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ANALYSIS OF A DUAL MODE DESALINATION  
SYSTEM FOR NAVAL BASES

E. E. Cooper

Naval Civil Engineering Laboratory  
Port Hueneme, California

May 1973

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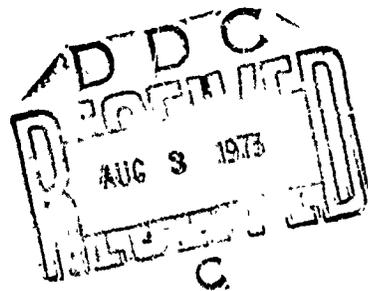
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ANALYSIS OF A DUAL MODE DESALINATION SYSTEM FOR NAVAL BASES

By

E. E. Cooper, Ph. D.

May 1973



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13. ABSTRACT A study was performed to determine the technical and economic feasibility of a dual mode desalination device combining a reverse osmosis unit and a multistage flash distillation unit. The function of the reverse osmosis unit would be to remove sufficient amounts of scaling salts from intake seawater to allow scale-free operation of the flash distillation unit at temperatures up to 350°F. Failure records of reverse osmosis equipment revealed that substantially higher membrane reliability can be expected if the saline water is pressurized to only 600-800 psi rather than the normal 1100-1500 psi used with seawater. A review of membrane technology revealed that at 600-800 psi, specially blended "open" cellulose acetate membranes or an ion exchange membrane can reject the necessary percentage of scaling salts with sufficient water flux to feed the flash distillation unit. Thus the dual mode desalination appears technically feasible. An economic evaluation of the dual mode device, however, reveals that the cost of its product water would be higher than that from a conventional 250°F flash distillation unit. A further result of the economic study indicates that the development of 350°F multistage flash distillation plants with fluidized beds should be pursued by the Navy.			

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## INTRODUCTION

The concept of a dual mode desalination system, the reverse osmosis-flash distillation (ROFD) system, resulted from ideas and experience gained during a long history of the Naval Civil Engineering Laboratory participation in seawater desalination. Most of the past effort is briefly reviewed in Reference 1.

Of particular interest are the tests conducted by NCEL personnel on two reverse osmosis units used to convert seawater. One was a 2500 gallon-per-day (gpd) unit manufactured by Universal Water Corporation, while the other was an 80,000 gpd barge-mounted unit manufactured by Aqua-Chem Corporation. Results of the tests are reported in References 2 and 3. Although the performance of the RO systems was somewhat disappointing, analysis of the test records pointed out which components were most subject to failure or malfunction. Both RO systems had two stages. Their first stages operated at feed pressures of 1000-1500 psi, while the second stages accepted the products of the first stages at pressures of 600-800 psi. The low pressure second stages experienced far fewer problems than the first stages.

Commercial RO units having brackish feed consistently operate for many months with no failures or detrimental loss of performance. Their feed is usually pressurized at 600-800 psi. The conclusion to be drawn is that the expected trouble-free lifetime of reverse osmosis membranes and systems is much longer when the system is operated at 600-800 psi feed water pressure.

It has been proposed that the ROFD plant utilize a reverse osmosis unit with a flash distillation unit in such a way that the weak features of both are avoided. The reverse osmosis unit is to be operated at a pressure of 600-800 psi. Feed seawater to the system enters the RO unit, which has as its main function the removal of a portion of the dissolved salts, particularly scaling salts. The partially desalted product water of the RO unit is then fed to the flash distillation unit. Because of the reduction in scaling salts, the flash still can be operated scale-free at high temperatures. Raising the water to 350°F in the heater of the flash distiller appears reasonable. High temperature operation of a flash still is desirable because of the resulting increased yield of fresh water. Approximately twice the output can be obtained from a 350°F still as from a 212°F unit for the same energy input.

The concept of using reverse osmosis membranes to reduce scaling salts is not unique. Erickson<sup>4</sup> conducted experiments to determine if a group of specially prepared membranes had suitable salt rejection and product flux for use as a water softener in distillation plants. During private communication, Milstead<sup>5</sup> related that his company is considering this as one possible application for a new line of membranes under development.

Basically three sizes of desalination systems are required by the Navy. For temporary advance bases, small units with an output in the order-of-magnitude of  $10^4$  gpd are needed. At larger semi-permanent bases, units producing nominally  $10^5$  gpd are required. At permanent installations such as Guantanamo,  $10^5$  gpd or more of pure water are needed.

Operation of flash distillation plants at  $350^\circ\text{F}$  is also a goal of the Office of Saline Water (OSW). The ROFD system has not been considered by OSW, but other techniques to permit scale-free  $350^\circ\text{F}$  operation have been researched and proved technically feasible. One technique called desulfation, is to remove sulfate ions from the feed water by an ion exchange process before pumping it into the flash distillation unit. Another procedure is to use a fluidized bed heat exchanger which is simply a modified heater. The desulfation process is currently favored by OSW. Several technically feasible schemes have been dropped from consideration on the basis of economics or reliability.

The sections below discuss in general terms several pertinent aspects of seawater conversion, then describe and analyze the ROFD system. Although the economics of  $350^\circ\text{F}$  operation of flash distillation units is only approximate, the cost of water production with the ROFD system is compared with production costs by the desulfation process, the fluidized bed process, and by a conventional  $250^\circ\text{F}$  flash distillation plant. Conclusions and recommendations are then outlined.

#### SALT CONTENT OF SALINE WATER

The U. S. Public Health Service<sup>6</sup> recommends that water to be used for human consumption (potable water) contain less than 500 parts per million by weight (ppm) of total dissolved solids (TDS). Water containing more than 1000 ppm should not be used for human consumption. Water containing in excess of 1000 ppm is defined as saline water.

The amount of dissolved solids in water depends upon its source. Table 1, compiled from References 4 and 7, compares the major salt constituents found in waters from different sources. It is seen that seawater normally has slightly less than 35,000 ppm TDS. This amount may differ from one location to another, particularly near continental shelves where dilution by fresh water streams can occur, but the proportion of various constituents is amazingly uniform.

Table 1. Salt Concentrations of Different Saline Waters  
(in ppm)

	Ocean	Roswell, N.M. Well	Buckeye, Ariz. Well	Webster, S.D. Well	Dead Sea	Great Salt Lake	Caspian Sea
Sodium (Na <sup>+</sup> )	10,561	5,000	598	124	32,000	67,300	3,200
Magnesium (Mg <sup>++</sup> )	1,272	303	7	103	35,700	5,600	773
Calcium (Ca <sup>++</sup> )	400	549	100	223	12,700	300	297
Potassium (K <sup>+</sup> )	380	Trace	Trace	12	6,400	3,400	70
Chloride (Cl <sup>-</sup> )	18,980	8,064	1,100	23	178,600	112,900	5,500
Sulfate (SO <sub>4</sub> <sup>--</sup> )	2,649	1,548	169	912	400	13,600	3,970
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	142	120	71	327	Trace	200	48
Bromide (Br <sup>-</sup> )	65	Trace	Trace	Trace	5,200	Trace	---
Other Solids	34	---	---	---	---	---	---
Total Dissolved Solids	34,483	15,564	2,045	1,724	271,000	203,300	12,658

Subterranean saline waters are found in large quantities around the world. These well-water sources are termed "brackish." Brackish waters normally have dissolved solid contents between 1,000 and 4,000 ppm, but may be as high as 25,000 ppm. The Roswell, New Mexico, well water is seen to contain over 15,500 ppm. Brackish water chemical compositions vary considerably with location.

Surface waters normally have low salt content, composed mainly of salts of calcium and magnesium. There are, however, bodies of surface water which cannot drain. Constantly fed by salt-bearing surface streams, but losing only pure water by solar evaporation, the waters become more and more laden with salt. The Dead Sea and the Great Salt Lake have accumulated salt concentrations many times higher than that of the ocean.

