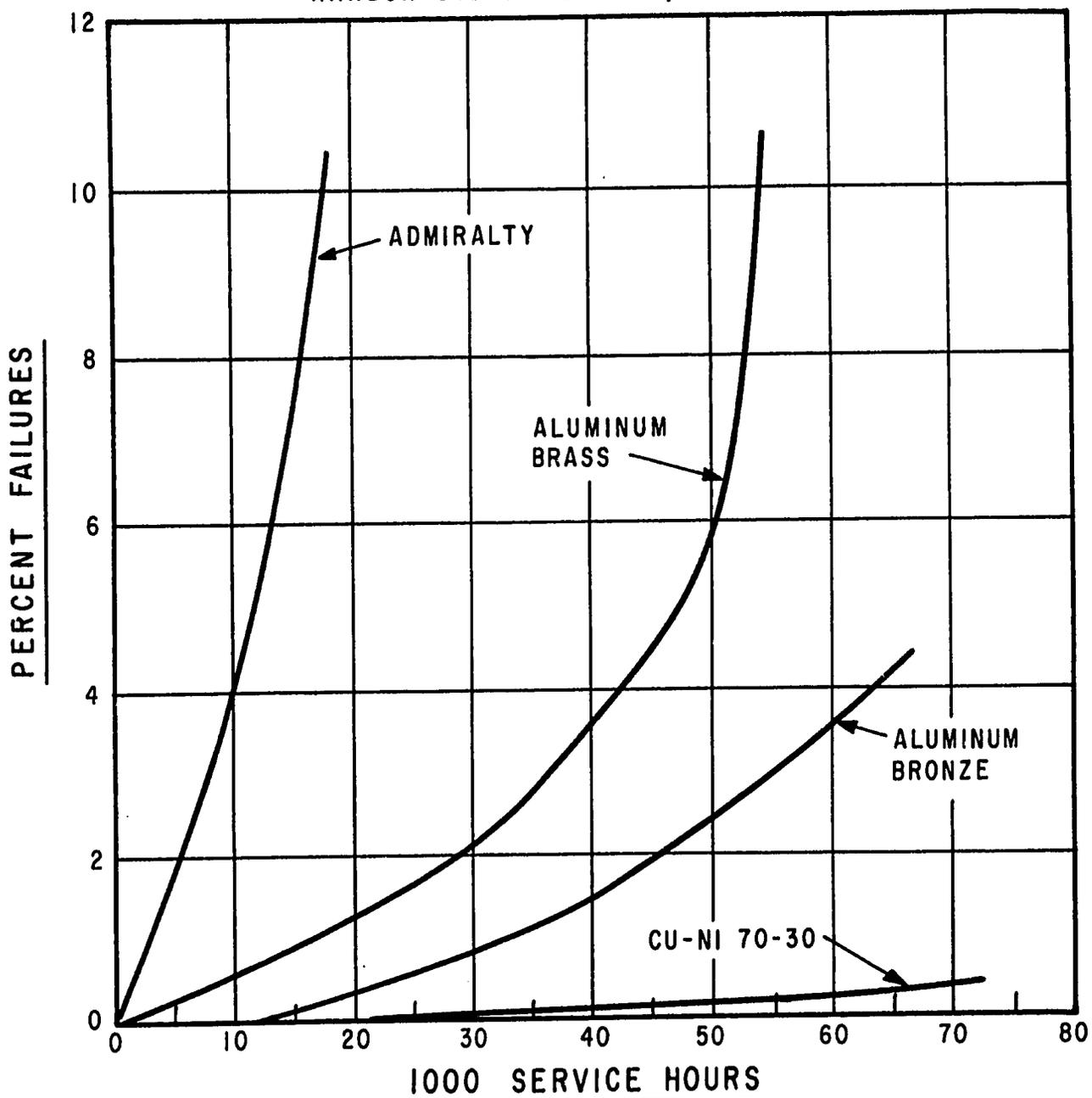


SOURCE: TUTHILL, A.H., "SUMMARY OF DURABILITY OF CONDENSER TUBE ALLOYS FOR LARGE SALINE WATER CONVERSION PLANTS," MARCH 15, 1965

FIGURE IV-39(b)

RELATIVE PERFORMANCE OF  
COPPER ALLOY TUBES IN SEAWATER

PERFORMANCE OF CONDENSER TUBES  
HARBOR STEAM PLANT 1947 TO 1959



SOURCE: TODHUNTER, H.A., "HARBOR PLANT  
STUDY SOLVES CONDENSER TUBE PROGRAM,"  
POWER ENGINEERING, JUNE 1960

TABLE IV-4CHEMICAL COMPOSITION OF HIGH-NICKEL ALLOYS  
RESISTANT TO SEAWATER (WEIGHT PERCENT) (33)

<u>Nickel Alloy</u>	<u>Ni</u>	<u>C</u>	<u>Fe</u>	<u>Cr</u>	<u>Al</u>	<u>Cu</u>	<u>Mn</u>	<u>Si</u>	<u>Other</u>
Monel	67.3	0.15	1.40	-	-	30	1.00	0.10	-
K-Monel	66	-	0.90	-	2.75	29	1.00	0.50	-
Inconel	75.4	0.15	8.00	15.5	-	0.50	0.20	0.20	-
Inconel-X	73	0.04	6.75	15.0	0.80	0.05	0.70	0.30	0.85Cb
Hastelloy-C	(55.4- 58.4)	0.08*	4-7	15.5	-	-	1.00*	1.00*	4W, 16Mo

\*Maximum

Source: Moore, R. E., "Materials for Water Desalting Plants,"  
Part 2, Chemical Engineering, October 14, 1963

Monel, however, Inconel is subject to pitting by stagnant seawater (33). Both Monel and Inconel are high-priced materials and their use is limited to applications where the corrosion and erosion resistance of less expensive materials is unsatisfactory.

Hastelloy-C, an alloy of nickel, molybdenum and chromium, has outstanding resistance to corrosion by hot seawater under both high-velocity and quiescent flow conditions. Again, this is a premium-priced material whose use should be limited to applications where less expensive materials are inadequate.

(e) Titanium

Generally, titanium has been reported to have outstanding resistance to seawater corrosion (30) (33). It is not susceptible to stress-corrosion cracking or impingement

attack in seawater flowing at velocities up to 50 feet per second. Recent observations at the Oak Ridge National Laboratory indicate that titanium may be susceptible to crevice-initiated corrosion in saline solutions above 100 C (27). This corrosion was initiated in crevices where semistatic flow conditions existed. Although the initiation was somewhat erratic, once the corrosion started it was often self-sustaining into regions beyond the crevice.

An MSF distillation plant built for Harvey Aluminum at St. Croix in the Virgin Islands is the first desalting plant to use titanium tubing. The plant employs over 100 miles of thin-wall (0.028 in.) titanium tubing, plus titanium tube sheets and flash evaporator components.

(f) Concrete

Concrete has been suggested as a material of construction for large vacuum vessels in MSF distillation plants (34). Some uncertainties in the use of concrete for reinforced concrete vessels include its resistance to corrosion by high-temperature seawater, possible corrosion of reinforcing steel by chlorides which might diffuse into the concrete, and whether lining materials will be required above some temperature level.

The Bureau of Reclamation has initiated an OSW-sponsored research program to determine the durability of concrete under long time exposure to high-temperature seawater (27). Concrete samples exposed for 180 days to 100 F seawater showed no deterioration in physical properties. Specimens which had been exposed to 290 F seawater showed a small degradation in compressive strength after 180 days exposure. This change was attributed to softening of the surface to form a paste extending to a depth of 1.5 to 5 millimeters. Distilled (product) water was found to cause rapid erosion and leaching of concrete specimens.

## B. Freezing and Crystallization Processes

### 1. Freezing and Crystallization Phenomena

#### a. General

The conversion of saline water to fresh water by freezing, as it occurs in nature, has been known for thousands of years. For example, fishermen collect sea ice from the Aral Sea during the winter and store it for summer use as fresh water (35). For many generations, inhabitants of Siberia have collected ice from saline water and allowed it to melt in the sunlight for use in watering their cattle (35).

Freezing and crystallization processes involve the removal of water, in the form of either ice crystals or hydrate crystals, from the surrounding brine; this leaves behind a more concentrated brine solution. Basically, these processes involve three steps. The first is a freezing or crystallization step, in which crystals containing essentially pure water are frozen in the brine. The second step is the separation and washing of these crystals. The third and final step is the melting or decomposition of the crystals to form fresh product water. There are a number of other auxiliary steps such as using the cold product water and cold brine reject streams to precool the incoming saline water stream, and providing auxiliary refrigeration to remove both heat which leaks into the system and work which is put into the system by compressors, pumps, scrapers, agitators and other mechanical devices.

When saline water is partially frozen, the individual ice crystals formed are pure water. The salts are left in solution, causing the remaining liquid to have a higher salt concentration. If the ice could be completely separated from the saline solution and melted, very pure water would be produced. As ice freezes, however, some of the brine is trapped in the interstices between the ice crystals. To produce potable water by freezing, a portion of the product water must be used to wash the occluded brine from the ice.

Figure IV-40 shows two pictures of growing ice, taken at the Westinghouse Research Laboratories. View (A) shows ice growing into distilled water with a planar interface. View (B) shows ice growing into seawater under the same conditions. Note that in View (B) the ice crystals are of the dendritic form. From View (B) it is easy to visualize how concentrated brine can become trapped in the interstices between ice crystals frozen from saline water.

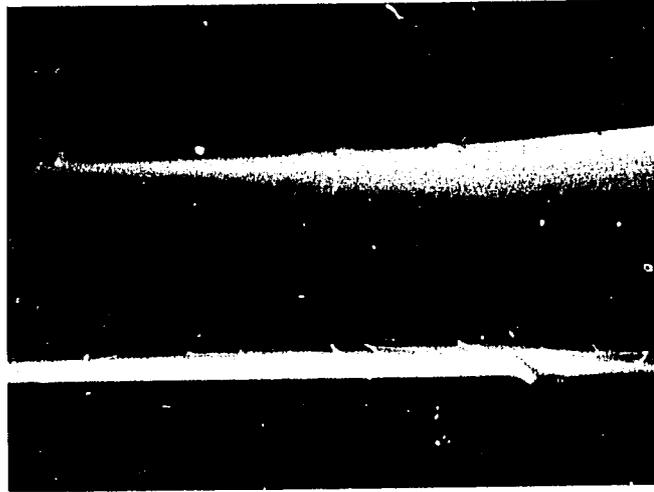
The mechanism of ice crystallization in saline water is not well understood, although considerable research has been done in this area and is continuing at a number of educational and research institutions. Primarily, the freezing of ice crystals involves both heat transfer and mass transfer. The freezing water must diffuse from the bulk brine solution to the solid-liquid interface, and salt must diffuse back into the bulk brine solution. The size and configuration of the crystals formed depends on a number of parameters, including the salinity of the surrounding solution, the amount of subcooling, the nucleation rate and the rate of solidification.

Ice crystals formed from pure water are essentially hexagonal plates (35). There are several ways in which the size of the ice crystals can be determined. One method which has been used by Carrier Corp. is based on permeability measurements; it yields an equivalent diameter of a spherical particle having the same volume as the ice crystal. The diameter of the hexagonal disk would be somewhat larger than this reported equivalent diameter. Another method of determining crystal sizes is by observation under a microscope (36).

Generally speaking, as the water from which the crystallization takes place becomes more saline, the crystals formed are smaller. Thus, under similar conditions one would expect larger ice crystals to be frozen from brackish water than from seawater (36). The idealized hexagonal ice crystal has been described (37) as having three a-axes mutually separated by 120 degrees in the basal plane, and a c-axis perpendicular to the basal plane. The dimensions of the unit crystal cells are  $a = 4.5A$

FIGURE IV -40

GROWING ICE CRYSTALS



View A Ice Growing in Distilled Water

Note Grain Boundaries on Planar Interface

Growth Rate	1 cm/hr
Thermal Gradient	10 C/cm
Magnification	30 X



View B Ice Growing in Seawater

Growth Rate	1 cm/hr
Thermal Gradient	10 C/cm
Magnification	30 X

Courtesy: Westinghouse Electric Corporation

and  $c = 7.4A$  (see Figure IV-41). Subcooling is defined as the difference between the temperature of the bulk brine solution and that of the crystal interface (37). As ice crystals are formed slowly with a low subcooling, the growth velocity along the a-axes and the c-axis are approximately the same. If the subcooling is increased and crystal growth is accelerated, the growth velocity in the a-direction increases faster than that in the c-direction. Thus, as one progresses to higher subcooling and more accelerated crystal growth, the form of the crystals becomes plate-like and then dendritic. Apparently the effect of increased salt concentration at the brine-crystal interface has a greater retardant effect on growth in the c-direction than in the a-direction.

Another factor involved in crystal growth is the nucleation rate. Nucleation can be brought about by a number of methods (35):

- (1) Changes in the physical or chemical environment
- (2) Presence of existing crystals or other nucleating agents
- (3) Attrition of existing crystals
- (4) Agitation of the liquid phase

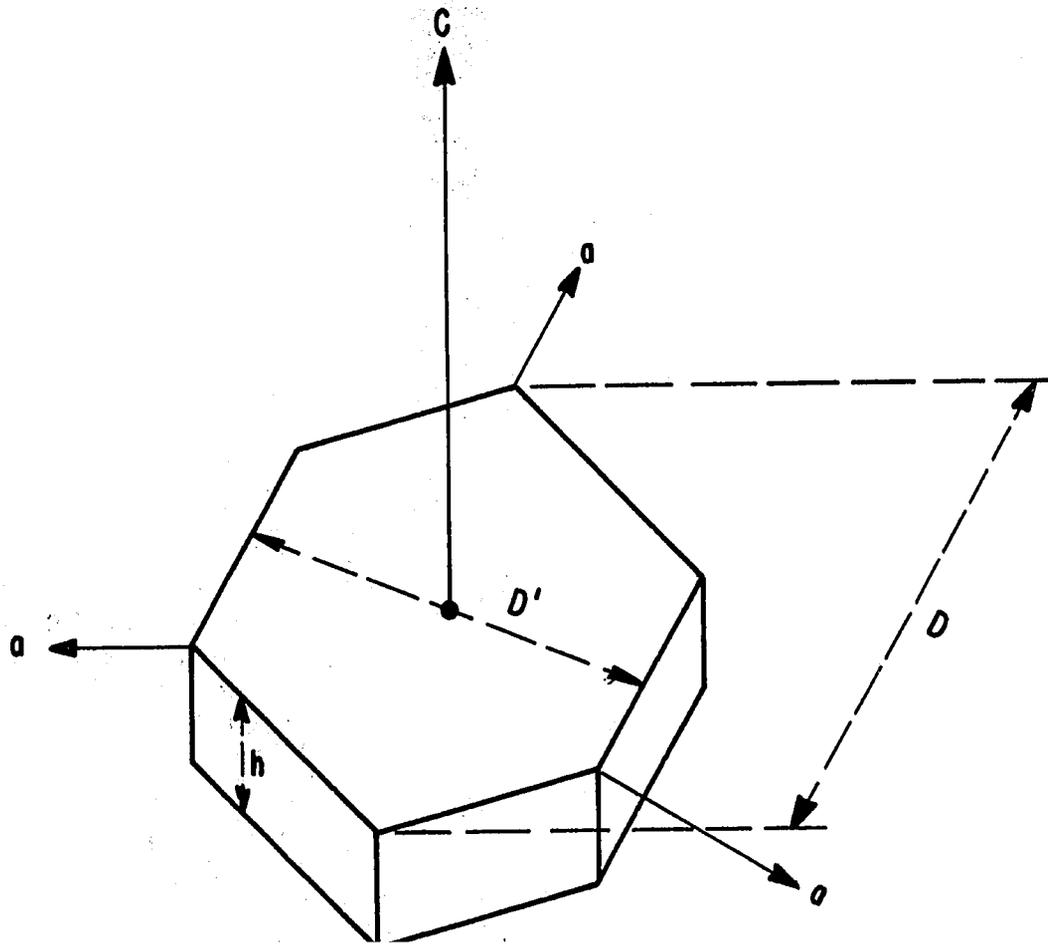
As the nucleation rate increases, the crystal size becomes smaller (37). In general, the nucleation rate increases as the subcooling increases.

When ice forms by growth at a cold surface, the crystal size and dendrite spacing increase as the solidification rate decreases (9).

The average sizes of crystals formed by various freezing and crystallization processes have been reported in the literature. The mean disk diameter of the ice crystals formed by the Carrier vacuum freezing process is approximately 190 microns ( $10^{-6}$  meter) (34). The mean disk diameter of the crystals formed by the Colt Industries vacuum freezing process is reportedly

FIGURE IV-41

IDEAL ICE CRYSTAL SHAPE



D = LONGEST DIAMETER  
D' = SHORTEST DIAMETER  
h = THICKNESS

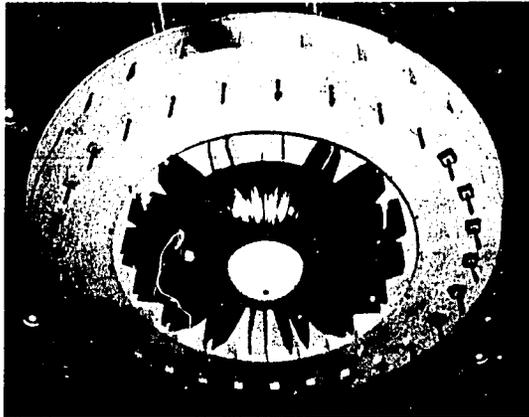
SOURCE: KAWASAKI, S. AND UMANO, S.,  
CORRELATION BETWEEN GROWTH RATE OF ICE  
CRYSTALS AND OPERATING CONDITION IN DIRECT  
CONTACT FREEZING PROCESS FOR CONCENTRATION  
OF SEAWATER, KAGAKU KOGAKU, 27, 218 (1963)

20% to 40% larger than that of the Carrier crystals (36). In both the Carrier process and the Colt process the residence time in the freezer was of the order of two to three minutes (36). Struthers Scientific and International Corp has reported on its controlled crystallization freezing process (37). In this process the residence time in the freezer varies from five to twenty minutes (36), and the crystal form is controlled by maintaining a low subcooling by agitation of the freezing brine-ice mixture in the freezer. Struthers has reported average crystallization sizes of 700 to 800 microns in diameter (37). The hydrate crystals formed by the Sweet Water Development Corp hydrate process are plate-like, and vary in size from 20 to 200 microns (38).

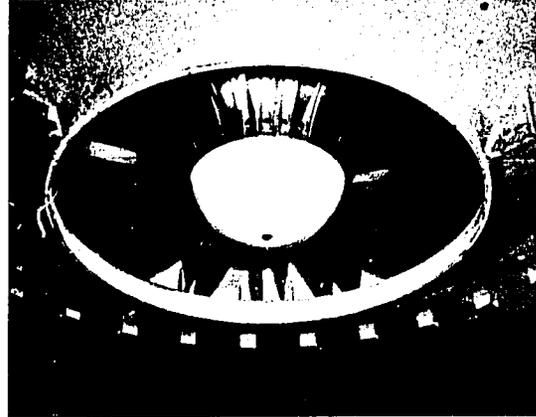
To freeze ice from a saline water solution, it is necessary to remove heat from the solution. This is accomplished in several ways, depending upon the process employed. In the indirect freezing processes, heat is removed through the wall of a tube containing a refrigerant or through the wall of a rotating drum as in a flake-ice type freezer. Thus, in indirect freezing, the heat must be transferred through the liquid film, through the solidified ice layer built up on the cold wall and through the wall into the refrigerant. In a vacuum freezing process, the heat removal is accomplished by rapid evaporation of water vapor from the surface of the freezing solution. Figure IV-42 shows the flexible bladed compressor employed in the vacuum freezing vapor compression process. The direct freezing processes using a secondary refrigerant introduce a liquefied refrigerant into the freezing brine solution. Figure IV-43 illustrates the mechanism of hydrate formation wherein liquid propane is introduced into freezing brine. Heat from the surrounding warmer brine is transferred to the cooler liquid drop. As this heat transfer takes place, a bubble of propane gas forms around the liquid drop, and heat must be transferred through the gas bubble to the drop. When the rising liquid drop reaches the brine surface, the bubble detaches itself from the drop and the drop is recirculated by the agitators. It is postulated that the hydrate crystals form at the interface between the liquid drop and the brine solution.

FIGURE IV -42

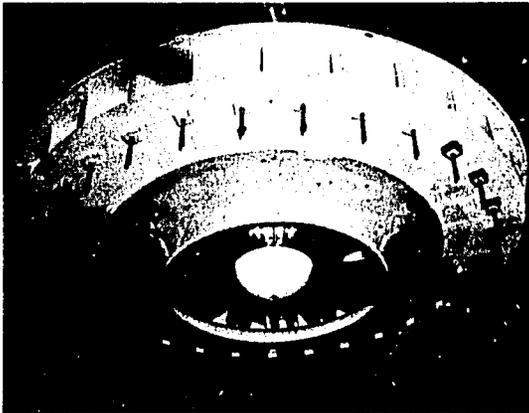
COMPRESSOR USED IN VACUUM FREEZING  
VAPOR -COMPRESSION PROCESS



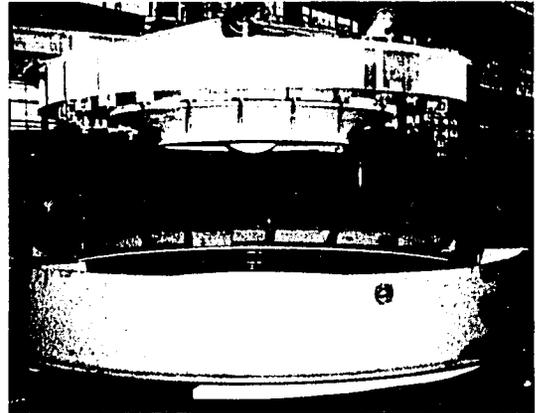
4 CM Compressor  
Lower shroud removed



Inlet eye, shroud installed



4 CM Compressor  
Lower shroud installed

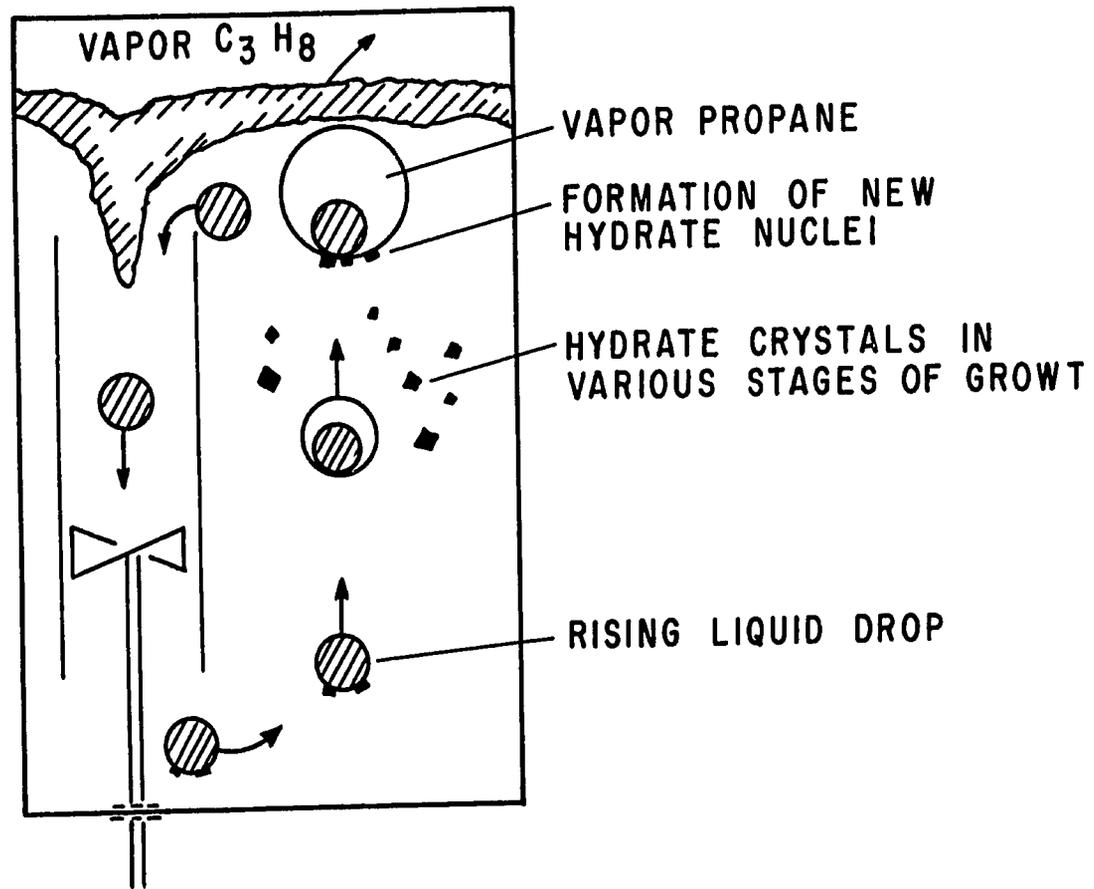


View showing adapter section  
with turning vanes

Source: U. S. Department of the Interior,  
Office of Saline Water

FIGURE IV-43

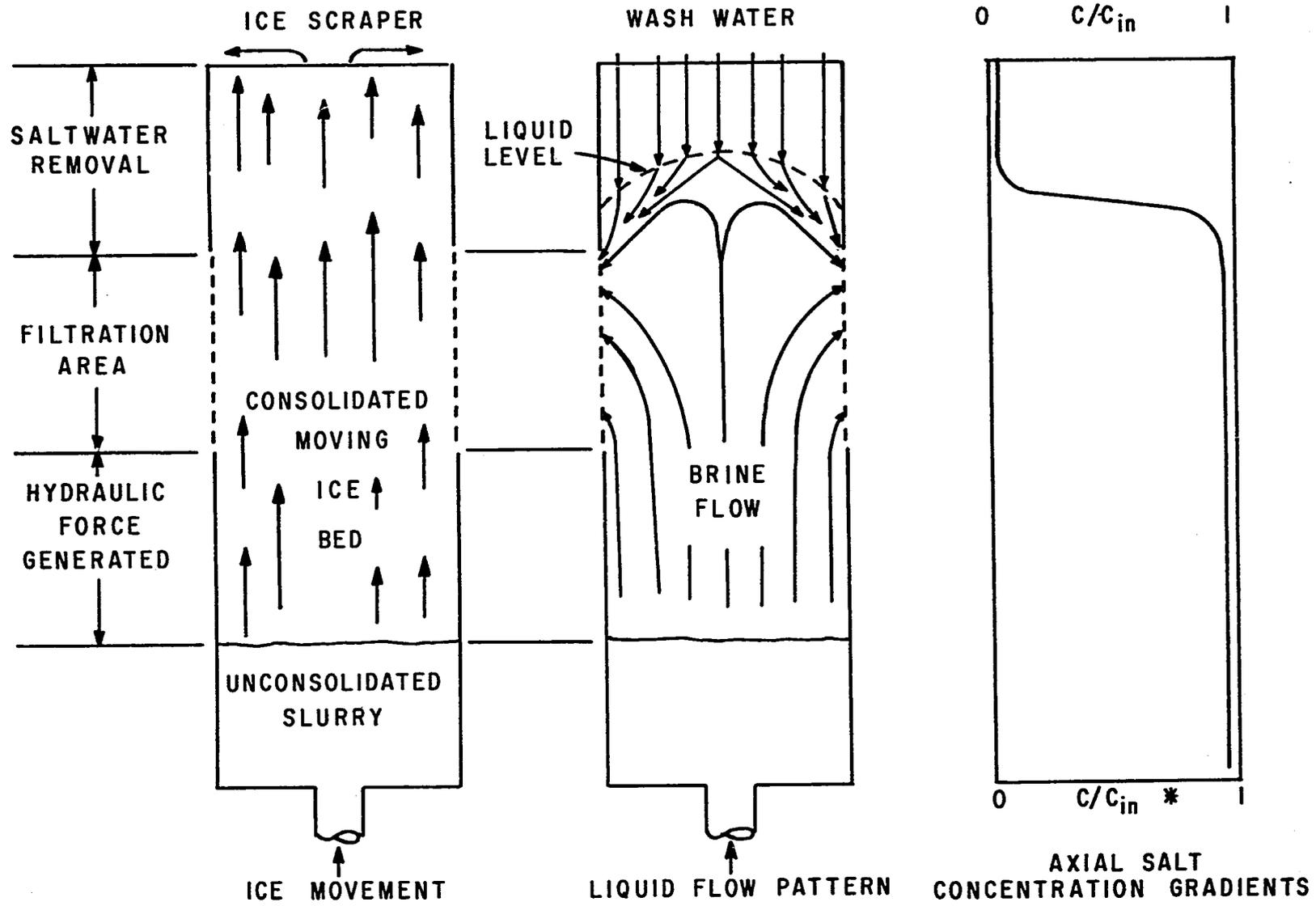
SCHEMATIC OF HYDRATE FORMATION PROCESS



SOURCE: WILLIAMS, V.C., ROY, C.L. AND  
WILLIAMS, R.A., "HYDRATE PROCESS PILOT  
PLANT," FIRST INTERNATIONAL SYMPOSIUM  
ON WATER DESALINATION, PAPER SWD/37  
OCT 3 TO 9, 1965

All of the freezing processes for desalting saline water require an efficient method for separating the ice crystals from the brine and holding to a minimum the loss of product water required for washing. Among the separation techniques which have been used for separating crystals from the liquid are vertical moving beds with countercurrent washing, centrifuges and cyclone separators. Professor Barduhn (36) has described the operation of the vertical moving-bed ice-brine separator with countercurrent washing, (see Figure IV-44). The unconsolidated slurry of ice and brine, containing 5% to 15% solids, enters at the bottom of the column and flows upward. The ice consolidates into a moving bed at some level. As the ice moves vertically past the screens in the side walls, the brine flows sideways out of the ice bed through the screens. Wash water comprising a small fraction of the fresh product water is introduced at the top of the column, and it washes the ice crystals countercurrently. The descending wash water stream removes any brine which is not drained from the ice. A scraper at the top of the column removes washed ice and any fresh water contained in the ice bed. The height of the ice bed below the filtration area is that necessary to provide the buoyant force necessary to push the ice column upward. The height of the bed above the filtration area is set by the vertical height necessary to provide space for the "brine hump" in the center of the column and to provide adequate drainage and washing. Professor Barduhn has developed an analytical model to describe the ice brine separation process. From this approximate analysis, it is concluded that larger crystals are no more easily washed than are small particles. By forming larger ice crystals, however, it should be possible to design a separation column with a higher ice flux without flooding the column. Actually there are two modes of operating such a column: one is a "drained" column condition and the other is a "flooded" column condition. As the column is operating "flooded," sufficient wash water is added so that there is a net flow of fresh water with the ice crystals out the top of the column. Table IV-5 lists the ice fluxes for different wash column designs from reference 36.

FIGURE IV-44  
WASH COLUMN MECHANICS



SOURCE: BARDUHN, A.J., "THE FREEZING PROCESS FOR WATER CONVERSION IN THE UNITED STATES," FIRST INTERNATIONAL SYMPOSIUM ON WATER DESALINATION, PAPER SWD/88, OCT 3 TO 9, 1965 WASHINGTON, D.C.

\* WHERE  $C$  = SALT CONCENTRATION IN LIQUID AT A GIVEN POINT IN COLUMN  
 AND  $C_{in}$  = INITIAL SALT CONCENTRATION

TABLE IV-5  
ICE FLUX FOR SOME  
WASH COLUMN DESIGNS

<u>Wash Column</u>	<u>Ice Flux (lb/hr per sq ft of column cross-section)</u>
Blaw-Knox (rectangular)	700
Colt	300
Carrier	165
OSW Column on Struthers' Wrightsville Beach North Carolina pilot plant	1,000

Source:

Barduhn, A. J., "The Freezing Processes for Water Conversion in the United States," SWD/88, FISWD, Oct 3 to 9, 1965, Washington, D. C.

As the amount of salt dissolved in water increases, the freezing point, i. e., the temperature level at which ice will form from the solution under equilibrium conditions, decreases. This phenomenon is referred to as freezing point depression. A chart of freezing point as a function of weight-percent sodium chloride is included in the Appendix. This freezing point depression is approximately proportional to the amount of salt dissolved in the water, and varies from 1.00 to 1.08 F per weight-percent sodium chloride, over a range of sodium chloride concentrations from 0 to 6% by weight (39). All hydrate crystals appear to have a similar depression at the formation temperature, which varies between 1.0 and 1.1 F per weight-percent sodium chloride up to 10% sodium chloride concentration (39).

It has often been stated that the energy requirements for freezing and crystallization processes are appreciably less than for distillation processes. This proposition is based on the fact that the latent heat of vaporization for water is approximately 7.7 times the heat of fusion for ice. However, this does not take into account the amount of latent heat which is recovered in the actual process. Energy inputs for various freezing processes have been quoted in the literature as 27 to 35 kwhr per 1,000 gallons of product water for the Struthers controlled freezing process (37) and 39 to 40 kwhr per 1,000 gallons of product water for the vacuum freezing processes of Colt Industries (9) and Carrier Corp (40). These are approximately the same as the energy input to a high performance distillation process when it is taken into account that, in general, freezing processes require energy input in the form of electrical power whereas distillation processes generally use heat. Also, the cost of removing a given quantity of heat is greater than the cost of adding it. Since distillation processes use heat they can be combined with power production in a dual-purpose power generation-water desalting plant, whereas the freezing processes use mechanical or electrical energy and cannot readily take advantage of the dual-purpose concept.

Basically, a freezing process is a heat pump which must transfer the latent heat of fusion from the temperature of the ice-brine mixture to that of the ice-water mixture. Assuming a recovery of 40% of the fresh water from the incoming seawater, the temperature difference between the freezer and melter will be approximately 6 F (32 F minus 26 F). In addition, there must be a 2 to 3 F temperature difference for heat transfer in both the freezer and the melter (37).

The principal advantage of freezing processes over distillation is that scale formation is negligible in the former. This is because the scale-forming compounds tend to stay in solution at the lower operating temperatures. Also, corrosion rates are lower at the lower temperature levels so that materials requirements are less stringent.

Some authorities feel that freezing process plants may be competitive for desalination of brackish waters also. This is because with less saline feedwater, it is possible to use multiple stages. With a seawater feed stream a concentration ratio of approximately 2 to 1 appears to approach the optimum. However, if one starts with a less concentrated feed, the designer may not be satisfied with a 2 to 1 concentration ratio, and it appears that a multiple-stage freezing process might be advantageous.

A number of small pilot plants have been operated using various freezing processes. The largest freezing-desalting plant in operation is of the vacuum freezing - vapor compression type and has a capacity of 240,000 gpd. Units of this type are offered commercially but none of the other freezing processes are ready for large-scale commercial, industrial or municipal applications.

#### b. Freezing and Crystallization Terminology

##### Dendrites

Branching or tree-like forms of crystals.

### Driving Force Temperature Difference for Freezing

The difference between the temperature of the bulk brine and the saturation temperature of the refrigerant at the pressure existing in the freezer vapor space (36).

### Freezing Point

The temperature at which ice is in equilibrium with a surrounding aqueous solution. For pure water the freezing point is 32 F (0 C). For a 3.5 weight-percent sodium chloride solution, the freezing point is depressed to approximately 28.8 F (41).

### Heat of Formation

The heat which must be removed from a freezing solution to form a given quantity of hydrate crystals. For propane hydrate, the heat of formation is 155 Btu per pound of fixed water.

### Heat of Fusion

The heat which must be removed from a freezing solution to solidify a given quantity of ice. The heat of fusion for ice is approximately 80 kcal per kg or 143 Btu per pound (6).

### Hydrate

A crystalline solid containing water molecules weakly bonded to a hydrating agent. The crystal structure is such that ionic impurities from the solution are excluded.

### Spontaneous Nucleation Temperature

The temperature at which ice crystal nuclei form rapidly without seeding or agitation. This is sometimes referred to as the labile region of supersaturation. A 0.2 weight-percent sodium chloride solution has a freezing point of -0.123 C (31.78 F) and a spontaneous nucleation temperature of approximately -5 C (23 F) (9).

### Subcooling

The temperature difference between the bulk brine and the ice crystal surface. In a direct-contact freezer using a secondary refrigerant, the brine temperature is lower than that of the solid-liquid interface. Subcooling is the driving force for crystal growth (37).