#### METHODS OF DESALINATION

Table 2 categorizes the principal processes by which the salt content of saline water can be reduced. A discussion of all the various techniques is beyond the scope of this report, but a simplified explanation of each, including clarifying sketches, is given in Reference 8. A discussion of the reverse osmosis and flash distillation processes is in order, however, since the ROFD system under study here is to utilize both techniques.

#### Reverse Osmosis

The normal osmotic process is depicted in Figure 1a. A semi-permeable membrane separates a salt water solution from pure water. At atmospheric pressure, pure water passes through the membrane to dilute the salt water solution. The migration of pure water can be stopped if the pressure of the salt water solution is raised while the pure water remains at atmospheric pressure (Figure 1b). The pressure required to stop the passage of pure water into the salt water compartment is the osmotic pressure. Osmotic pressure increases with the salt concentration. For brackish waters, the osmotic pressure is usually below 200 psi. For seawater it is about 350 psi.

When the pressure of the salt water solution is raised above the osmotic pressure, water is forced from the salt water compartment to the fresh water compartment (Figure 1c). In other words, a reverse osmosis occurs.

An ideal semipermeable membrane would allow passage of only water during the reverse osmosis process. No membrane is perfect, however, and some salt is transferred along with the water. The effectiveness of a membrane is expressed in terms of its salt rejection and flux corresponding to some particular pressure imposed on the saline water solution. Membrane effectiveness is dependent upon many factors including the type of membranes, method of fabrication and curing, operational temperature and pressure, composition of the feed water, membrane mounting procedure, and state of membrane degradation due to fouling or compaction during use.

Table 2. Desalination Processes

Distillation:

Vertical tube  
Multistage flash  
Multieffect multistage  
Vapor compression  
Solar

Membrane:

Electrodialysis  
Transport depletion  
Reverse osmosis

Crystallization:

Vacuum freezing-vapor compression  
Secondary refrigerant freezing  
Hydrate formation

Chemical:

Ion exchange

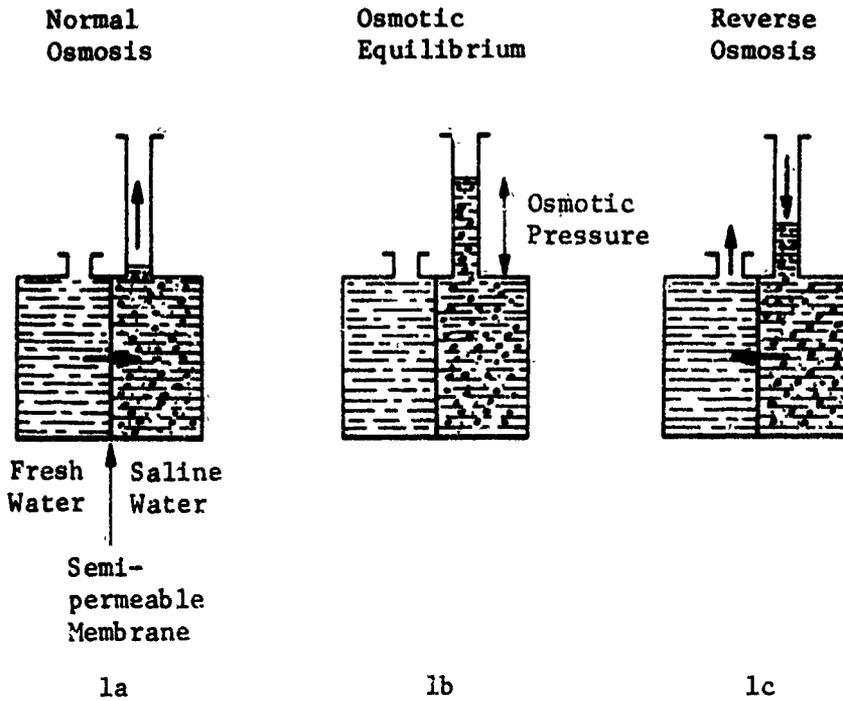


Figure 1. Osmotic process.

There are three types of RO membranes developed for commercial use. By far the most commonly used are cellulose acetate membranes. The characteristics and expected performance of cellulose acetate membranes are fairly well understood due to the extensive experience with them. Another concept in reverse osmosis membranes, called hollow fibers, has also been introduced. The fibers appear as hair-like tubes, the hole in the center being microscopic. Several types of material can be used to manufacture the fibers, but a nylon blend is favored at present. In operation, pressurized saline water surrounds the fibers, and fresh water passes through the tube walls and out through the hollow center. A third type of membrane is sometimes designated as a charged membrane, but is more appropriately called an ion exchange membrane. At present only the General Electric Company has developed a product in this category, a sulfonated polyphenylene oxide membrane. In principle, membranes may be of either the cation or anion type, depending on the material used to accomplish the ion exchange. The GE membrane is a cation type.

The ROFD system is to be a versatile device capable of desalting seawater, so obviously the reverse osmosis membranes used must operate efficiently and be compatible with seawater. The nylon hollow-fiber membranes may be ruled out for several reasons. Their close packing makes them subject to easy clogging and fouling. Pressures in the 600-800 psi range are sufficient to collapse many of the fibers. And, most seriously, the nylon is chemically attacked by the chlorine in seawater. Thus, either a cellulose acetate or an ion exchange membrane must be used in the ROFD system. Only special types of cellulose acetate membranes will operate efficiently in the ROFD system. Since the osmotic pressure of seawater is about 350 psi, operation of the RO unit at 600-800 psi gives a driving potential of only 250-450 psi. Actually the potential is even less throughout most of the RO unit because the osmosis of fresh water concentrates the brine and raises the osmotic pressure. The low driving potential normally results in a low flux of fresh water. In order to improve the flux, so-called "open" membranes must be specially prepared. Practically all development efforts have had the objective of producing "tight" membranes in the hopes of improving the economics of RO desalination of both brackish and seawater. With open membranes, a high rate of salt passage accompanies the increased water flux. Figure 2 shows salt rejection versus water flux for three cellulose acetate membranes, each cured at a different temperature. Data were taken by Erickson<sup>4</sup>. The flux through open membranes usually decreases with use due to their susceptibility to compaction.

Very little can be said at present concerning the use of ion exchange membranes with seawater. The membranes were developed specifically for wash water treatment and have never been tested with seawater. They have been used with dirt laden, soapy water and showed no decrease in flux due to fouling even after 90 days of continuous use. They are chemically stable in very acidic or very basic waters (pH = 4 to 13), whereas cellulose acetate membranes must be exposed only to water having the pH controlled so that it is slightly acidic. Ion exchange membranes have demonstrated almost complete rejection of the sulfate ( $\text{SO}_4^{--}$ ) ions in tests with brackish water feeds. Dr. A. B. LaConti<sup>10</sup> of General Electric has projected that the ion exchange membranes will show a 90% salt rejection with a corresponding flux of 10 gal/ft<sup>2</sup>-day when seawater is the feed. An interesting feature of the ion exchange membranes is that they show best performance when operated at 165°F.

The large pressure drops across membranes dictate that they be supported to prevent bursting. Several arrangements for mounting and supporting the membranes have been devised. The arrangements may be classified as plate and frame, tubular, and spiral wound. Hollow fibers are bundled into a cylinder which does not fit any of the three above classifications, but fibers will not be considered for use in the ROFD system for reasons given above. The plate and frame arrangement is often used in laboratory work, but the manifolding and space required make other arrangements more attractive for commercial units. The spiral wound arrangement has good packing density and is used on many commercial units for brackish water desalination, waste water treatment, and polishing of water for industrial uses. The small passageways between layers of the spiral result in susceptibility to easy clogging and fouling when used with seawater. The tubular arrangement is better for reducing fouling problems. Disadvantages of the tubular arrangement include low packing density and difficulty in detecting and replacing defective membranes. The tubular arrangement is preferred for seawater use.