### Triple Point

The condition of pressure and temperature at which the solid, liquid and gaseous phases can coexist in equilibrium.

### Zone Freezing

A process by which a narrow zone of frozen water is made to traverse a tube of saline water. The formation of ice crystals tends to concentrate the salt in the solution ahead of the crystals. This results in one end of the tube becoming depleted in salt and the other end becoming more concentrated.

## 2. Freezing and Crystallization Process Descriptions

### a. Freezing Processes

#### (1) Indirect Freezing

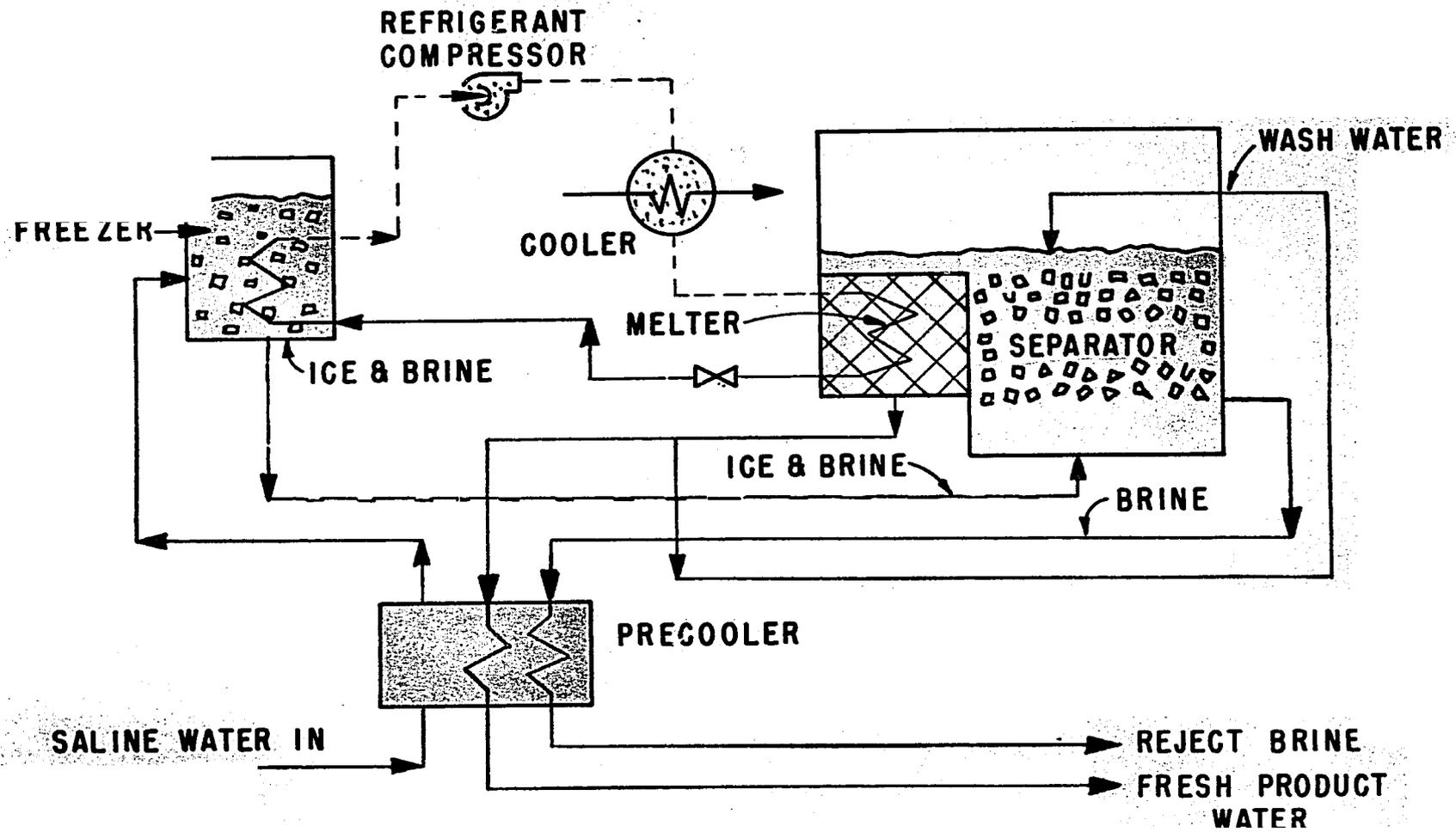
A schematic flow diagram of the indirect freezing process is shown in Figure IV-45. Incoming saline water is passed through a pre-cooler, where it transfers its heat to the brine and product water leaving the process. The saline water flows next through the freezer where additional heat is removed from it by transfer through tube walls to a refrigerant. Ice forms on the exterior of the coils or surface containing the evaporating refrigerant, and is removed from these surfaces mechanically. The refrigerant is circulated in a closed system. The liquefied refrigerant entering the freezer is vaporized by the latent heat extracted from the freezing brine. The vaporized refrigerant is then compressed, cooled by seawater in the cooler and further cooled and condensed by giving up heat to melting ice in the melter unit. The condensed liquid refrigerant is then cooled by adiabatic expansion and recycled to the freezer unit.

The slurry of ice crystals and brine is pumped to the separator where the brine is washed from the ice crystals. In the vertical moving-bed type of separator, the ice-brine slurry enters near the bottom. Most of the brine is removed by filtration. The ice crystals float toward the top of the separator where the adhering brine is washed away by the downward-flowing wash water. The washed ice crystals are mechanically harvested and directed into the melter. The ice is melted by the heat given up by the condensing refrigerant. A portion of the melted fresh product water is recycled as wash water for the separator.

The indirect freezing process is relatively inefficient because all heat must be transferred to and from the refrigerant through metallic tube walls. The temperature difference between the evaporating refrigerant and the freezing brine in the freezer, and that between the condensing refrigerant vapor and the melting ice in the melter, must be added to the temperature

FIGURE IV-45

INDIRECT FREEZING PROCESS



difference between the freezing brine and melting ice to determine the overall temperature difference across which a heat pump must operate. Early studies at the University of Washington on using conventional ice-making machines concluded that using indirect heat transfer for a freezing process would be uneconomical (34).

## (2) Direct Freezing Using Vapor Compression

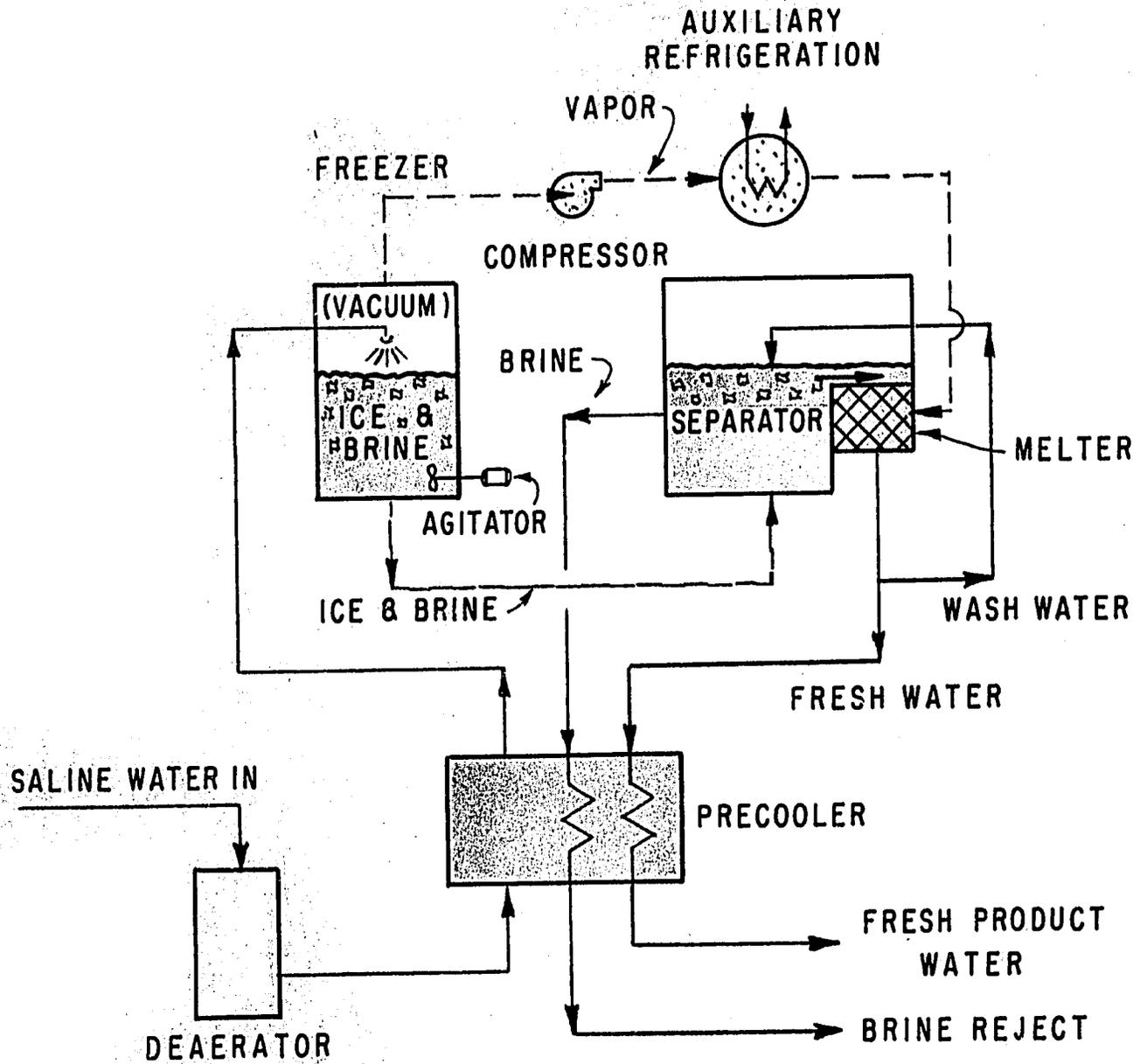
The freezing process can be made more efficient by eliminating the metallic heat-exchange surface used in the indirect freezing process and allowing direct transfer of heat to take place between the refrigerant and the freezing saline water. One direct freezing method, sometimes called the "Zarchin" process, uses the water itself as the refrigerant. The schematic flow diagram for this direct freezing process is illustrated in Figure IV-46. As precooled seawater is introduced into the freezer unit, which is maintained at a vacuum, a portion of the water flashes to vapor. The heat required to vaporize the flashing water is taken from the remaining brine solution, thereby cooling it. If the freezer pressure is maintained below the vapor pressure of the brine solution at its freezing point, ice will be formed. The ice-brine slurry is conveyed to the separator where the ice crystals are separated and washed.

Approximately one gallon of water is vaporized or flashed in the freezer for every seven gallons of water frozen. This vapor leaving the freezer is compressed by the vapor compressor and conveyed to the melter. The compressed freshwater vapor is condensed in the melter, giving up its heat to melt the ice. Also, some auxiliary refrigeration must be provided to condense the vapor completely and discharge part of the heat to the surroundings.

One drawback to the process is the very low pressures which must be maintained in the freezer, melter and wash column. This has required the development of vapor compressors capable of handling large volumes of water vapor at low pressure.

FIGURE IV-46

DIRECT FREEZING PROCESS  
USING VAPOR COMPRESSION



A related problem is that of maintaining the large equipment components in a vacuum-tight condition.

The vacuum freezing-vapor compression process, also known as the Zarchin process, was developed jointly by Desalination Plants Ltd., a joint venture of Colt Industries Inc., and the Government of Israel. A 60,000-gpd prototype module was built by Colt Industries at Beloit, Wisconsin. The prototype module went into operation at Beloit in 1962, and formed the basis for the design and construction of a 240,000-gpd four-module plant at Eilat, Israel; this plant started up in January 1964. The Eilat plant, shown in Figure IV-47 is the largest freezing-desalting plant in operation, but is still subject to developmental work.

The 60,000-gpd Beloit module has been moved to the OSW test station at Wrightsville Beach, N. C. This module, shown in Figure IV-48, has operated successfully at production rates as high as 110,000 gpd. The freezer operates at 3.5 mm Hg pressure and the melter operates at 4.8 mm Hg. Thus, the water vapor compressor must develop a compression ratio of approximately 1.5 and handle water vapor with a high specific volume. With a freezing point depression of approximately 5 F, the brine in the freezer is held at approximately 27 F. The original vapor compressor was a flexible-bladed compressor using stainless steel blades, rotating at 3,600 rpm. This older compressor unit was 9 feet in diameter and had a capacity of 300,000 to 350,000 cfm. It has been replaced with a new unit to stretch plant output to 125,000 to 137,000 gpd. Approximately 2% to 5% of the product water is consumed in washing the separated ice crystals.

The freezing solution in the freezer must be continually agitated by a mechanically-driven agitator to prevent formation of an ice crust on the surface of the freezing brine. The ice crystals formed are quite small because of the relatively low residence time in the freezer.

FIGURE IV -47

ZARCHIN DIRECT FREEZING DESALINATION PLANT  
EILAT, ISRAEL

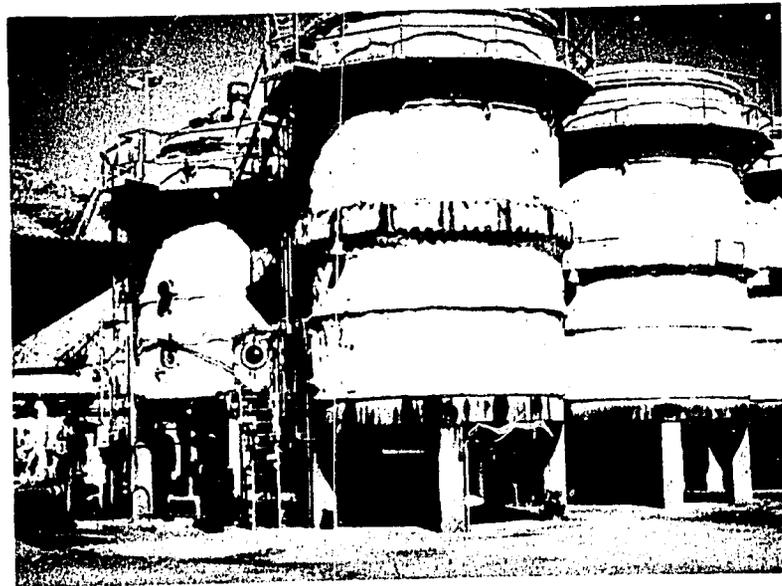
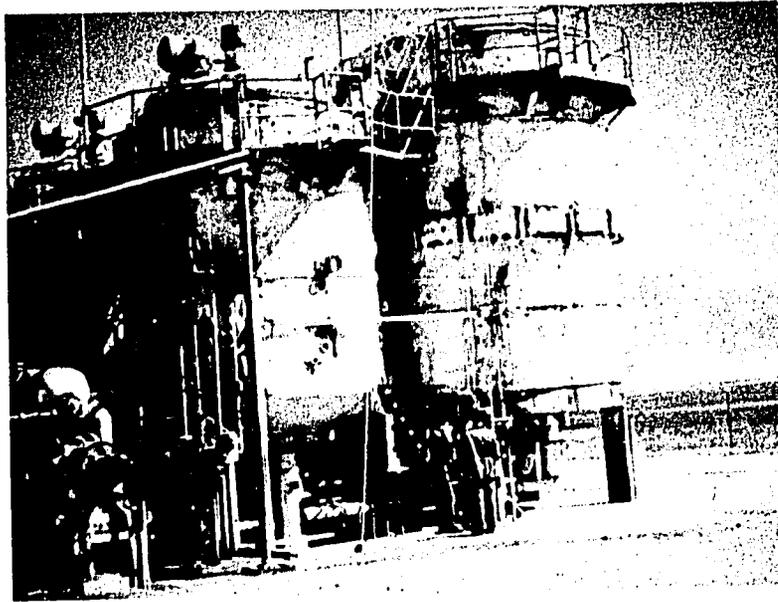
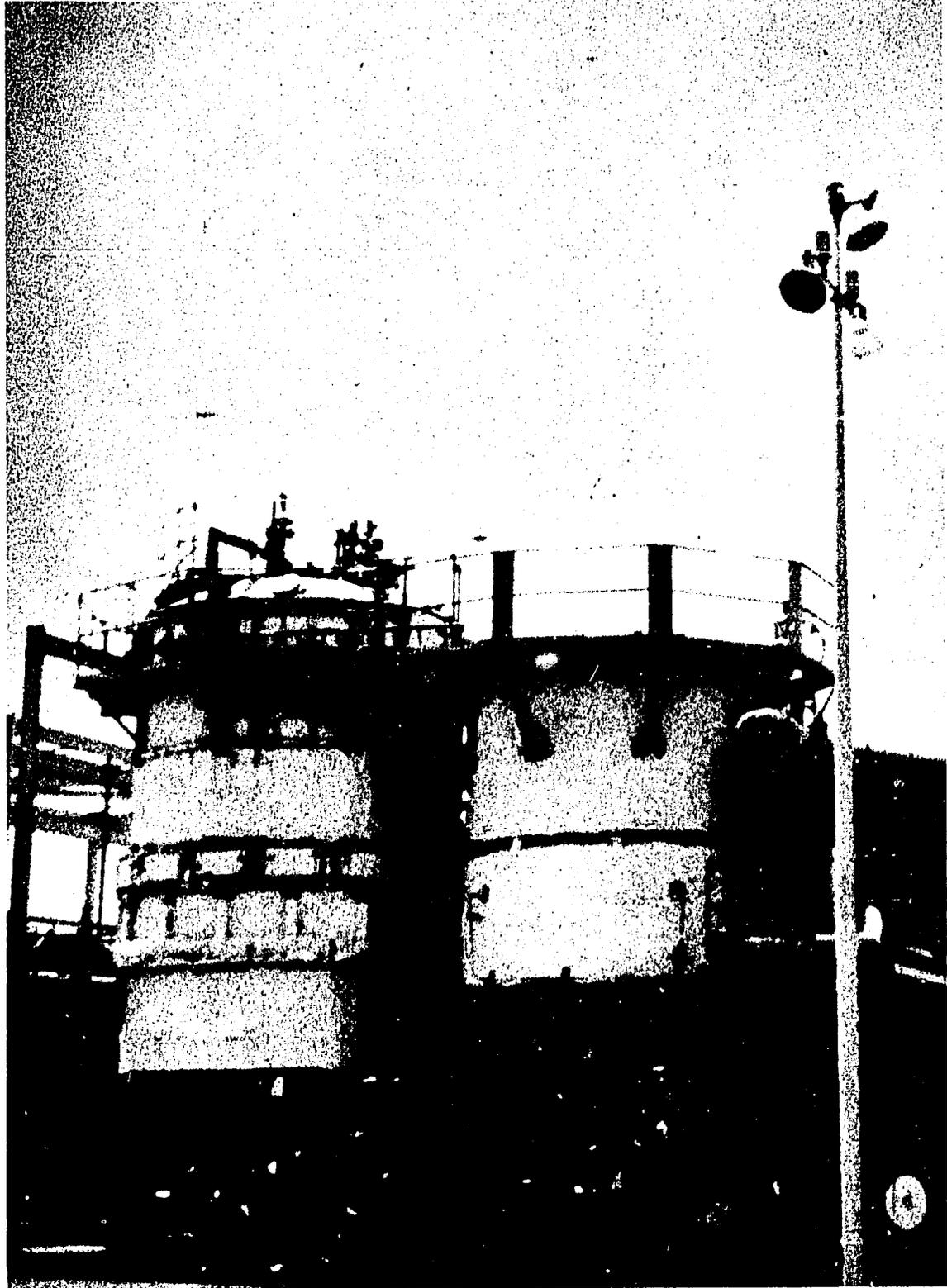


FIGURE IV-48

COLT INDUSTRIES' NOMINALLY-RATED 60,000-GPD  
VAPOR COMPRESSION VACUUM FREEZING PROCESS (HAS PRODUCED 110,000 GPD)  
WRIGHTSVILLE BEACH, N. C.



Some of the problems encountered have been control valves sticking and cavitation of the brine pumps which take suction from the deaerator. The deaerator reduces the oxygen concentration in the incoming seawater from 8 ppm to 1 ppm.

There also has been trouble in the past with a vane-type entrainment separator located in the freezer compartment. This entrainment separator is supposed to knock out any water drops which are entrained in the water vapor stream exiting from the top of the freezer chamber. However, there had been a tendency for drops to freeze on the vanes, and these frozen drops had to be removed by mechanical knocking. There has been installed a new type of entrainment separator which employs radial vanes heated with incoming seawater. In addition to preventing ice formation on the vanes, this pre-cools the seawater.

The experience gained from the operation of the 240,000-gpd four-module plant at Eilat and the prototype module at Wrightsville Beach, N. C. make the vacuum freezing-vapor compression process the most advanced of the various freezing and crystallization processes at the present time.

Under OSW contract, design studies were performed by the Carrier Corporation on the vapor compression freezing process. These studies concluded that the size of a freezing plant module using this process is limited by the physical size of the vapor compressor. With a centrifugal compressor operated at 3,450 rpm, the impeller diameter was 6 feet and the equivalent plant capacity was 75,000 gpd. Using a 1,725-rpm compressor, the compressor impeller was 12 feet in diameter and the plant capacity was 300,000 gpd (40). To build plants with higher water production capacities would require using more than one primary compressor. It has been stated that scale-up of this process beyond 5 mgd would be difficult (36). However, it appears that the economics of vacuum freezing-vapor compression may well be attractive in plants rated at less than several million gallons per day.

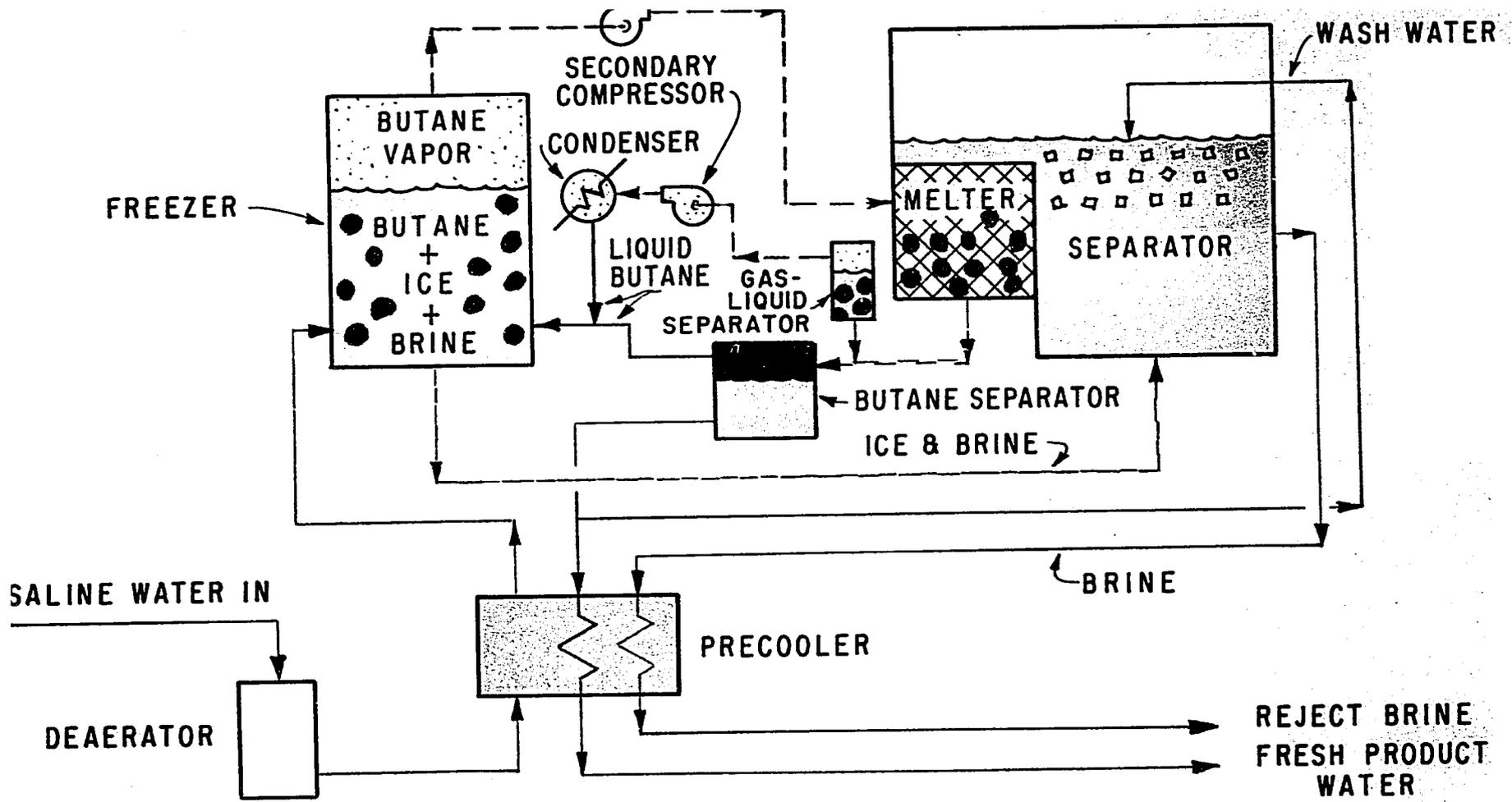
A variation of the direct freezing process, using the cooling effect of flash evaporation, absorbs the water vapor in a suitable medium such as lithium bromide, instead of compressing it. The water vapor leaving the freezer is taken up by the absorbent and later driven out by heat. Although this variation circumvents the difficulties attendant with developing large vapor compressors, it involves the added complexity of the vapor-absorption and desorption systems.

The Carrier Corporation designed and operated a 300-gpd pilot plant using the vapor absorption principle at its research laboratories in the middle 1950's. Results obtained from this small pilot plant were used to design a 15,000-gpd unit which was operated successfully at Wrightsville Beach, N. C. This plant used lithium bromide to absorb the water vapor which flashed in the freezer. These two pilot plants demonstrated the practicability of using the continuous vertical ice column washer-separator. Recent studies (40) on plants with a capacity of 165,000 gpd concluded that the direct freezing plant using water vapor compression could produce water at a lower cost than one using vapor absorption equipment.

### (3) Direct Freezing Using a Second Refrigerant

Another variation of the direct freezing process is shown schematically in Figure IV-49. A liquefied refrigerant is sprayed directly into the saline water in the freezer unit. Ideally, the refrigerant should be insoluble in water and have a boiling point lower than the freezing point of the freezing saline water. Various réfrigerants have been used, including n-butane, isobutane and fluorocarbon refrigerants. The refrigerant evaporates as it absorbs heat from the brine and produces ice. Refrigerant vapor from the freezer is compressed, condensed and recycled. Part of the refrigerant is condensed in the melter, giving up heat to the melting ice. The secondary compressor and condenser liquefies the refrigerant which does not condense in the

FIGURE IV-49  
DIRECT FREEZING  
USING SECONDARY REFRIGERANT



melter. The liquefied refrigerant is separated from the product water and returned to the freezer unit. The separation and washing of ice crystals is accomplished in a manner similar to that used in other freezing processes.

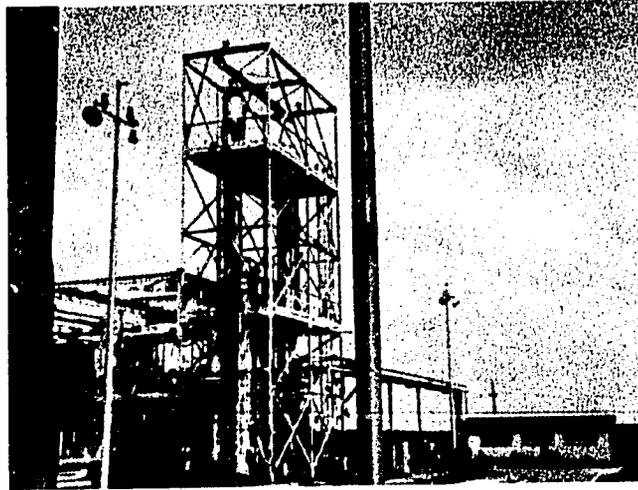
A 35,000-gpd pilot plant using butane as a direct-contact refrigerant was operated for several years by the Blaw-Knox Co. at St. Petersburg, Florida (see Figure IV-51). Following design improvements, the pilot plant's design capacity was uprated to 55,000 gpd. Blaw-Knox combined its efforts with those of Professor Wiegandt of Cornell University, who also had been working on a direct freezing process using a secondary refrigerant. The St. Petersburg, Florida pilot plant tested both the use of the Blaw-Knox Rotocel as a freezer and washer, and the use of the Wiegandt column which combines the freezing, washing and melting operations in one vessel (30).

The Struthers Scientific and International Corp has designed and constructed two freezing-desalting plants at OSW's Wrightsville Beach, N.C. test station (see Figure IV-50). These plants utilize Struthers' direct-contact controlled crystallization process. This process combines developments and experience acquired by Struthers Scientific and International Corporation from their own work and that of Struthers Wells Corp, North American Aviation (Rocketdyne Division), Dr. M. H. Gorin, Dr. Ludwig Rosenstein and Dr. Shuji Umano (37). Dr. Umano, while with the Government Chemical Industrial Research Institute in Tokyo, Japan, directed most of the Japanese research on the direct-contact controlled crystallization freezing process (37). A pilot plant with a water capacity of 57,000 gpd was built in Japan to produce a concentrated brine for feed to salt production evaporators. Using an auger-type centrifuge, 900-ppm water was produced with no washing (37).

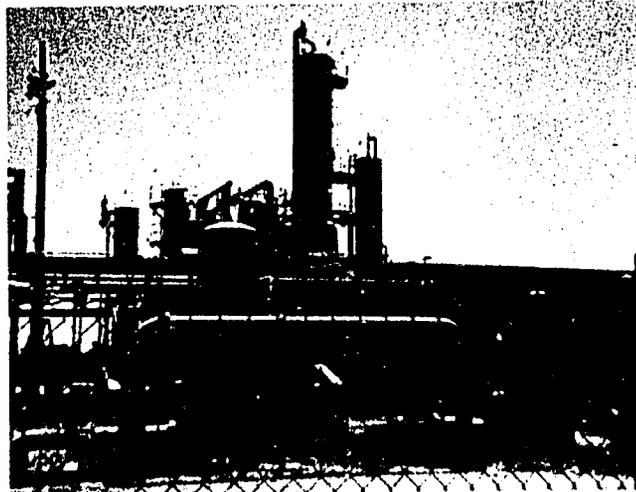
The 15,000-gpd Struthers Wells pilot plant, completed in 1963, was built to test equipment designs which could be scaled up to production plants of larger capacity. The Struthers' process

FIGURE IV-50

STRUTHERS SCIENTIFIC FREEZING-DESALTING PLANTS



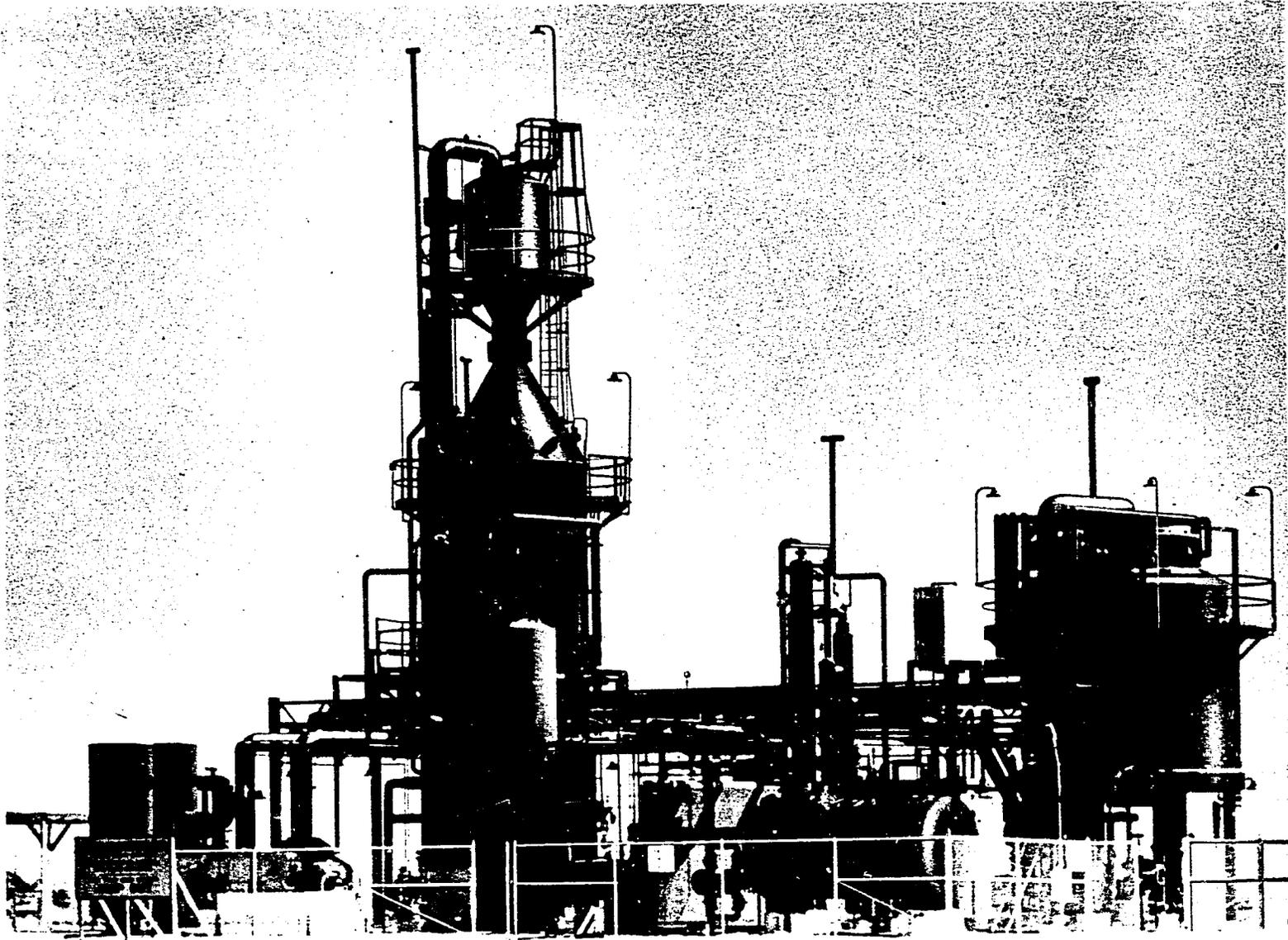
15,000-gpd Pilot Plant  
Wrightsville Beach, N. C.



200,000-gpd East Coast Demonstration Plant  
Wrightsville Beach Test Station (Shut Down)

FIGURE IV-51

BLAW-KNOX 35,000-GPD PILOT PLANT



Source: U. S. Department of the Interior,  
Office of Saline Water

uses a mixture of n-butane and isobutane as the direct-contact refrigerant. The freezer operates at 3 to 4 psig and the melter operates at 7 to 8 psig. The plant uses a horizontal vibratory conical-basket centrifuge for separating ice crystals from brine; however, operating difficulties were encountered with centrifuge operation due to a slow accumulation of ice, glazing and sticking to the centrifuge basket. A vertical wash column has replaced the centrifuge as a means of separating ice from the brine.

The 200,000-gpd East Coast Experimental Conversion Plant at Wrightsville Beach, N. C. was completed by Struthers Scientific and International in 1964. Operational difficulties were encountered, including severe vibration of the main compressor and problems with the separation of water-refrigerant mixtures in the presence of seawater. The vibration problems were eliminated by installation of pulsation dampeners on the suction and discharge of the main compressors and by a pipe support system. The 200,000-gpd plant presently is shut down, pending completion of a study of recommended system and equipment modifications.

The Carrier Corporation has performed design and experimental work on a direct-freezing process using R-C318 (octafluorocyclobutane) as a direct-contact secondary refrigerant. This refrigerant has the desirable characteristics of low toxicity, high stability and nonflammability. An OSW-sponsored study showed that, although the cost of water produced using R-C318 as a direct refrigerant in a 165,000-gpd plant would be somewhat above that for a vapor compression freezing plant of the same capacity, the R-C318 process could be extrapolated to module sizes of at least 600,000 gpd (40). Recent OSW-sponsored work has included the design and construction of a bench-scale freezer unit using R-C318 as a direct secondary refrigerant, and on the stability and recovery of R-C318. The principal limitation of the process is the necessity of minimizing losses of the relatively expensive R-C318 (\$2 per pound). A loss of 1 ppm with the brine and product would add 3¢ per 1,000 gallons to the cost of water (40).