All dissolved species are not rejected equally by RO membranes. It has been well established that bivalent ions are more readily rejected than univalent ions. Using data from Reference 4, rejection characteristics of two identical membranes, one with a brackish water feed and the other with a synthetic seawater feed are shown in Table 3. It is seen that the bivalent scaling ions ( $\text{Ca}^{++}$ ,  $\text{SO}_4^{--}$ ,  $\text{Mg}^{++}$ ) are preferentially rejected at a greater rate than the non-scaling ions. The univalent bicarbonate ion, which also contributes to scale, is highly rejected from seawater. No such data are presently available for ion exchange membranes, but it is known that they selectively reject the  $\text{SO}_4^{--}$  ion very well. According to Dr. LaConti<sup>10</sup>, however, the rejection rate is reduced when large amounts of  $\text{Cl}^-$  are present, as in seawater.

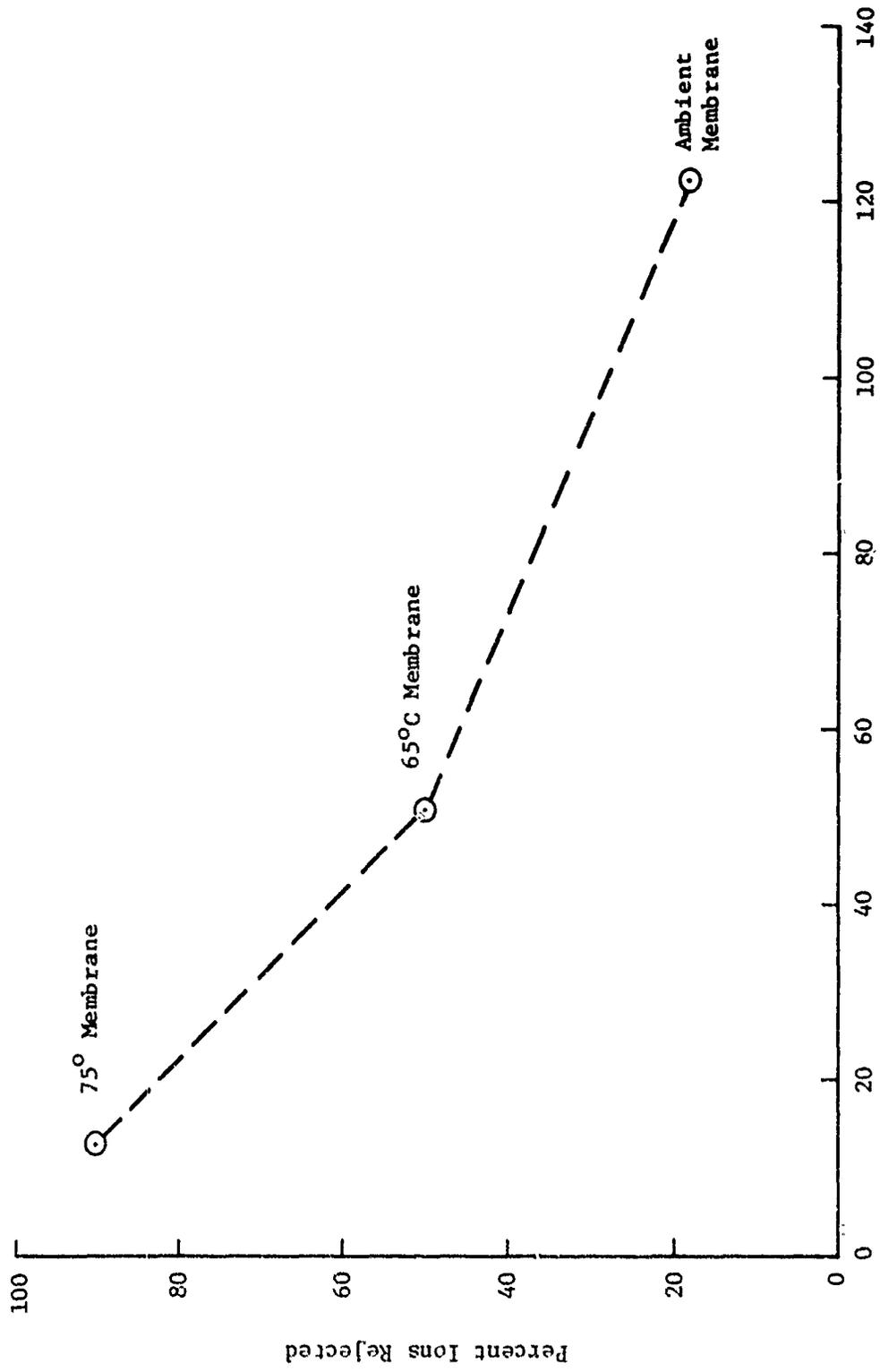


Figure 2. Salt rejection vs flux (UCLA membranes).

Table 3. Membrane Rejection of Dissolved Ions  
(UCLA Membrane Cured at 75°C, Pressure = 600 psig)

Ion	Rejection Rate, % Synthetic (Well) Water Roswell, N. M.	Rejection Rate, % Synthetic Seawater
SO <sub>4</sub> <sup>--</sup>	98.1	99.5
Ca <sup>++</sup>	97.8	95.7
Mg <sup>++</sup>	95.8	96.0
HCO <sub>3</sub> <sup>-</sup>	87.5	91.4
Na <sup>+</sup>	94.4	90.0
Cl <sup>-</sup>	93.8	90.0
K <sup>+</sup>	----	86.8
Br <sup>-</sup>	----	83.0

### Flash Distillation

Figure 3 depicts a multistage flash distillation (MFD) device. The unit is composed of a series of chambers, or stages, each having a lower pressure than the one before it. The unit takes advantage of the fact that the boiling temperature of water decreases as pressure decreases. When hot water at equilibrium in one chamber flows into the adjacent lower pressure chamber, some of the water flashes to steam.

Heat is added to the feed water just prior to its entry into the high pressure chamber. The amount of heat added is much less than that needed to evaporate the product water. In an efficient distillation unit, 90 percent of the energy required to evaporate steam from the brine can be recovered during recondensation of pure water. Cool feed water is pumped through the condensers of each stage. It enters the condenser of the low pressure stage and is pumped through the condenser of each stage before passing through the heater and into the flash chambers. Preheating of the feed by the condensing steam obviously results in less heat input being required at the heater.

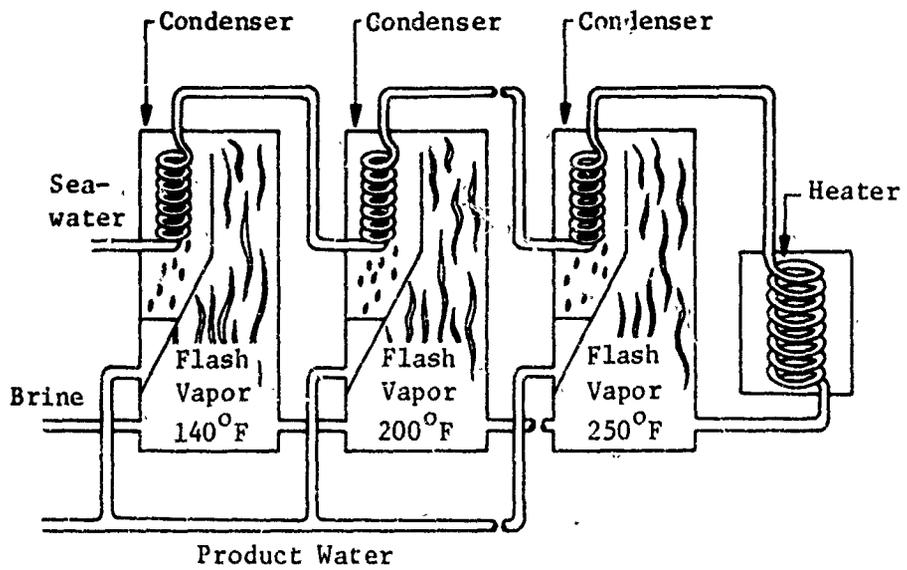


Figure 3. Multistage flash distillation process.