### b. Hydrate Formation Crystallization

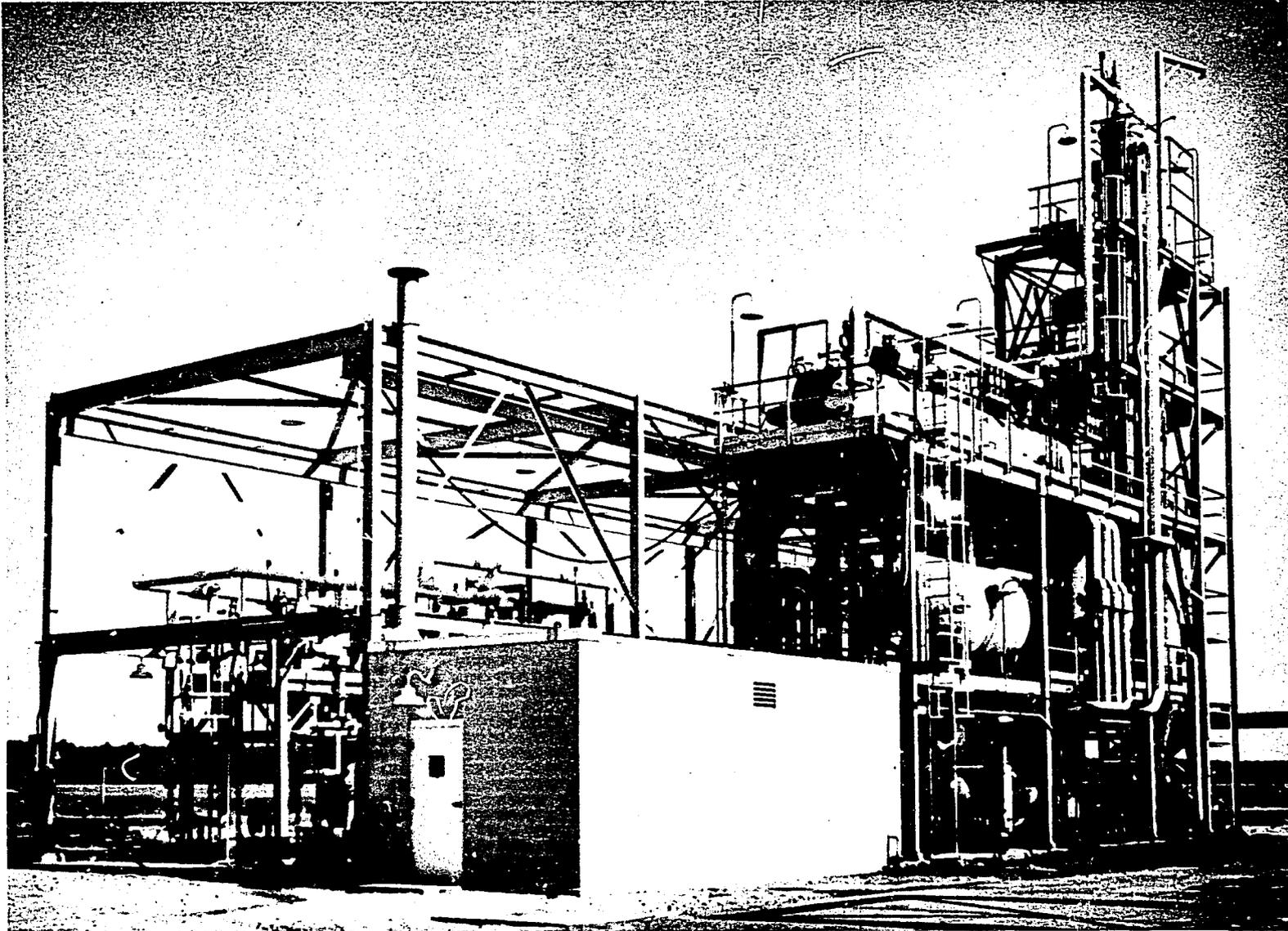
The hydrate desalting processes are very closely akin to freezing processes. Hydrates are solid compounds formed by water and some other material. Whereas ice crystals are formed in the freezing processes, in hydrate crystallization processes, hydrate crystals are produced and later decomposed to yield the product fresh water. The crystals formed are insoluble in water and have the property of excluding salt from their lattices. Various hydrating agents can be utilized including propane, chlorofluoromethanes, chlorine and carbon dioxide. Most of the pilot plant operations to date have used liquid propane as the hydrating agent. Propane forms insoluble clathrate crystals with water, having an approximate composition of 17 mols of water to each mol of propane.

The flow diagram for the hydrate desalting process using propane is essentially the same as that depicted in Figure IV-49 for the direct freezing process using a secondary refrigerant. After the hydrate crystals are produced in the hydrate formation unit, the crystals are separated from the brine and washed; they are then decomposed into product water and the immiscible liquid hydrating agent, which is recycled. The hydrate formation unit is analogous the freezer unit employed in the freezing process, and the hydrate decomposition unit corresponds to the melter.

The Sweet Water Development Co. has developed a hydrate process which uses propane as the hydrating agent. A 20,000-gpd pilot plant using the propane-hydrate process began operation at Wrightsville Beach, N. C. in 1965 (see Figure IV-52). The hydrate crystallizer is a horizontal vessel, divided internally into six compartments by horizontal semicircular baffles. The liquefied propane is injected into the bottom of each compartment where it is mixed with the brine by agitators. The crystallization or melting temperature of the hydrate is 42.4 F and the crystallizer operates at 55 to 60 psig. The crystals formed are plate-like and have a size distribution from 20 to 200 microns. The separation of hydrate crystals from brine is accomplished in

FIGURE IV -52

SWEET WATER DEVELOPMENT CORP, 20,000-GPD PILOT PLANT  
PROPANE HYDRATE PROCESS, WRIGHTSVILLE BEACH, N. C.



Source: U. S. Department of the Interior,  
Office of Saline Water

a series of cyclones. The hydrate crystals are washed with a cocurrently moving stream of liquid propane which is used to displace the brine.

The principal process limitation has been in obtaining satisfactory separation of the hydrate crystals and brine in the cyclone separators. The most efficient removal of brine from hydrate crystals which has been achieved to date is 85%. However, this is not sufficient to achieve the required salinity level of drinking water.

A 10,000-gpd hydrate process plant was designed and built by the Koppers Co. at OSW's Wrightsville Beach, N. C. test station. This pilot plant, shown in Figure IV-53, employs Freon-12 as the hydrating agent; the plant was completed in 1966.

Until sufficient operating experience has been accumulated on these pilot plants and a larger demonstration plant has been operated, the hydrate process cannot be regarded as ready for large-scale commercial, municipal or industrial applications.

FIGURE IV-53

KOPPERS CORP - FREON HYDRATE PROCESS, 10,000-GPD PILOT PLANT  
WRIGHTSVILLE BEACH, N. C.



## C. Electrodialysis Processes

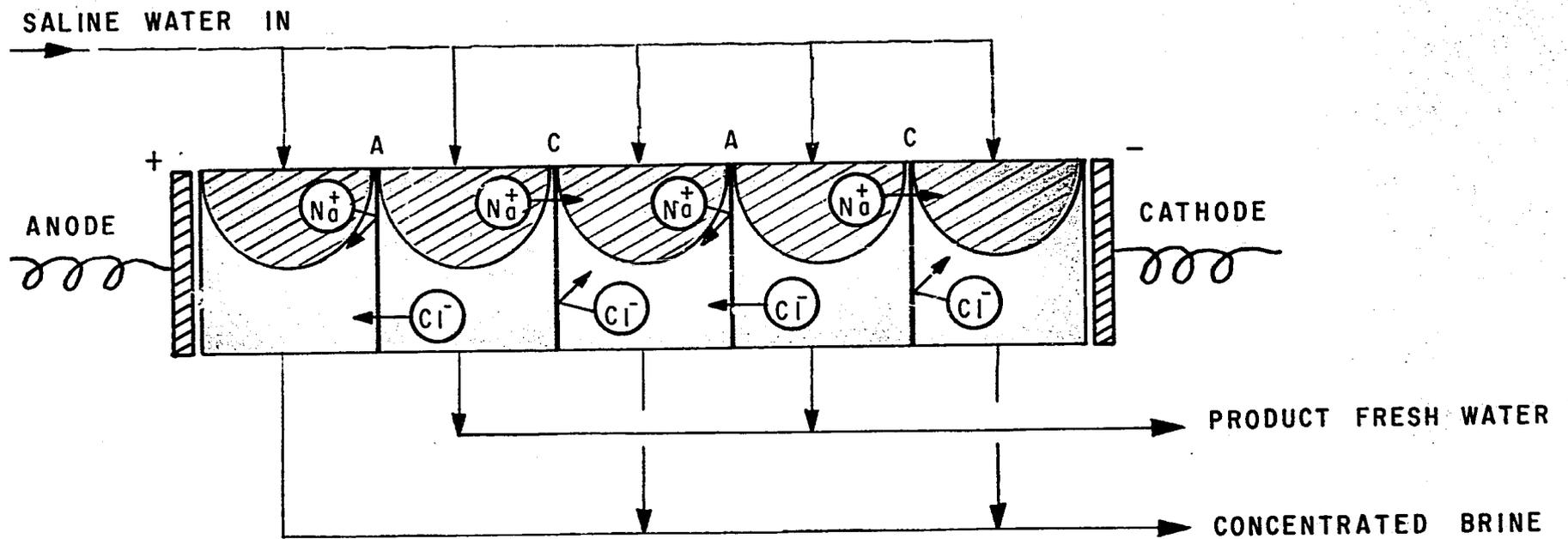
### 1. Electrodialysis Phenomena and Process Description

#### a. General

Unlike the distillation and freezing processes and the reverse osmosis process (refer to Subsection IV. D), which separate product water from the saline water feed, the electrodialysis process removes the salt from the saline water. Figure IV-54 is a schematic flow diagram for the electrodialysis process. The saline water is fed to a number of narrow compartments formed by alternate anion-permeable and cation-permeable membranes. The salt in saline water consists of positively charged ions (cations) and negatively charged ions (anions). Although seawater and most brackish waters contain a large variety of cations and anions, the cations are represented in Figure IV-54 by sodium ions ( $\text{Na}^+$ ) and the anions by chloride ions ( $\text{Cl}^-$ ). The electrodialysis cell consists of several hundred pairs of anion-permeable and cation-permeable membranes sandwiched between two electrodes. When an electromotive potential, or voltage, is applied across the cell, the negatively charged anions are attracted toward the anode, or positive electrode; the positively charged cations are drawn toward the negative cathode. The anion-permeable membrane (A) selectively passes anions but blocks the passage of cations. The cation-permeable membrane (C) allows cations to pass through but stops anions. Thus, the water passing through every other compartment is depleted in salt, and is withdrawn as the product; the water in the intervening passages becomes more saline and is rejected as concentrated brine. Electrodialysis can be used either to purify saline water by removing the salt (where fresh water is the desired product), or to concentrate the dissolved salts (where brine is needed).

The cation permeable membrane contains cation-exchange resin; similarly, the anion-permeable membrane contains anion-exchange

FIGURE IV-54  
ELECTRODIALYSIS PROCESS



- FRESH WATER
- SALINE WATER
- BRINE

resin. The ion-exchange resin either is cast in the form of continuous sheets or is contained in a base film. A heterogeneous film is obtained by dispersing finely divided ion-exchange resin with an inert plastic binder material and compacting the mixture with heat and/or pressure (6). The Southern Research Institute has been doing research, under OSW contract, to prepare membranes wherein the ion-exchange material is graft-polymerized to the base film by the use of cobalt-60 gamma radiation or a chemical cross-linking agent. Some ion-exchange membranes employ glass or Dynel fibers to give them mechanical strength. Other membranes employ no reinforcing and rely on the spacers between the membrane sheets for mechanical support. The usual thickness of ion-exchange membranes varies from 0.1 to 1.0 millimeter (6). Usually, the cation-exchange material is a sulfonate such as sodium styrene sulfonate, whereas the anion-exchange material usually is an ammonium salt (43). Normally the cation-exchange membranes are less expensive and less susceptible to fouling than the anion-exchange membranes. The rejection of ions by an ion-selective membrane is due to a combination of coulombic repulsion and salt exclusion (43). For the coulombic repulsion to function, the average pore size in the membrane must be less than 30 Ångströms (Å). The effective pore size available in commercial ion-exchange membranes varies from 10 to 15 Å (43).

After the ion-selective membranes have been installed in an electro dialysis stack, the electrical resistance of the membrane stack will undergo a gradual increase over a prolonged period. This increase may be caused by fouling with large organic ions or by the formation of inorganic scale deposits such as calcium carbonate, magnesium hydroxide and calcium sulfate on the membrane surface. With proper acid pretreatment, the inorganic scaling by calcium carbonate and magnesium hydroxide can be effectively controlled. Using proper pH control, tests in the Netherlands have been conducted up to 28,000 hours without the limitation of inorganic scaling. Under reasonable operating conditions, a membrane life of three to five years can be expected (44).

Usually, the principal effect of membrane degradation is a gradual increase in electrical resistance rather than rupture or failure of the membrane. Defective membranes are detected by probing the stack with a voltage indicator.

Membranes made by different manufacturers may not be interchangeable from one electro dialysis unit to another.

To reduce the overall resistance to current flow through the membrane stack it is desirable to maintain as close a spacing as possible between the adjacent membrane sheets. This is accomplished by a separator between membranes. These separators also form the flow path in which the liquid is forced to flow in a tortuous path across the membrane surface. The separators also promote stirring of the liquid to reduce polarization effects. Figure IV-55 shows a typical intermembrane spacer and a membrane sheet from an Ionics Mark-III stack. The polyethylene spacers are approximately 0.04 inch thick (45).

The electrodes for the electro dialysis stack must be made of materials which will resist the corrosive electrode reaction products to which they are exposed. The anode, or positive electrode, is subject to the corrosive action of the oxygen and chlorine which are evolved. The anode typically is made of a material such as titanium, coated with a thin coat of platinum. The cathode material is either stainless steel or Hastelloy C. If polarity reversal is used to counteract polarization effects, both electrodes must be platinum coated.

Figure IV-56 shows an exploded assembly drawing of the Ionics Mark-III stack. The assembly of anion- and cation-selective membranes, spacers and electrodes is combined into an assembly similar to a plate and frame filter. Figure IV-57 shows Ionics Mark-III stacks installed in a 240,000-gpd electro dialysis plant in Kuwait.

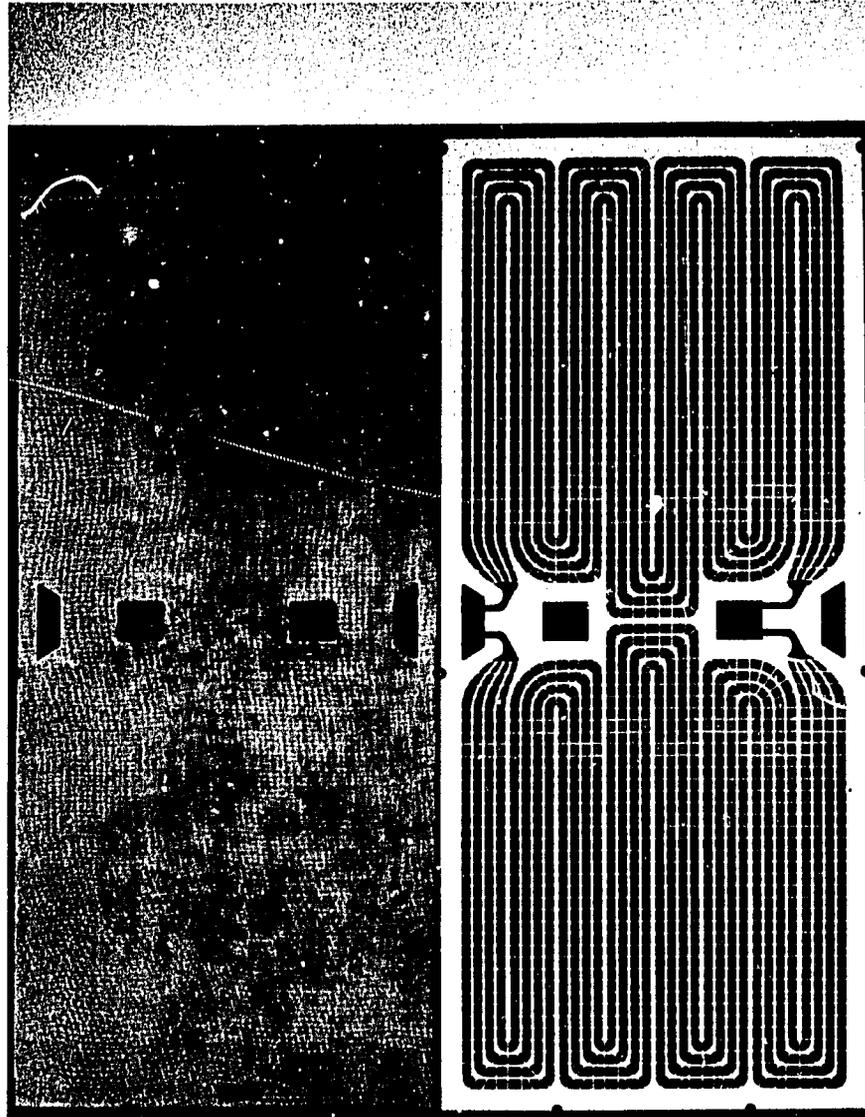
#### b. Electro dialysis Terminology

##### Anion

A negatively charged ion present in a solution, which is attracted toward a positively charged electrode (anode).