The brine and distilled water discharged from the low pressure stage are at a higher temperature than the feed water entering the condenser. This temperature difference, along with heat loss through the walls of the distillation unit, plus some inefficiencies in the flash chambers, account for the fact that all the heat added in the heater is not recovered in the condensers. Even more than 90 percent of the heat of vaporization can be recovered, but the weight and cost involved makes this economically impractical. The condenser heat exchangers usually operate with at least a 10°F temperature difference between the feed water and the condensing steam.

Each flash still is designed for optimized performance at some specified heater temperature. In some stills the heater temperature is below 212°F, while others are designed to heat the water as high as 350°F. For reasons explained in the next section, all flash units are subject to scaling. The major scaling problems occur in the heater, but scale sometimes also forms on the feed water side of the condenser tubes, particularly in the high pressure and temperature stages. On the other hand, scale which attempts to form in the flash chambers is washed through the system and does not form on the surfaces. Scale problems can be minimized by operating at relatively low heater temperatures. For example, if all stages are operated at pressures below atmospheric, water will flash in the first chamber even when introduced below 212°F. Scale formed in a 212°F heater is primarily magnesium hydroxide,  $Mg(OH)_2$ , which can be prevented or removed by adding the proper amount of acid to the feed water, either continuously or at intervals.

It is proposed, however, that the ROFD system can be designed to heat the feed water to 350°F. At such high temperatures, untreated seawater will deposit calcium sulfate scale in the heater. By passing the seawater through an RO unit before it reaches scaling temperatures, however, the concentrations of calcium and sulfate ions may be reduced to such an extent that scale will not form. Operation of a still with a high temperature heater allows more stages to be used with a corresponding increase in product water.

In each stage, an ideal heat balance equates the heat required to vaporize product water to the heat given up by the remaining brine.

$$M_V(\Delta h)_{L-V} = M_L c_p \Delta T$$

$$\frac{M_V}{M_L} = \frac{c_p \Delta T}{(\Delta h)_{L-V}}$$

In actual practice the ideal situation is never quite realized.<sup>11</sup> Unless design features are incorporated to reduce them, nonequilibrium effects in the flash chambers will reduce the amount of vapor formed.

Of concern are temperature gradients in the brine, temperature differences between the vapor and the brine, and violent boiling which lofts brine into the vapor. In conventional multistage flash equipment, small temperature differences between stages help minimize the nonequilibrium effects. A 10°F temperature drop is a common value. Since  $(\Delta h)_{L-v} \approx 1000 \text{ Btu/lb}_m$  and  $c_p \approx 1.0 \text{ Btu/lb}_m \cdot ^\circ\text{F}$ ,  $M_V/M_L$  is approximately 0.010 per stage. That is, each 10°F stage flashes about 1.0 percent of the saline water entering it. A flash still taking in seawater at 75°F and heating it to 210°F would use 13 stages and ideally distill about 13 percent of the feed water. But if the water were heated to 350°F, 27 stages would be used and approximately 26-27 percent of the feed water would be converted under ideal conditions. Actual yields of 10 percent and 20 percent could be expected for the two cases described.

### SCALE FORMATION

Badger<sup>12</sup> defines scale as a deposit formed by precipitation from solution of a substance which has a solubility that decreases with an increase in temperature (inverse solubility). This definition is not strictly true since some scale can form from salts with normal solubilities, but the major scaling salts have inverse solubility. In raw seawater, the chemical compounds causing scaling problems are calcium carbonate ( $\text{CaCO}_3$ ), magnesium hydroxide ( $\text{Mg(OH)}_2$ ), and calcium sulfate ( $\text{CaSO}_4$ ).

Unless measures are taken to prevent it, scale appears in almost all processes of desalination. It can form on heat exchangers and boiler tubes of distillation units. It can coat the membranes of electro-dialyzers and reverse osmosis units. The occurrence of the scale leads to operating difficulties and/or loss of efficiency unless the layer is very thin.

In reverse osmosis units the primary scaling problem arises from calcium carbonate deposition on the membranes. This fouling can be prevented by the combined actions of acid addition to the feed water to keep the pH low and by discharging the salt water before it has become excessively concentrated, i.e., before excess water has been removed. In distillation, the type of scale formed depends primarily upon the temperature of the heating surface. Scale has a low thermal conductivity. Thermal conductivity values listed in Reference 7 show that calcium sulfate scale conducts heat only 3 percent as efficiently as aluminum, and only 14 percent as efficiently as steel. Thus the building of scale on a heat transfer surface rapidly degrades the heat transfer effectiveness of the surface.

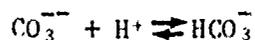
An oversimplified explanation of scale formation states that when the concentration of a salt dissolved in water surpasses the solubility limit of that salt, the excess salt is precipitated. The explanation is oversimplified by omitting discussion of kinetic effects, influence of other salts in solution, possibility of supersaturated solutions,

and influence of surface irregularities or particles in the water which act as nuclei for scale formation. Langelier<sup>13,14</sup> performed the first quantitative measurements of solubility limits for calcium sulfate, calcium carbonate, and magnesium hydroxide. His findings, as well as the observations of numerous investigators, indicate that calcium carbonate scale is formed when the heating surface is below 180°F, magnesium hydroxide scale is formed above 180°F, but calcium sulfate becomes the most prevalent scale at high temperatures, usually above 250°F. Figure 4 shows the relative composition of scale formed at different water temperatures and heating rates.

In his experiments, Langelier introduced an excess quantity of a scaling salt into water at a known temperature, allowed time for an equilibrium solution to establish, and determined the amount of salt going into solution. In order to explain the results, two terms should first be defined. The ionic product of a salt is the product of the concentrations of the ions which combine to form the salt. Consider calcium sulfate, for example. The ionic product of CaSO<sub>4</sub> is the product of the concentrations, C<sub>Ca<sup>++</sup></sub> × C<sub>SO<sub>4</sub><sup>--</sup></sub>. The units of C<sub>Ca<sup>++</sup></sub> and C<sub>SO<sub>4</sub><sup>--</sup></sub> in this report are ppm/10<sup>6</sup> (gram weight of ions/10<sup>6</sup> grams water). The solubility product is the highest value of the ionic product possible in a stable solution at a given temperature. Langelier's data is basically a presentation of the solubility product as a function of temperature for the three scaling salts.

#### Calcium Carbonate

Precipitation of calcium carbonate scale occurs when the ionic product exceeds the solubility product. The concentration of calcium ions in aqueous solution can be easily determined. There is difficulty, however, in directly measuring the concentration of carbonate ions. One must instead resort to indirect means. Carbonate and hydrogen ions react reversibly to form the bicarbonate ion.

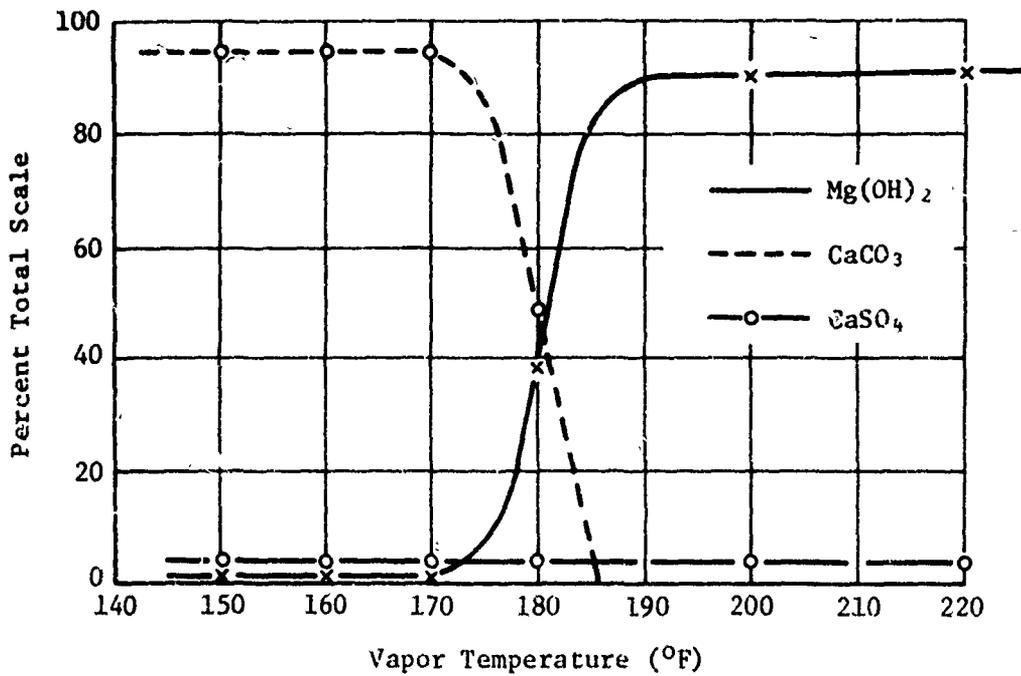


The law of mass action states that

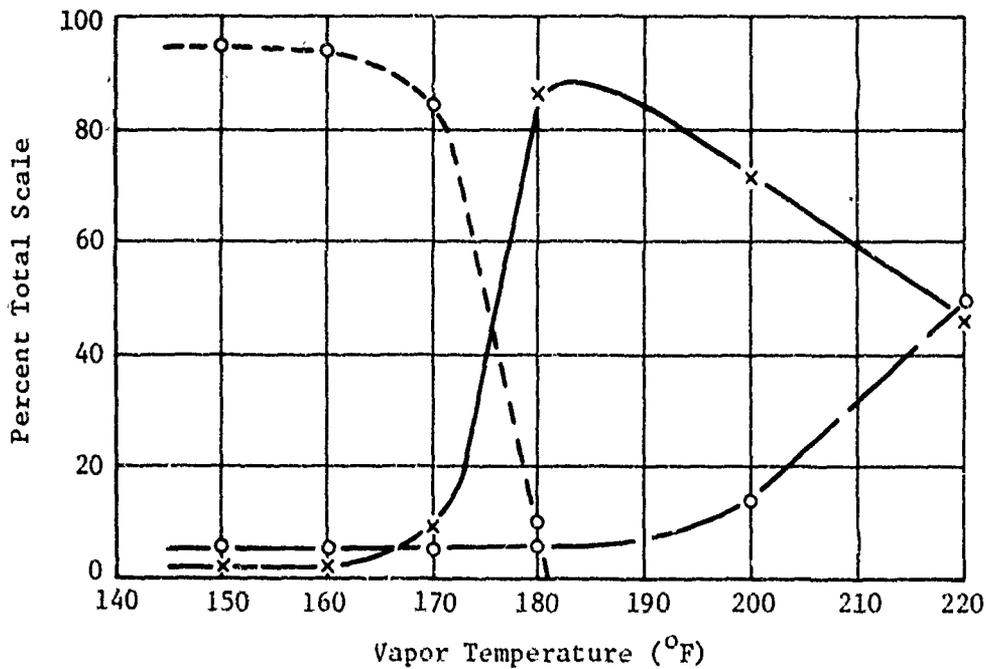
$$\frac{C_{\text{CO}_3^{--}} C_{\text{H}^+}}{C_{\text{HCO}_3^-}} = K_1(T)$$

$$C_{\text{CO}_3^{--}} = \frac{K_1(T) C_{\text{HCO}_3^-}}{C_{\text{H}^+}}$$

Concentration of the bicarbonate ion in a solution can be determined by titration with acid. Concentration of the hydrogen ion determines



Nominal Temperature Difference =  $22^{\circ}\text{F}$   
 Between Heating Surface and Vapor



Nominal Temperature Difference =  $80^{\circ}\text{F}$   
 Between Heating Surface and Vapor

Figure 4. Scale formation as a function of temperature and heating rate.

the pH of the solution, since by definition

$$\text{pH} = -\log_{10} C_{\text{H}^+}$$

so the ionic product of calcium carbonate is

$$C_{\text{Ca}^{++}} C_{\text{CO}_3^{--}} = C_{\text{Ca}^{++}} \frac{K_1(T) C_{\text{HCO}_3^-}}{C_{\text{H}^+}}$$

If the complicating effects noted above are neglected, then at a given temperature there is a single value of the solubility product. Call this  $S_{\text{CaCO}_3}(T)$ . Then

$$S_{\text{CaCO}_3}(T) = C_{\text{Ca}^{++}}^* \frac{K_1(T) C_{\text{HCO}_3^-}^*}{C_{\text{H}^+}^*} \quad (1)$$

where the superscript \* denotes a concentration at the solubility limit.

Graphical representation of Equation (1) is most conveniently given on log-log plots. Taking the decimal logarithm of both sides and rearranging,

$$\log_{10} C_{\text{Ca}^{++}}^* = \left[ \log_{10} S_{\text{CaCO}_3}(T) - \log_{10} K_1(T) \right] - \left[ \log_{10} C_{\text{HCO}_3^-}^* - \text{pH} \right]$$

Choosing a temperature, a straight line relationship exists between  $\log_{10} C_{\text{Ca}^{++}}^*$  and pH, with  $\log_{10} C_{\text{HCO}_3^-}^*$  as a parameter. Langelier<sup>13,14</sup> determined the solubility limit of  $\text{CaCO}_3$  at temperatures of 60°C and 100°C. Figures 5 and 6 show plots of calcium concentration versus pH for these two temperatures. Data for other temperatures must be interpolated or extrapolated. Note that the parameter of the figures is the concentration of calcium carbonate rather than the bicarbonate ion. The equivalent bicarbonate concentration is obtained by multiplying the  $\text{CaCO}_3$  concentration by the ratio 61/50.

To use the curves, concentrations of calcium, hydrogen, and bicarbonate ions are measured at 25°C. Enter the 60°C plot at the measured pH and bicarbonate concentration and read the equilibrium calcium concentration. If the measured calcium concentration is greater than the equilibrium value, precipitation of scale is expected when the water is heated to 60°C.

#### Magnesium Hydroxide

Figures 5 and 6 are somewhat misleading when applied to seawater.