FIGURE IV-55

THE BASIC COMPONENTS OF AN IONICS MARK-III STACK

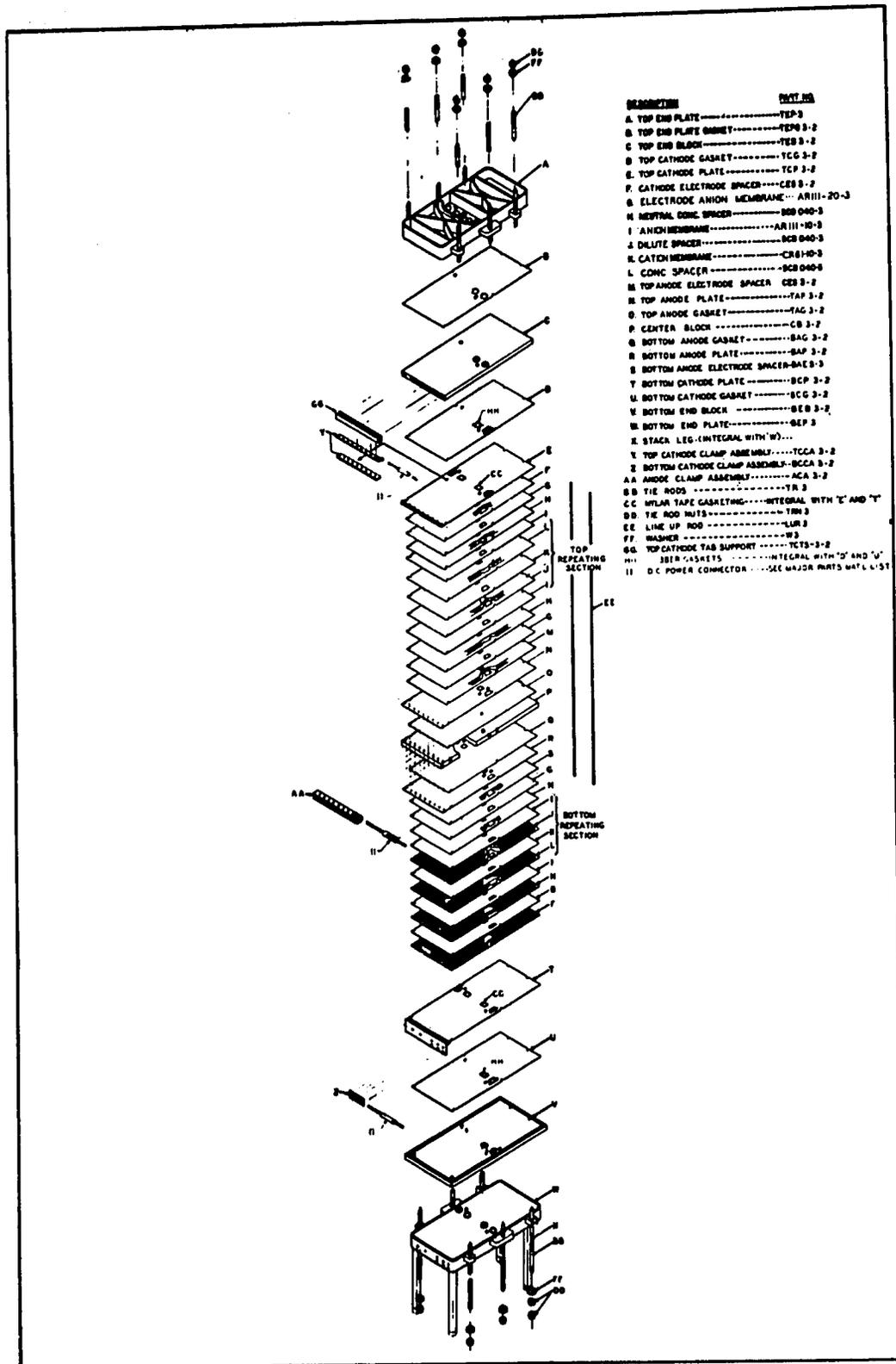


At the right is an 18-inch x 40-inch membrane with center manifold hole punchings. At the left is an 18-inch x 40-inch intermembrane spacer showing corresponding central manifold hole punchings, liquid entry channels and the four-path tortuous spacer with turbulence promotion straps. Spacer thickness is 0.040 inch and membrane thickness is 0.023 inch. A full Mark-III stack contains 550 such spacers and 550 membranes. The stack is constructed by laying a spacer between each pair of membranes so that the manifold holes correspond.

Source: Ionics, Inc

FIGURE IV -56

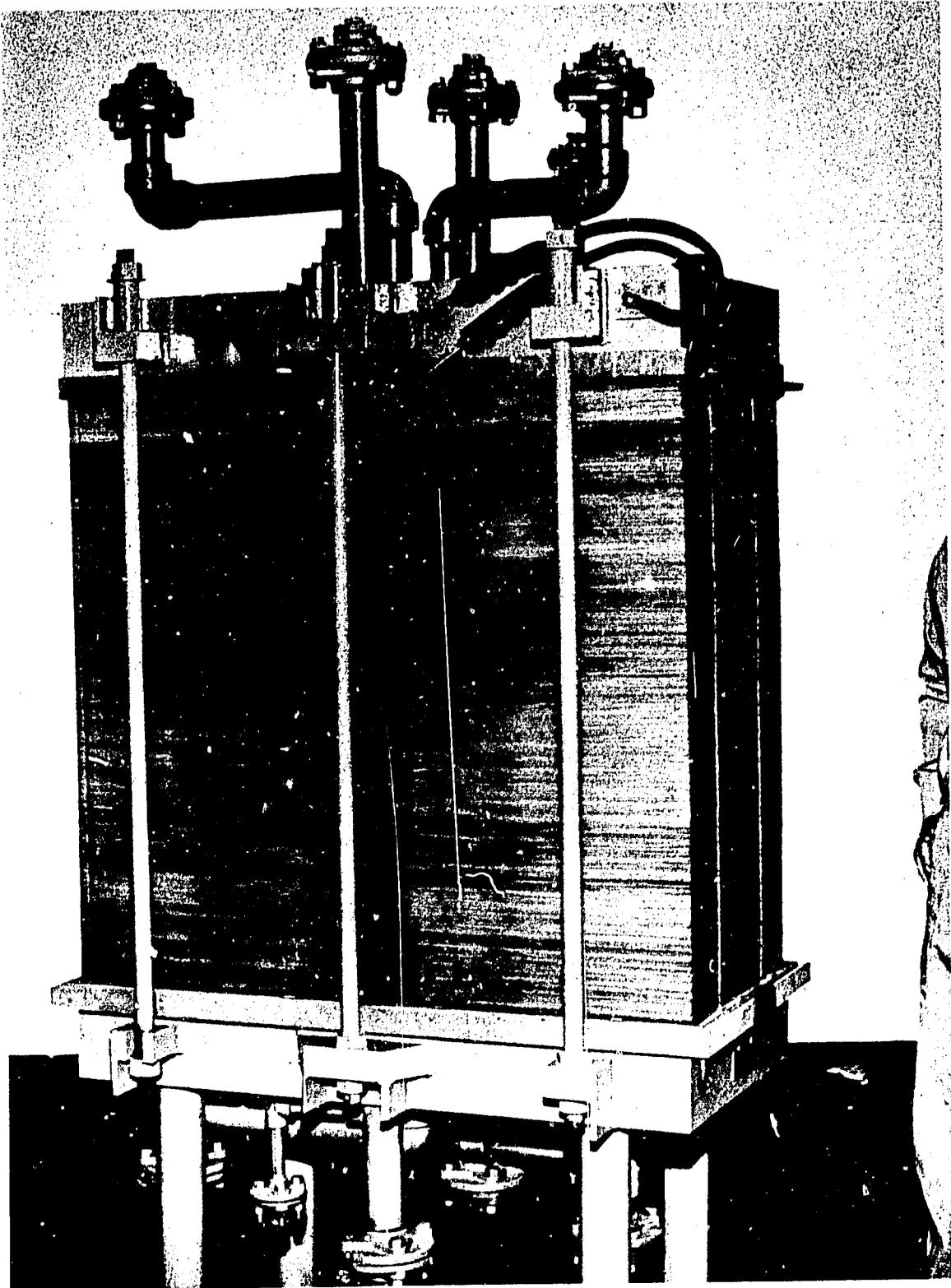
ARRANGEMENT OF MEMBRANES, SPACERS AND ELECTRODES  
IN AN ELECTRODIALYSIS STACK



Source: Gilliland, E. R., "The Current Economics of Electrodialysis," Paper SWD/90, First International Symposium on Water Desalination, Oct 3 to 9, 1965

FIGURE IV-57

IONICS MARK-III STACKS IN KUWAIT ELECTRODIALYSIS PLANT



Courtesy: Ionics, Inc

### Anion-Selective Membrane

A membrane made of an anion-exchange material which will allow anions to pass selectively through the membrane under the influence of an electric field. It is also called an anion-exchange membrane or an anion-permeable membrane. Anions from the solution exchange freely with the anion-exchange resin, but cations cannot enter the membrane.

### Anode

A positively charged electrode.

### Cathode

A negatively charged electrode.

### Cation

A positively charged ion present in a solution, which is attracted toward the negatively charged electrode (cathode).

### Cation-Selective Membrane

A membrane made of a cation-exchange material which will selectively allow cations to permeate the membrane under the influence of an electric field. It is also called a cation-exchange membrane or a cation-permeable membrane. The cation-exchange material exchanges freely with positively charged cations in the solution; however, no negatively charged ions can enter the membrane.

### Current Density

The flow of electric current through an electro dialysis cell per unit area of membrane stack cross section (amp per square cm).

### Electro-Osmosis

A phenomenon by which water is carried along with ions migrating under the influence of an electric field (6).

### Hydrolysis

The splitting apart of water molecules into hydrogen ions ( $H^+$ ) and hydroxyl ions ( $OH^-$ ) under the influence of an electric field. This occurs when there are insufficient salt ions present in solution to maintain the electrical current transport through the cell.

### Neutral Membrane

A membrane such as parchment or cellophane which is neutral or nonselective in its tendency to pass anions or cations.

### Permselectivity

A measure of the efficiency with which an ion-exchange membrane discriminates between anions and cations.

### Polarization

The increase or decrease in salt concentration near the surface of a membrane in an electro dialysis cell due to the passage of current through the cell.

### Power Index

The ratio:

$$\text{power index} = \frac{\text{electric power (dc) per unit fresh water produced}}{\text{production rate divided by total membrane area}}$$

Both the numerator and denominator are proportional to current; therefore, the power index is independent of applied voltage, current or rate of production. A comparison between different electro dialysis units must be made at equal raw water and product water salinities (6).

### Spacers

Separators placed between the membrane sheets to maintain a fixed distance between the membranes. The spacers also force the liquid streams to follow a tortuous path and enhance mixing of the liquid stream. Also, the spacers may perform the function of mechanically supporting the membrane.

### Transport Number

The fraction of the current passing through a membrane, which is carried by the "counterions." In an anion-permeable membrane the counterions are the negative ions. Similarly, in a cation-permeable membrane the counterions are positively charged ions. The transport number of the counterions should be close to unity in an ion-selective membrane (6).

## 2. Electrodialysis Plant Experience

There are more than 200 electrodialysis plants desalting brackish water throughout the world (43). These plants have an aggregate production capability which exceeds 3 mgd (45).

Four U. S. communities (Webster, South Dakota; Coalinga, California; Buckeye, Arizona; and Port Mansfield, Texas) receive all or part of their water supply from electrodialysis plants.

The largest electrodialysis plant built and operated has been the 2,880,000-gpd plant at Weldom, Orange Free State, South Africa. This plant was built by the South African Council for Scientific and Industrial Research, the Anglo-American Corporation of South Africa, Ltd. , and Rand Mines, Ltd. It was designed to demineralize mine waters from 3,100 ppm to 525 ppm total dissolved solids, and employed inexpensive membranes made from modified parchment paper. The plant operated for over 18 months but never achieved more than 71% of its rated capacity. The mine seepage problem, which the plant was designed to solve, disappeared and the plant was shut down since there was no further incentive to bring it to reliable operation at rated capacity.

The OSW demonstration plant at Webster, South Dakota, shown in Figure IV-58, was supplied by Asahi Chemical Industries, Ltd. It began operation in 1962 and has a rated water production capacity of 250,000 gpd.

The 28,000-gpd Ionics electrodialysis plant at Coalinga, California has been in operation since 1959, producing water with 300 ppm total dissolved solids from a 2,000-ppm brackish water feed. Previously, Coalinga's water supply had been brought in by tank car.

The city of Buckeye, Arizona obtains its entire freshwater supply from a 650,000-gpd electrodialysis plant. This plant, shown in Figure IV-59, was built by Ionics, Inc. It has been in operation since 1962, treating brackish well water containing 2,100 ppm total dissolved solids and producing 500 ppm product water.

FIGURE IV -58

ELECTRODIALYSIS DEMONSTRATION PLANT  
WEBSTER, SOUTH DAKOTA

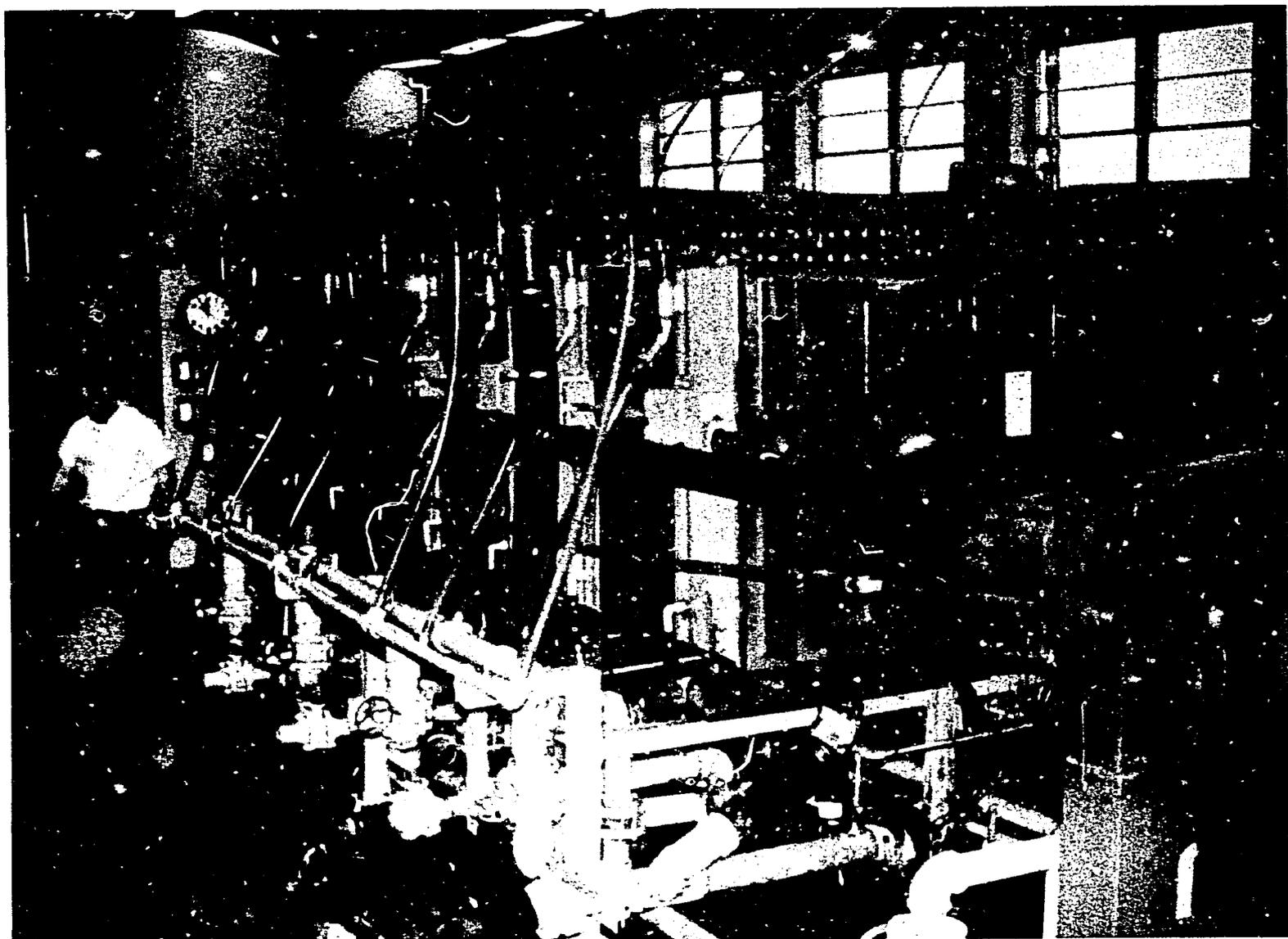
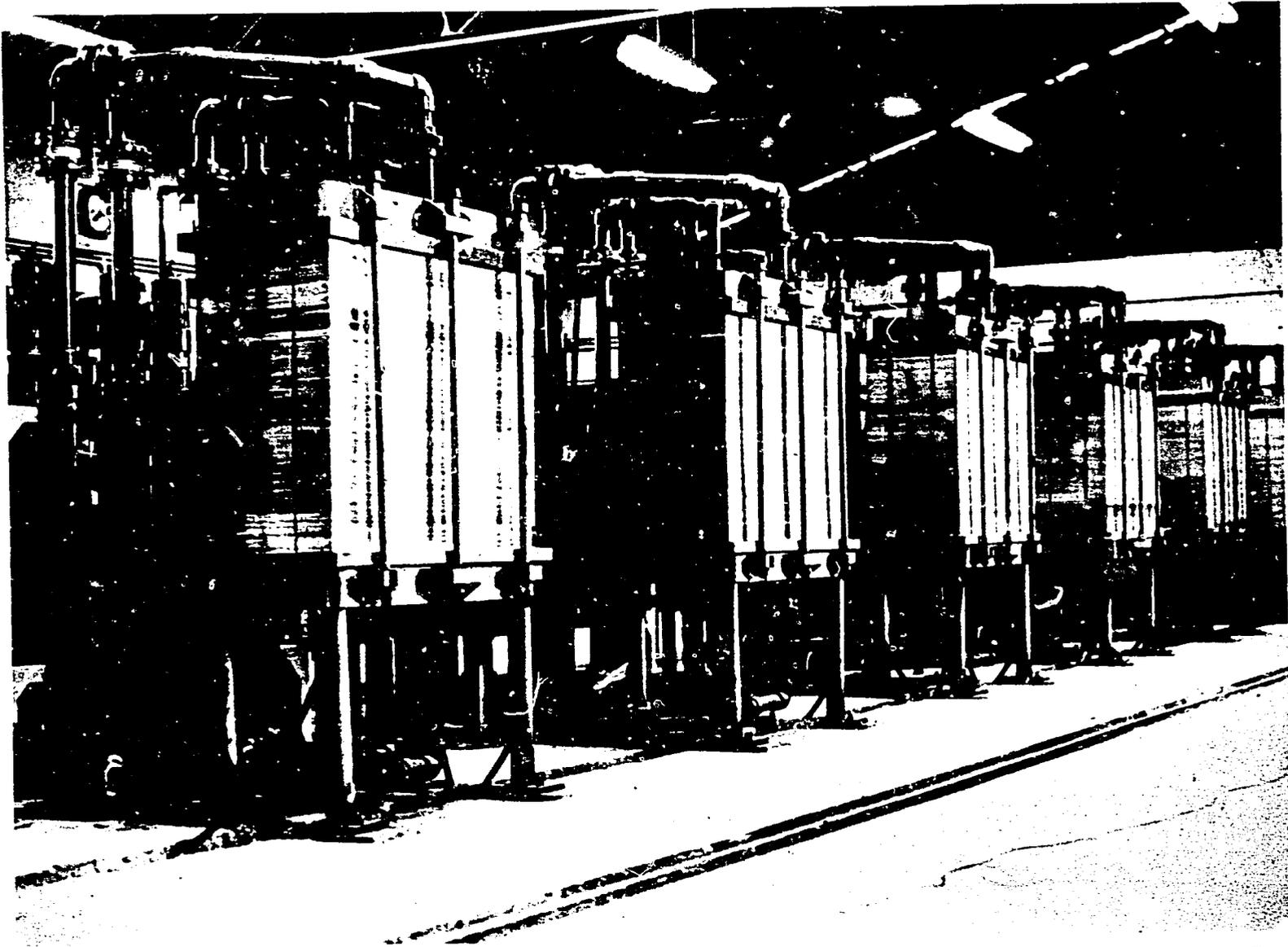


FIGURE IV-59

ELECTRODIALYSIS PLANT, BUCKEYE, ARIZONA



Courtesy: Ionics, Inc

A 250,000-gpd electro dialysis plant built by Ionics, Inc. went into operation in 1965, supplying the entire freshwater requirements for Port Mansfield, Texas. Brackish well water with 2,400 ppm total dissolved solids is supplied to the plant through an 18-mile pipeline.

In Japan, the electro dialysis process has been used to obtain concentrated brine from seawater.

In summary, the electro dialysis process is suitable for desalting brackish waters but, presently, is not competitive with other processes for desalting seawater.

### 3. Electrodialysis Process Limitations

#### a. General

One of the limitations on the electrodialysis process is the salinity of the available feedwater. The electrodialysis process is best suited to the demineralization of brackish waters containing less than 5,000 ppm total dissolved solids. The electric power consumed, and the resulting freshwater cost using the electrodialysis process, are roughly proportional to the amount of salt which must be removed from the saline water feed stream. This is in contrast to other distillation processes, in which the cost of desalting water is largely independent of its initial salinity. Electrodialysis is not presently economical for desalting seawater, which has an average salinity of 35,000 ppm because of the excessive energy requirements. The modular characteristics of electrodialysis desalination plants are such that the unit capital cost is less sensitive to capacity than in the case of other processes, and in smaller water-production capacities this process is more economical than the distillation processes.

Another limitation on the electrodialysis process is the purity of the product water stream. Generally it is not economical to use electrodialysis to reduce the dissolved solids in the product below 100 to 300 ppm. As the product water decreases in salinity, its resistance increases and a higher voltage is necessary to maintain the same current flow. Thus, the power required to reduce the salt concentration from 4,000 ppm to 3,000 ppm is less than that required to reduce it from 1,300 ppm to 300 ppm (6). Generally, ion exchange would be more economical than electrodialysis to purify further the product water. It should be noted that the distillation processes can produce high purity product water from seawater; however, high product water purity is not required for every use. For domestic consumption, 500 ppm total dissolved solids is satisfactory.

If electro dialysis is being used to concentrate a solution, there is a limit to the amount of possible concentration. This upper limit on achievable concentration is due to the water of hydration, which is carried along with the ions transferred through the membrane. This phenomenon is known as electro-osmosis.

Another limitation on the electro dialysis process is the maximum achievable current density (electric current per unit stack cross-section). This limit is a function of the feedwater composition, the fluid velocity and the particular spacer design (6). The allowable current density, as a function of salinity, goes through a maximum at intermediate concentrations. At low ppm total dissolved solids, the current density is limited by polarization. At high ppm, it is limited by burning of the membrane material.

Polarization is the increase or decrease in salt concentration which occurs near the membrane surfaces because of the passage of electric current. As the current density increases, the salt concentration near the membrane surfaces facing the brine stream increases, while that near the membrane surface facing the product stream decreases. Polarization has three effects (6):

- (1) The stack resistance increases.
- (2) Inorganic scales may deposit on the membrane.
- (3) Local pH changes occur at high current densities.

The overall stack resistance increases because the decreased resistance in the brine stream (due to increased salt concentration) does not compensate for the increased resistance in the product stream (due to salt depletion).

Deposition of inorganic scale compounds may occur if the saturation concentration of the particular scale-forming compounds is exceeded. These solubility limits are, of course, a function of the solution pH. At the current densities (20 ma per square cm) normally employed in electro dialysis plants, water hydrolysis occurs in the depleted region of the freshwater

stream (43). This hydrolysis is the splitting apart of water molecules into hydrogen ( $H^+$ ) and hydroxyl ( $OH^-$ ) ions. It has the effect of increasing the current-carrying capability of the freshwater stream. As a result of this hydrolysis, the local pH on the anode side of the anion-exchange membrane will become more basic or alkaline. Similarly, the cathode side of the cation-exchange membrane will become more acidic. There is a tendency for the alkaline scale compounds, calcium carbonate and magnesium hydroxide, to deposit in the alkaline environment of the brine stream on the anion-exchange membrane.

The usual method of preventing alkaline scaling of the anion-exchange membrane is to use acid pretreatment of the feed stream. Another technique is periodic reversal of stack polarity. However, if polarity reversal is employed, provision must be made to change the flow connections when the polarity is reversed.

Occasionally, brackish waters are encountered which are saturated or even supersaturated in calcium sulfate. In these cases a potential calcium sulfate scaling problem may exist. The remedy is to treat the waste stream (the stream being concentrated) with a polyphosphate material and then increase the amount of brine blowdown.

The ion-exchange membranes may have their resistance increased also by colloids, organic matter, algae and solids contained in the feed stream. Most of these materials can be removed by filtration and/or coagulation.

Sulfonic acid groups from the cation resin may contaminate the anion resin and neutralize charged sites thereon, thus limiting the ability of the anion resin to pass anions.

Brackish well-waters may contain impurities such as iron and manganese, which will require special pretreatment of the saline water feed stream. Investigations conducted at the Bureau of Reclamation field test station near Denver, Colorado disclosed that the principal fouling agent associated with the long-term rise in the electrical resistance of electrodialysis stacks was iron hydroxide. These tests have indicated that acidification of the dilution feed stream holds promise of controlling this resistance rise (27).

An on-site evaluation in 1965-66 by Kaiser Engineers of the operations of the OSW Webster, South Dakota Demonstration Plant indicated that the principal problems in this operation involved removal of certain elements in the saline water which were detrimental to good current efficiency and membrane life (46).

The brackish well-water which comprises the feed stream to the plant contains iron, manganese and organic contaminants. Manganese zeolite filter units were provided to remove iron and manganese from the feed water. Some difficulty was experienced with the breakthrough of fine zeolite sand during backwashing and rinsing of the filter beds, primarily because of excessive flow through the operating filter units when a filter was being backwashed. Some of this fine sand was carried over, and it clogged the polishing filters and occasionally entered the electro dialysis stacks (9). A study was made by Johns-Manville Products Corp. on methods of improving the quality of brackish feed water containing iron, manganese and organic contaminants. Pilot plant studies used a preconditioning step and diatomite filtration, followed by an adsorption bed of granulated activated carbon to remove organics (27). With well-waters, such as those at Webster, containing metallic organic complexes, the process was able to reduce the iron and manganese content to less than 50 micrograms per liter (27).

b. Research to Overcome Process Limitations

Research programs are being carried out under OSW sponsorship at a large number of research institutions and companies to develop more efficient ion-exchange membranes at lower cost.

The Bureau of Reclamation, Office of the Chief Engineer, conducts a continuing testing program of permselective membranes and electro dialysis equipment at its Denver, Colorado laboratories and at its Dalpra Farm field test station near Longmont, Colorado. Tests have been carried out, under OSW sponsorship, on electro dialysis demineralizing units supplied by various firms. These investigations include determination of limiting current densities, long-term resistance rise and polarization.

Southern Research Institute of Birmingham, Alabama is working under OSW sponsorship to develop electro dialysis membranes prepared using a cellulosic substrate. Among the cellulosic base films which have been investigated are cellophane film, parchment denitrated nitrocellulose and cellulose diacetate (27). Anion-selective membranes have been prepared using 4-vinylpyridine as the ionic monomer which is graft-polymerized onto the cellulosic substrate (27). In preparing cation-selective membranes, sodium styrene sulfonate has been employed as the ionic monomer (27). Cross-linking of the ionic monomers to the substrate has been achieved using gamma radiation and various chemical agents (27).

The OSW has sponsored studies by the Negev Institute for Arid Zone Research at Beersheba, Israel. These studies are directed toward decreasing the energy requirements for desalination by operating the electro dialysis unit at elevated temperatures. The resistance of electro dialysis membranes decreases at elevated temperatures; however, other detrimental effects occur also, such as increased salt leakage by diffusion and membrane swelling. Operation at elevated temperatures is achieved by using heat exchangers to recover the electric energy dissipated as heat in the electro dialysis stack. Heat recovered from the effluent streams is used to preheat the incoming saline water. It is planned to design and construct a small pilot plant (up to 2,500 gpd) to evaluate further high-temperature electro dialysis using heat recovery (27).

## D. Reverse Osmosis Process

### 1. Reverse Osmosis Phenomena

#### a. General

Osmosis is a natural process by which water flows through a semipermeable membrane separating two saline solutions. The water flow takes place from the less concentrated solution, on one side of the membrane, into the more concentrated solution on the other. This tends to equalize the concentrations on either side of the membrane. The semipermeable membrane has the characteristic that it is permeable to water but not to dissolved salts. Figure IV-60 illustrates normal osmosis. If the water level is allowed to rise in the more concentrated saline solution, flow will continue until a condition of osmotic equilibrium is reached. The difference in water levels corresponds to the osmotic pressure. At this condition of osmotic equilibrium, there is no net flow of water across the semipermeable membrane.

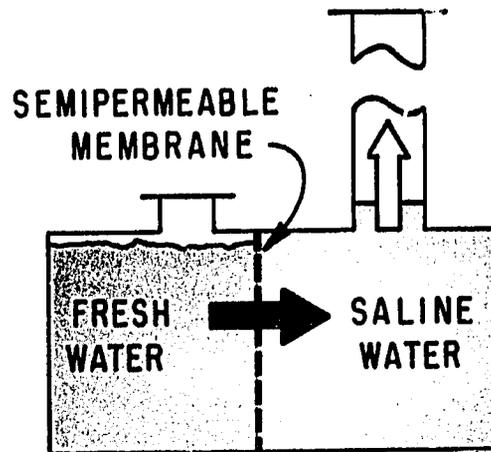
By applying a mechanical pressure which exceeds the osmotic pressure and acts in the opposite direction, the flow of water can be reversed. Thus, by applying high enough pressure, water is forced through the semipermeable membrane from the more concentrated side to the less concentrated side. This process is known as "reverse osmosis" or "hyperfiltration" or "ultrafiltration."

Since the reverse osmosis process does not involve a change of phase, as do distillation and freezing processes, it has the potential of achieving a high thermodynamic efficiency (or low energy input per unit of product).

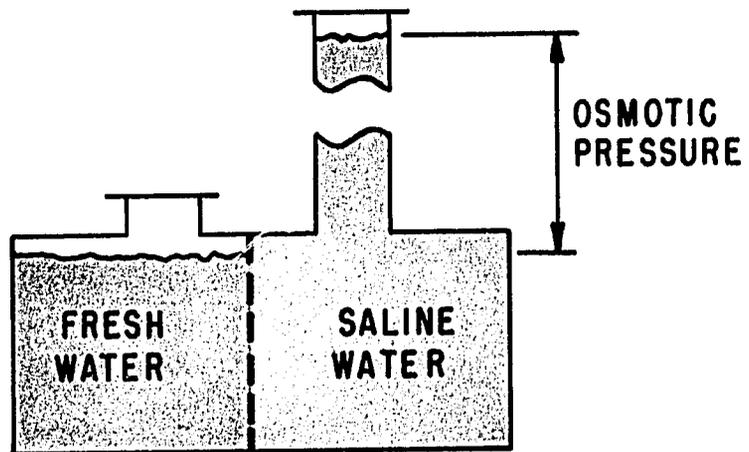
Another advantage of the reverse osmosis process is its simplicity. The essential components consist of a pressurizing pump, a reverse osmosis desalination unit and the associated instrumentation to control pressure and measure product purity. The membrane material not only acts as a barrier to ions but also to un-ionized material. Thus, reverse osmosis can be used to exclude organic materials and viruses from the freshwater product.

FIGURE IV-60

OSMOSIS



(a) NORMAL OSMOSIS



(b) OSMOTIC EQUILIBRIUM

The pressure differential required to force water through the membrane is a function of the difference in concentration between the two solutions. The greater this difference, the higher the required pressure differential. The curve included in the Appendix presents the osmotic pressure as a function of temperature and seawater concentration. The osmotic pressure between seawater and fresh water is approximately 22 atmospheres (or 320 psi). To achieve an appreciable flow of product water through the membrane, the applied pressure must be considerably in excess of the osmotic pressure. To obtain fresh water from seawater by reverse osmosis, the required pressure differential is approximately 1,500 psi, whereas with brackish waters pressure differentials in the range 500 to 750 psi are sufficient.

Reverse osmosis units operate at ambient temperatures, and no heating or cooling of the saline water feed stream is necessary as long as the temperature lies between 60 F and 100 F (47). A reverse osmosis plant treating a typical brackish water would operate at 750 psig and achieve a product-to-feed recovery ratio of 80%. Under these conditions, the electrical energy consumption would vary from 6.5 to 7.5 kilowatt-hours per 1,000 gallons depending on whether the plant was large enough to justify energy recovery (47).

With a seawater feed, typical operating conditions are 1,500 psi and a product-to-feed recovery ratio of 33% (47). The electrical energy input would be approximately 19 kilowatt-hours per 1,000 gallons without energy recovery, and approximately 11 kilowatt-hours per 1,000 gallons with energy recovery (47).

There are two mechanisms by which a solvent can move through a membrane. The first mechanism is convective flow through interconnected pores in the membrane. Membranes with a crystalline structure pass only those molecules which are smaller than the pore size (43). With these crystalline membrane materials, the exclusion of larger molecules is almost complete but the penetration rates are slow.

The second mechanism by which a solute can pass through a membrane is known as permeation. In permeation, the penetrant is dissolved in the membrane, moves through the membrane by a process of activated diffusion and is desorbed on the other side of the membrane (43).

The "standard" reverse osmosis membrane used today is an asymmetric membrane of modified cellulose diacetate, developed by Loeb and Sourirajan at UCLA. This membrane consists of a spongy substructure and a thin (approximately 0.3 micron), dense skin layer formed by a special casting technique. The spongy substructure is made by casting a 2 to 4 mil thick film containing a hydrophilic compound (magnesium perchlorate or formamide) (43). The hydrophilic compound draws water into the membrane as a plasticizer, thereby creating a spongy substructure. The composite structure is referred to as a "skinned" membrane (43).

Actual membranes do not achieve complete rejection of salt. To produce potable water from seawater without staging, a salt rejection of 98.6% is required (43). If as much as half of the fresh water is to be recovered from the seawater feed as product, an even higher salt rejection would be required. Membranes prepared under laboratory conditions have achieved as high as 98% to 99% salt rejection. However, membranes produced in larger quantities average approximately 96.5% (43).

For a particular membrane material, the achievable salt rejection is a function of both the operating pressure and the difference in salt concentration between the saline feed stream and the product water stream. Generally speaking, the higher the operating pressure the higher the salt rejection. As the salinity of the treated water increases, the salt rejection decreases. This means that with presently available membranes, the reverse osmosis units must be operated in series to produce potable water from seawater. Conversion of brackish water of drinking quality can be accomplished with a single reverse osmosis stage.

## b. Reverse Osmosis Terminology

### Activated Diffusion

The process by which a penetrant molecule moves through a membrane from one transient vacancy to another, with an energy interaction between the penetrant and the membrane.

### Asymmetric Membrane

A permeable membrane which has a laminated structure affecting its solute transporting properties (41).

### Concentration Polarization

The buildup of salt concentration near the membrane surface on the more saline side of a reverse osmosis membrane. This increased local salt concentration either reduces the water flux through the membrane, or increases the required operating pressure. The salt is carried to the membrane wall by the permeating water, but must leave by back-diffusion.

### Hyperfiltration

Also called ultrafiltration and reverse osmosis. It is a process by which a pressure differential is applied across a membrane, permeable to solvent but not to the solute, to cause the solvent (water) to flow from the more concentrated solution into the less concentrated solution. The term is applied to the pressure-induced separation of a spectrum of particles, macromolecules, simple molecules and ions from a solute (43).

### Osmosis

The natural process by which water flows through a semi-permeable membrane from a less concentrated solution into a more concentrated solution.

### Permeability

The quantity of the permeant per unit area, thickness, time, driving force (43).

### Reverse Osmosis

A process in which pressure is applied to the more saline solution to force water into the less saline solution, thereby overcoming the osmotic pressure due to the concentration differences. It is also called ultrafiltration and hyperfiltration.