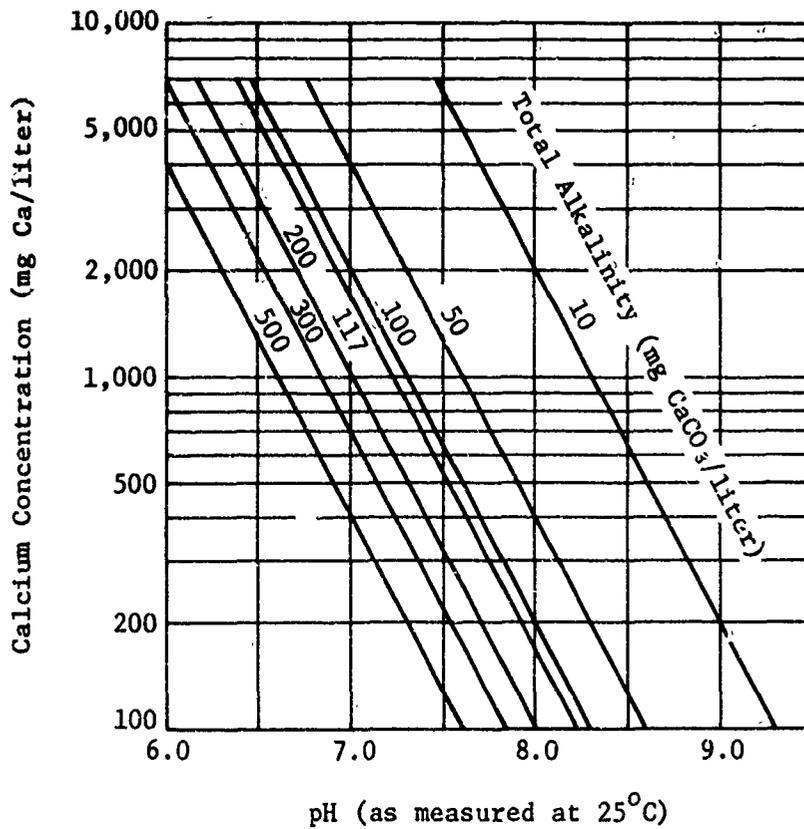


Figure 5. Solubility of CaCO<sub>3</sub>, T = 60°C.

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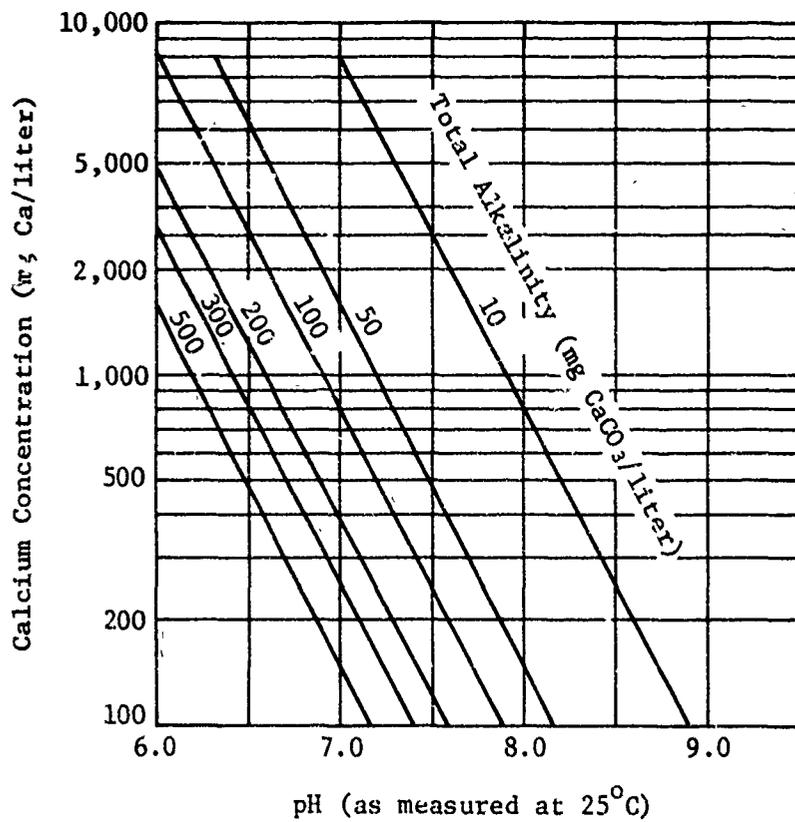


Figure 6. Solubility of CaCO<sub>3</sub>, T = 100°C.

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At a given pH and bicarbonate concentration, they show a lower calcium ion solubility at 100°C than at 60°C. But Figure 4 shows less calcium carbonate formation at the higher temperature. In seawater other dissolved constituents react in a way to curtail the scaling of CaCO<sub>3</sub>. Up to 180°F (83°C) calcium carbonate is the primary scaling agent, but above that temperature, magnesium hydroxide becomes the major scale. This is explained as follows.

Bicarbonate concentration tends to decrease with increasing temperature due to the decomposition reaction.

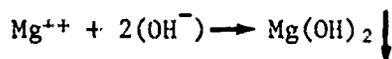


The CO<sub>2</sub> gas generated goes out of solution, leaving the OH<sup>-</sup> ion. In turn, the increase in OH<sup>-</sup> ions drives the water decomposition reaction further to the right.



Decomposition of bicarbonate suppresses the formation of calcium carbonate, while it will be seen below that the increase of OH<sup>-</sup> enhances the formation of Mg(OH)<sub>2</sub>.

Raw seawater contains 1200 ppm magnesium which can react with the hydroxyl ion to form magnesium hydroxide.



Langelier experimentally determined the solubility limits of Mg(OH)<sub>2</sub> as a function of temperature also. In terms of the solubility product,

$$S_{\text{Mg}(\text{OH})_2}(T) = C_{\text{Mg}^{++}}^* (C_{\text{OH}^-}^*)^2 \quad (4)$$

Rather than measure the concentration of the hydroxyl ions, the concentration of the hydrogen ions is measured. In accordance with Equation (3) they are in equilibrium with the hydroxyl ions. By the law of mass action, the equilibrium constant for Equation (3) is

$$\frac{C_{\text{H}_2\text{O}}}{C_{\text{H}^+} C_{\text{OH}^-}} = K_2(T)$$

Since the concentration of H<sub>2</sub>O is practically constant, it can be grouped with K<sub>2</sub>(T)

$$K_3(T) = \frac{K_2(T)}{C_{\text{H}_2\text{O}}} = \frac{1}{C_{\text{H}^+} C_{\text{OH}^-}}$$

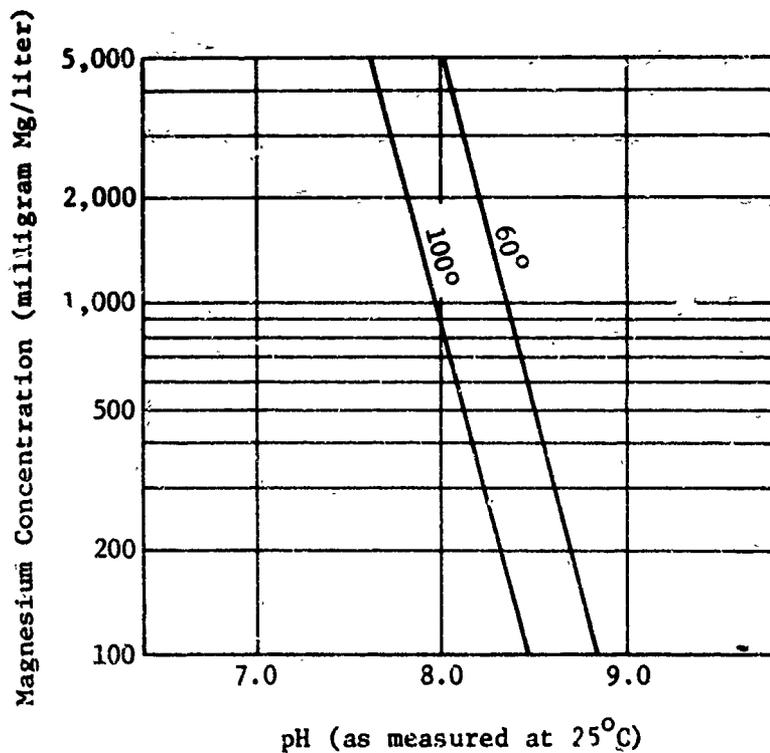


Figure 7. Solubility of  $Mg(OH)_2$ .

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Substituting into (4)

$$S_{\text{Mg(OH)}_2}(T) = C_{\text{Mg}^{++}}^* \left[ \frac{1}{K_3(T) C_{\text{H}^+}^*} \right]^2$$

Taking decimal logarithms and rearranging,

$$\log_{10} C_{\text{Mg}^{++}}^* = \left[ \log_{10} S_{\text{Mg(OH)}_2}(T) + 2 \log_{10} K_3(T) \right] - 2 \left[ \text{pH} \right]$$

Again a straight line relationship is obtained, this time between pH and the logarithm of the equilibrium magnesium concentration. Langelier's data is plotted in Figure 7 with temperature as the parameter.

### Calcium Sulfate

Calcium sulfate,  $\text{CaSO}_4$ , is the third saline water salt which contributes to the scaling problem. It is usually precipitated when seawater is heated to 250°F or above. Calcium sulfate is the most difficult scale to remove once it has formed.

At least six hydrated forms of calcium sulfate are chemically possible, but fortunately all of these do not contribute to scaling. The three forms which do are  $\text{CaSO}_4$  (anhydrite),  $\text{CaSO}_4 \times 1/2\text{H}_2\text{O}$  (hemihydrate), and  $\text{CaSO}_4 \times 2\text{H}_2\text{O}$  (gypsum). The solubility limit of each form is different, but for all forms is expressed as the product of concentrations of the calcium and sulfate ions.

$$S_{\text{CaSO}_4}(T) = C_{\text{Ca}^{++}}^* C_{\text{SO}_4^{--}}^*$$

Since the concentrations of both ions in solution can be measured directly, it is not necessary to present the solubility data in the same oblique manner as was used for  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$ .

Calcium sulfate deposition seems to be strongly influenced by some of the complicating factors mentioned above. For example, Emmett<sup>15</sup> shows that the solubility product of calcium sulfate increases appreciably in the presence of sodium chloride or magnesium chloride. The same conclusion was reached by Denman.<sup>16</sup> Reference 17 presents two solubility plots for the scaling forms of calcium sulfate. One plot is based on a pure water solvent, while the other is the solubility curve for seawater. Solubility in seawater is much higher. Since seawater is the working fluid of interest in this study, seawater solubility curves for the three scaling forms of calcium sulfate are presented as functions of temperature in Figure 8.

Because the solubility curve for hemihydrate lies above that for anhydrite in Figure 8, it would be expected that anhydrite would precipitate more readily than hemihydrate. Such is not usually the case in flowing systems, however, because of different kinetic behavior of the two forms. Anhydrite can remain in a supersaturated state for a considerable

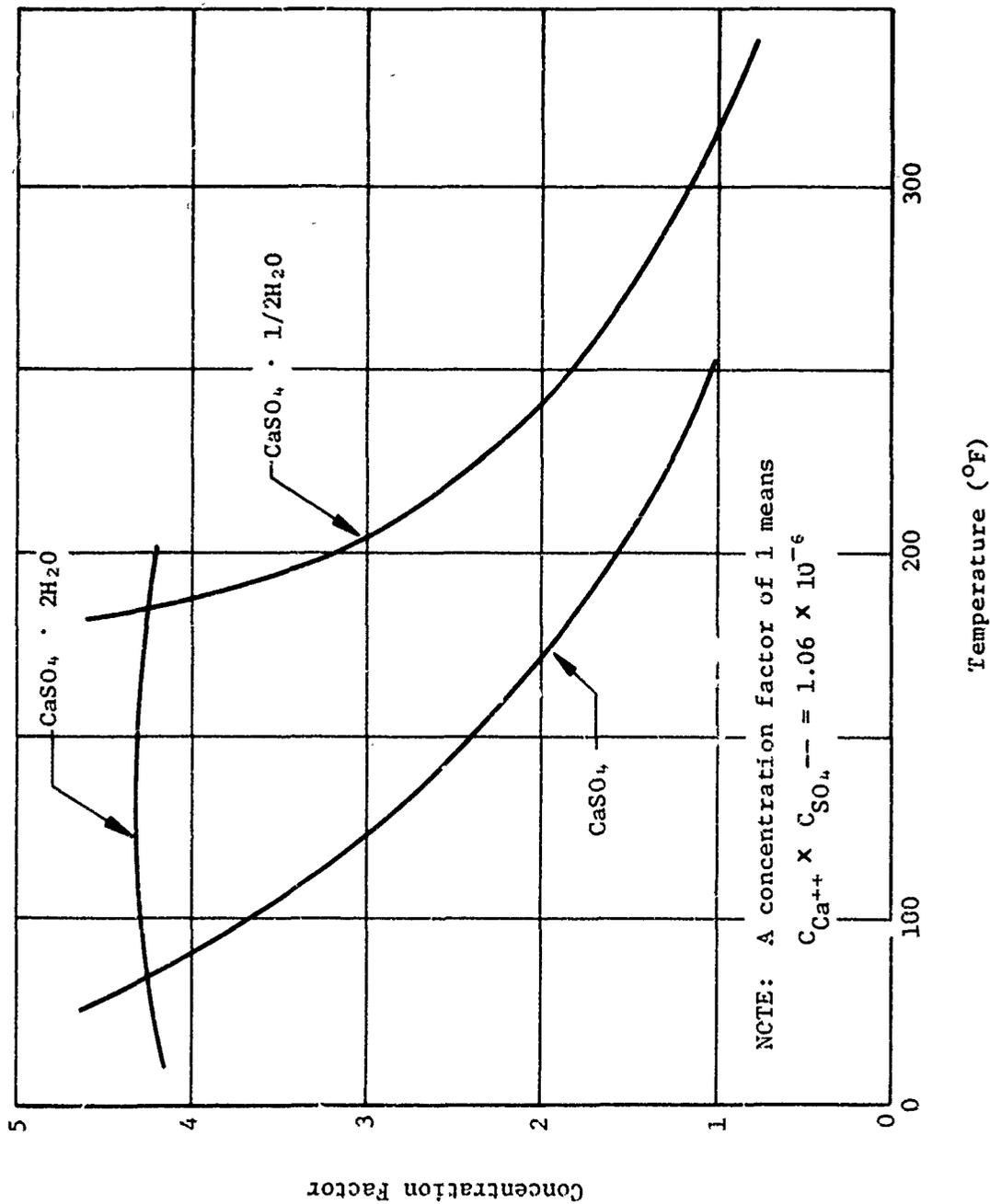


Figure 8. Approximate solubility limits of CaSO<sub>4</sub> in seawater concentrates.