### Ultrafiltration

See hyperfiltration and reverse osmosis

### Water Flux Rate

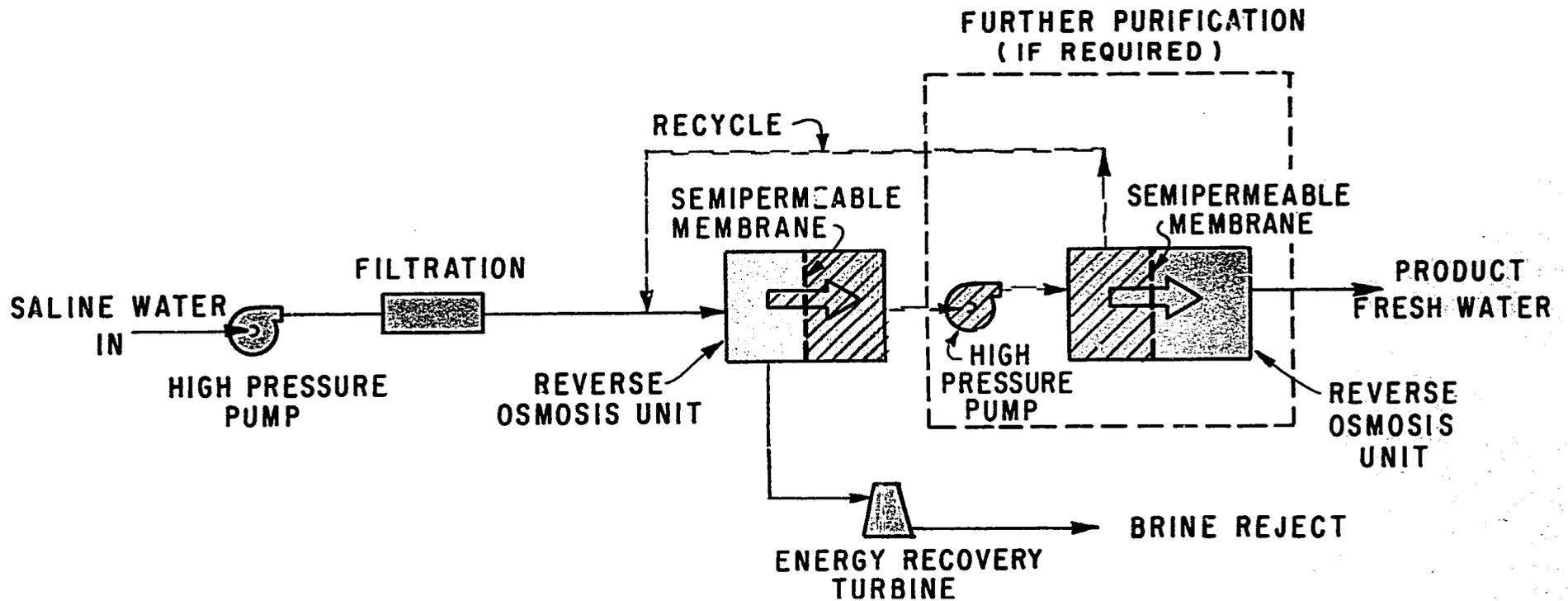
The flow of water which can be achieved through a semipermeable membrane per unit area of membrane surface (gpd per square foot).

## 2. Reverse Osmosis Process Description

Figure IV-61 is a schematic flow diagram of the reverse osmosis process. The entering saline water feed stream is filtered to remove any particulate matter which might erode or foul the membrane surface, thereby impeding the flow. The high pressure saline water feed enters the concentrated side of the first reverse osmosis unit. Fresh water is forced through the semipermeable membrane to the low-concentration product water side of the unit. Approximately 50% of the saline water feed is recovered as product. Typically, the product-to-feed recovery ratio may vary from 80% for brackish water to 33% for seawater (27). The brine reject stream from the first reverse osmosis unit flows through a turbine or other energy recovery device. Because of the high pressure to which the saline stream must be raised, it is necessary to recover energy from the brine reject, at least for a large seawater conversion plant. For brackish water conversion, energy recovery may not be economical since both the operating pressure and quantity of concentrated brine are lower than for a plant which processes seawater. Also, energy recovery generally is not warranted for small capacity plants (47). If the saline water input has a relatively high salt concentration, further purification may be required. This is indicated in Figure IV-61 by a second reverse osmosis unit in series with the first. The brine from the second unit would be recycled to the first unit.

The principal technological limitation on the reverse osmosis process is the development of a membrane with suitable characteristics. Ideally a membrane material should be inexpensive and have high water flux rate, high salt rejection and a long performance life. Also, it is necessary to achieve a uniform membrane quality on a production basis.

FIGURE IV-61  
REVERSE OSMOSIS PROCESS



The performance of reverse osmosis membranes declines with time. This degradation is a function of a number of variables, including the type of membrane, feedwater contamination, operating temperature and operating pressure. The membrane degradation is attributed to the combined effect of membrane compaction due to pressure, biological attack, erosion and the deposition of precipitates or coatings on the membrane surface (47). Also, membranes may fail prematurely due to pinholes, tears or other structural defects. The long-term test data presently available are insufficient to predict membrane life reliably. It is estimated that an average membrane life of six months might be expected; however, no performance guarantees can yet be given (47).

Generally, fouling of the membrane surfaces by suspended matter in the feedwater can be prevented by filtration to remove particles larger than 5 microns (47).

Acidification of the feedwater may be required if the pH is higher than 7, since cellulose acetate may be damaged by prolonged exposure to alkaline solutions (47). Biological attack of reverse osmosis membranes can be controlled by chlorination of seawater or brackish water which is biologically contaminated (47).

Another limitation on the reverse osmosis process is the need to develop efficient energy-recovery devices. The high pressure reject brine stream from a reverse osmosis unit contains energy which could be utilized to supply part of the feedwater pumping energy. Energy recovery is most likely to be economical in large capacity plants, and has not been used in any of the small plants built to date.

Concentration polarization is the increase in salt concentration near the wall on the more saline side of the membrane. The salts are carried along to the wall by the water permeating through the membrane, and can leave by back-diffusion only. Concentration polarization is a technical limitation on the reverse osmosis process, since, as the local concentration builds up near the wall, the water flux will decrease unless the imposed pressure differential is increased.

Considerable research effort is being directed toward finding a suitable membrane material. Among the organizations presently conducting research on reverse osmosis membranes for OSW are

North Star Research and Development Institute, Westinghouse Electric Corporation, Montana State University, Arthur D. Little Research Institute, the Weizmann Institute of Science (Israel) and Dartmouth College. Two promising new developments have resulted from this research activity: an ultra-thin cellulose acetate membrane and an organic membrane deposited continuously on a porous backing (11). The dynamic deposition of the inorganic membrane material is accomplished by adding small amounts of the membrane-forming material to the influent stream. The use of polysaccharides and polyelectrolytes is also under investigation.

The problem of concentration-polarization is being attacked by several different approaches. One approach is the use of turbulence promoters near the membrane surface to stir the boundary layer. Dorr-Oliver, Inc. and Amicon Laboratories are investigating the use of a thin-film approach to minimize concentration-polarization. The theoretical basis for this approach is based on maintaining a small concentration difference between the bulk fluid and the membrane solution interface (27).

A number of analytical investigations are being conducted to define the theoretical basis for reverse osmosis desalination in various systems configurations. Some of the organizations performing such analytical evaluation are Syracuse University Research Institute, Clarkson College of Technology and the University of California, San Diego.

Because of the relatively undeveloped state of reverse osmosis processes, a number of design concepts are being examined as alternative configurations for arranging the membrane and its support in a complete system. Some of these designs are the plate and frame, spiral wrapped module, tubular and thin film concepts.

During 1962, Aerojet-General Corporation began work on a reverse osmosis pilot plant utilizing a plate and frame design. This pilot plant contains 100 square feet of membrane and has a nominal capacity of 1,000 gpd when processing seawater, or 2,000 gpd when operating on brackish water. Aerojet-General presently is operating four of these units under an OSW contract. The purpose of these units is to investigate membrane performance on both seawater and brackish water, to obtain information on membrane life and to evaluate the pretreatment which would be required for the saline water feed to the reverse osmosis unit. One deleterious effect encountered was the effect of ferrous ions in the feedwater.

This was successfully eliminated by diatomaceous earth filtration and also by periodic treatment of the membrane material with either citric acid or a dilute mineral acid. Figure IV-62 shows a trailer installation with two similar 1,000-gpd reverse osmosis units.

A prototype of a commercial reverse osmosis unit containing 460 square feet of membrane was put into operation by Aerojet-General Corporation in July 1965. This unit has a nominal capacity of 10,000 gpd on 1,000 ppm brackish water feeds (47).

A second prototype commercial unit, with a nominal capacity ranging from 20,000 gpd to 40,000 gpd, was put into operation by Aerojet-General in May 1966; it is described in more detail in Section V.

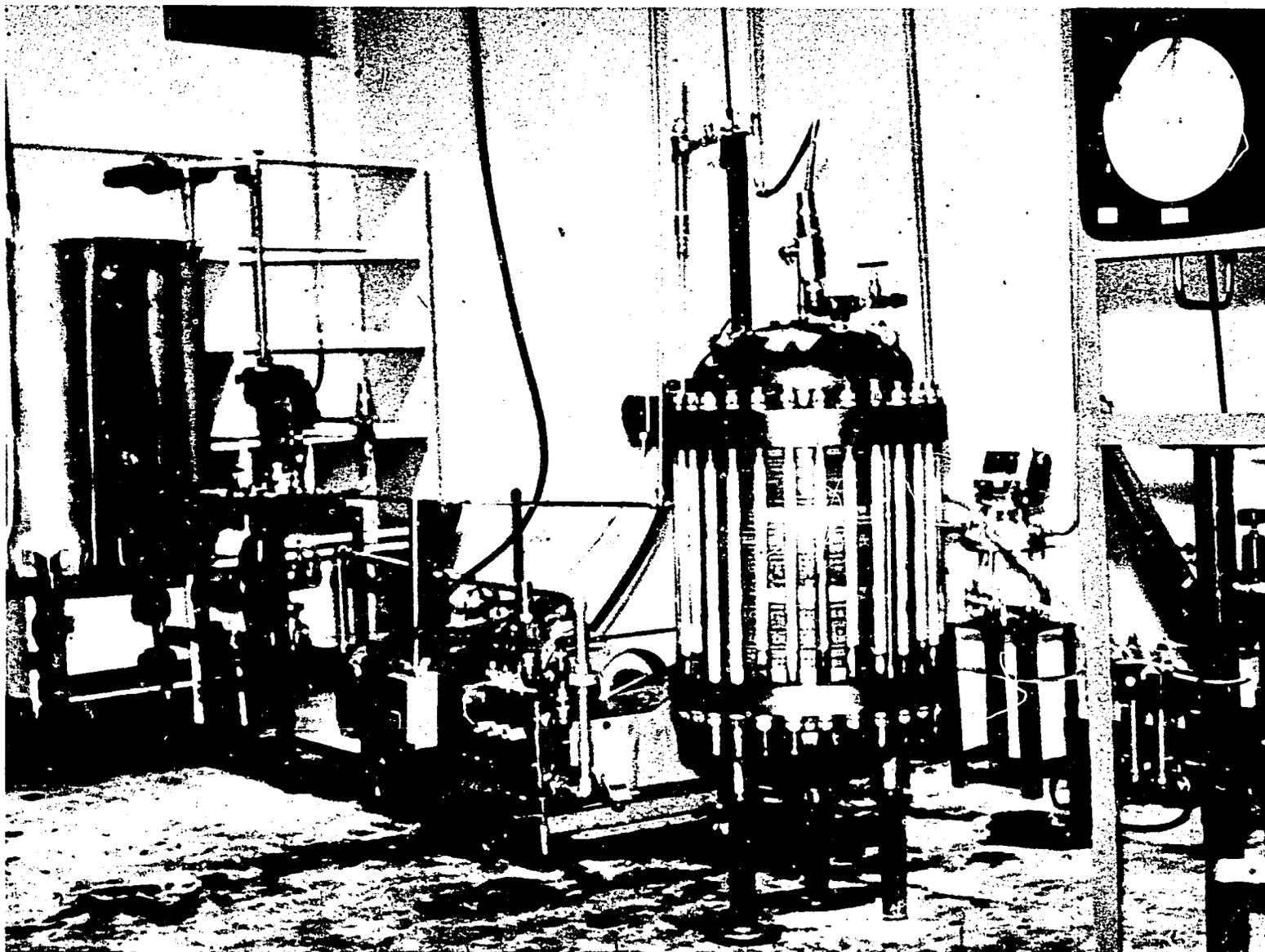
At present, under an OSW contract, Aerojet-General Corporation is fabricating a larger pilot plant, containing 2,500 square feet of membrane. This pilot plant has a nominal capacity of 50,000 gpd and will test cell components suitable for use in a large-capacity reverse osmosis plant. The size of the components used in this unit represents a considerable scale-up over previous units. It is planned to operate the 50,000-gpd plant on well-water containing calcium and magnesium salts.

A spiral-wound sandwich module has been developed by the General Atomic Division of General Dynamics Corporation (see Figure IV-63). This spiral-wound sandwich consists of a pair of membranes covering a porous flexible backing material. The resulting three-layer sandwich is glued together at the edges. The membrane sandwich is rolled on a perforated tube together with a separator. The perforated tube serves as the conduit for product water. General Atomic has constructed test loops using this spiral-wound module, both for operation at low pressures with brackish water and at high pressures with seawater. A 1,400-gpd reverse osmosis unit was built by General Atomic and exhibited at the First International Symposium on Desalination in Washington, D. C. during 1965. The unit was used to conduct tests on reverse osmosis purification of Potomac River water. Bacteria and coliforms were almost completely eliminated from product water. A 10,000-gpd pilot plant is presently being built by General Atomic at San Diego, California.

A tubular osmotic-membrane assembly is being operated at Coaltinga, California in a 7,000-gpd reverse osmosis plant. The tubular assembly consists of a membrane made from a cellulose acetate, formamide and acetone. The membrane is cast on a tube

FIGURE IV-62

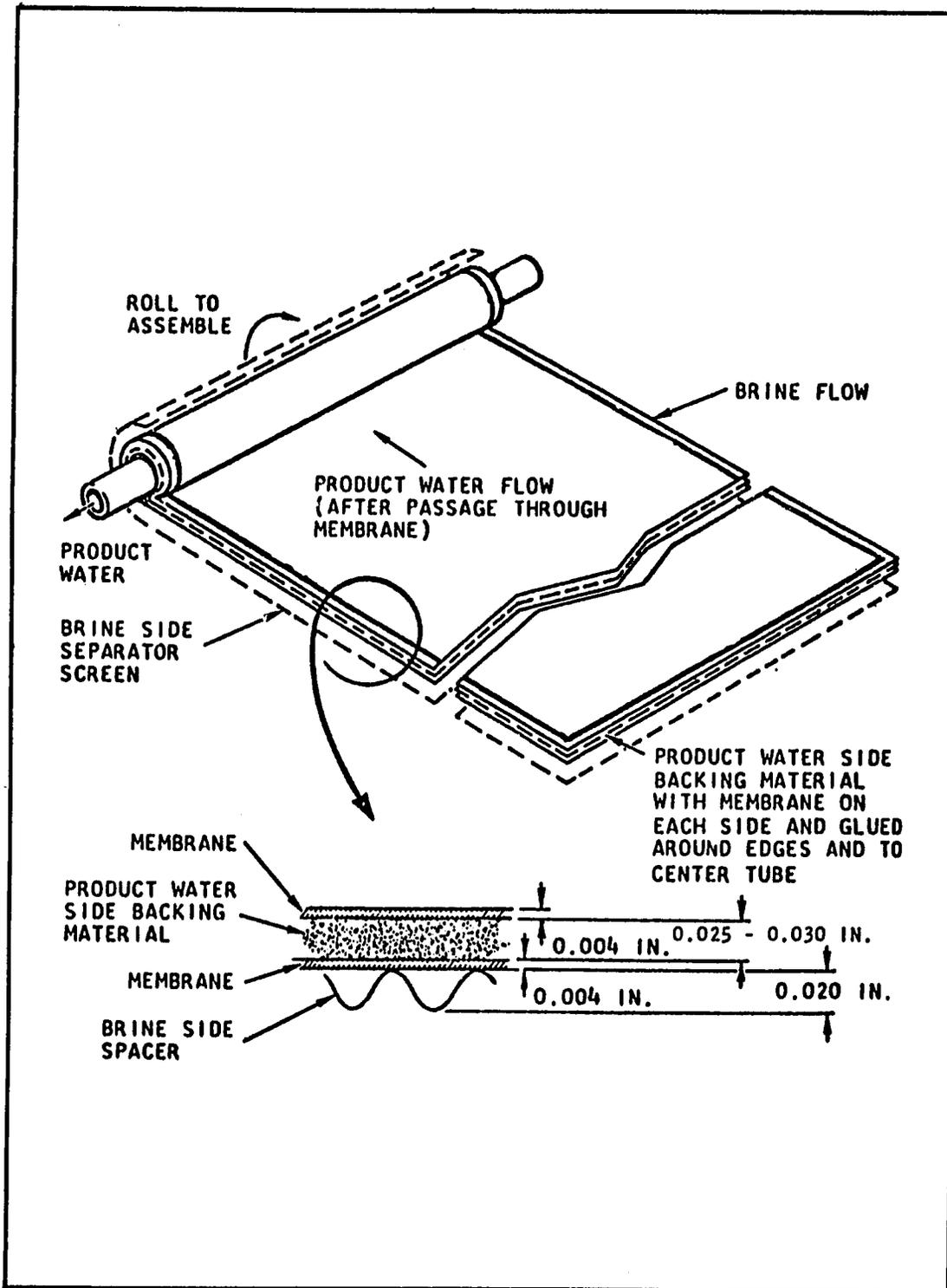
AEROJET-GENERAL CORP 1,000-GPD PILOT PLANT  
INTERIOR VIEW OF TRAILER SHOWING REVERSE OSMOSIS UNIT



Source: U. S. Department of the Interior,  
Office of Saline Water

FIGURE IV -63

SPIRAL-WOUND REVERSE OSMOSIS MODULE  
DEVELOPED BY GENERAL ATOMIC DIV, GENERAL DYNAMICS CORP



Source: U. S. Department of the Interior,  
Office of Saline Water

having a 0.004-inch wall, and wrapped in two layers of filter paper and a nylon mesh material. The entire assembly is placed inside a 1-inch copper tube. The Coalinga plant demineralizes brackish water at an operating pressure of 600 psi. Havens Industries also has built a small reverse osmosis pilot plant using tubular assemblies. The Havens unit employs reusable porous fiberglass tubes coated with a cellulose diacetate surface.

Although reverse osmosis offers considerable promise as a future process for economically desalting both seawater and brackish water, the process is not sufficiently developed for large-scale commercial, municipal or industrial applications. Considerable uncertainty exists with regard to the type, life and cost of the membrane, membrane support costs and equipment arrangement.

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