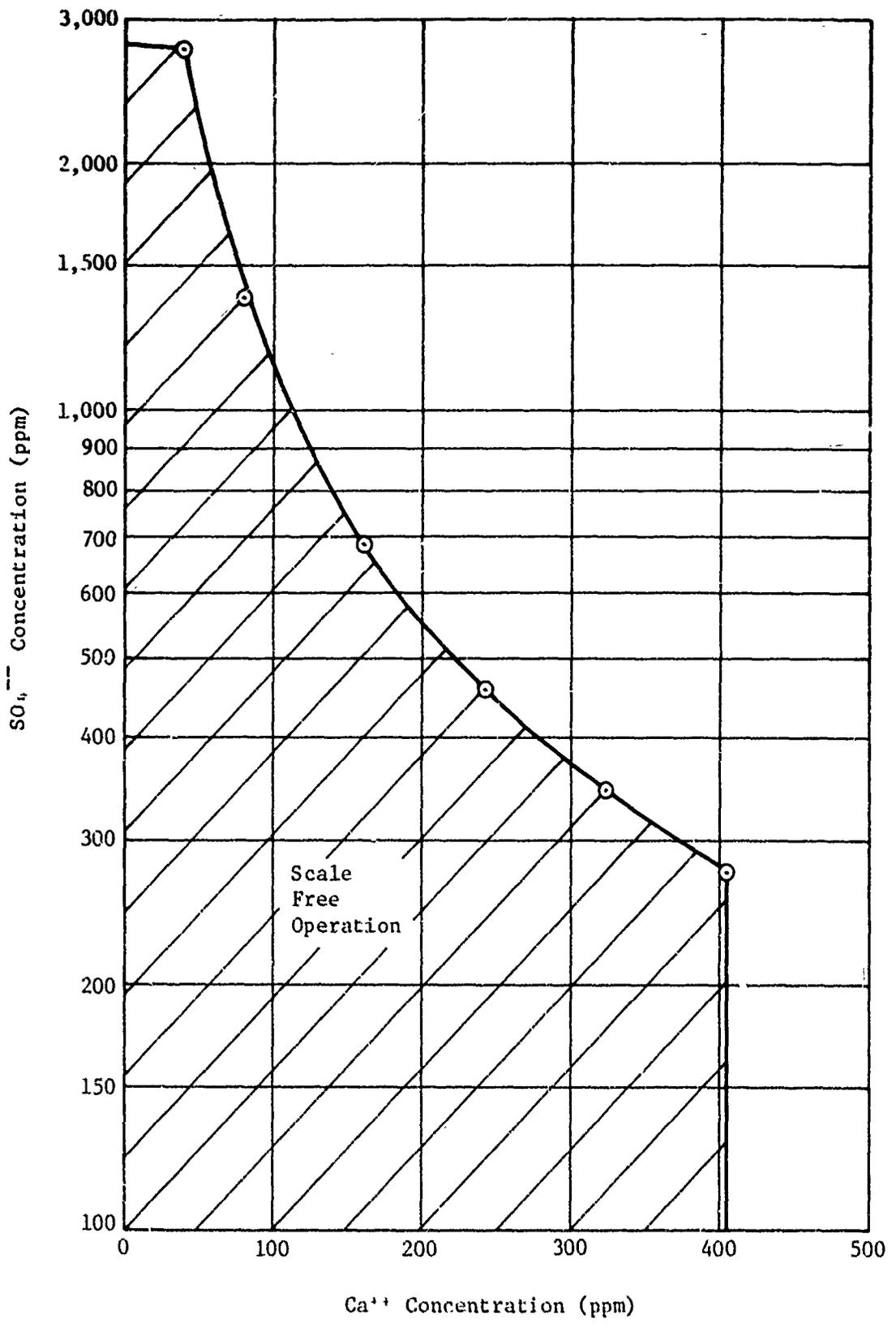


Figure 9. CaSO<sub>4</sub> scale threshold at 350°F.

length of time, while hemihydrate rapidly deposits out of a supersaturated solution

The calcium sulfate scaling threshold for 350°F operation of a multistage flash distillation plant is presented in Figure 9. Data is taken from Reference 18. It is seen that the curve is based upon a concentration product of  $S_{CaSO_4}(350^\circ F) = 1.12 \times 10^{-7}$ . This value will be used as the upper limit for scale-free operation of the dual mode system.

## SCALE PREVENTION AND REMOVAL

A number of methods is available for scale prevention or removal. The choice of one, however, depends upon various factors such as the type and concentration of material dissolved in the water, the temperature of the heating surfaces, the quantities of water being handled, and level of training of personnel operating the purification units.

Of the three types of scale discussed in the previous section, calcium sulfate is the most difficult to remove once it has formed. In addition, when operating temperatures are high enough for  $CaSO_4$  precipitation from seawater, the procedures presently used for scale prevention are costly. The most economical scale control measure for seawater distillation units has been to operate below 250°F and become concerned only with the "soft" scales,  $CaCO_3$  or  $Mg(OH)_2$ .

Figures 5, 6, and 7 show that the pH factor of the feed water influences the solubility of  $CaCO_3$  and  $Mg(OH)_2$ . Acid addition to the feed water lowers the pH and brings conditions to the left of the scaling limit lines of the figures. Periodic addition of heavy doses of acid is often preferred to continuous injection. Thin films of scale formed since the previous dose, are removed each time. Sulfuric or hydrochloric acids are used in large units, but weaker, more expensive acids are sometimes preferred in smaller installations to avoid the corrosive effects of the stronger acids.

Although much less commonly practiced, chemicals other than acids are sometimes added to the feed water for soft scale control.<sup>7</sup> There are salts which, in aqueous solutions, decompose by hydrolysis to form acids. There are also mixtures which act to delay scale deposition and retard dropout until the flow has moved past the heater. Finally, other mixtures added to seawater cause the scale to become softer and less adherent, thereby facilitating removal.

The  $CO_2$  content of the water being heated is also believed to influence the soft scale formation. A study by Partridge<sup>19</sup> shows the solubility of calcium carbonate and magnesium hydroxide to be increased appreciably by the addition of  $CO_2$  to water. In addition, dissolved  $CO_2$  retards the decomposition of bicarbonate shown in the chemical Equation (2). The end result is a reduction in pH and less formation of the hydroxyl radical. Hence, there is less formation of  $Mg(OH)_2$ .

Considerable research and testing have been devoted to control of calcium sulfate scale at temperatures above 250°F. Most efforts have had the objective of removing sufficient amounts of the calcium and/or sulfate ions so that the ionic product will not exceed the solubility product at the operating temperatures of the distillation units. For their multimillion gallon-per-day plants, OSW has favored chemical removal of either calcium or sulfate. Numerous reactions have been proposed for precipitating scaling ions before they reach the distillation units. Two have been tested on large pilot plants. A process for removing calcium, called the lime-magnesium carbonate method, has been tested at the Clair Engle plant in San Diego.<sup>20</sup> A more effective method, which desulfates the seawater by ion exchange to form barium sulfate precipitate, has been developed and successfully tested at the OSW Wrightsville Beach pilot plant.<sup>21</sup> Not only is the desulfation scheme effective, but the sale of byproducts makes it economically attractive.

The purpose of the RO unit in the dual mode system is also to remove enough calcium and sulfate ions so that  $\text{CaSO}_4$  will not precipitate at 350°F in the distillation unit.

Recent tests with a fluidized bed heat exchanger have shown that seawater without pretreatment can be heated to 350°F without scale formation on the walls.<sup>21</sup> The fluidized bed heater is simply a tube partially filled with metallic particles. Cool water enters the bottom and flows upward, lifting and agitating the particles as it is heated. Particle motion prevents scale buildup on the walls. Scale which does precipitate is entrapped by the particles, but calcium sulfate is in a supersaturated state as the flow leaves the heater.

Another approach to prevent accumulation of calcium sulfate scale on heating surfaces is to coat the surfaces with a non-adhering material such as Teflon<sup>®</sup> or smooth glass. The low thermal conductivity of the available coating materials defeats the purpose, however. This approach appears uneconomical for large systems. Various other schemes involving flexure of the heating surface walls or mechanical systems to mechanically crack off accumulated scale have been proposed, but their complexity has made them unfeasible.

Still another scheme calls for a heat exchanger wall made of porous material such as carbon. Pure water seeping through the walls into the saline water reduces the ionic product at the walls to the point that scale does not form. Laboratory tests have been only moderately successful.

The above discussion, though by no means all inclusive, points out many of the options available for scale control. A comparison of the economics of water production between the ROFD system and other systems is in order.

#### ROFD SYSTEM MODEL AND ANALYSIS

Compatibility must be established between the reverse osmosis unit

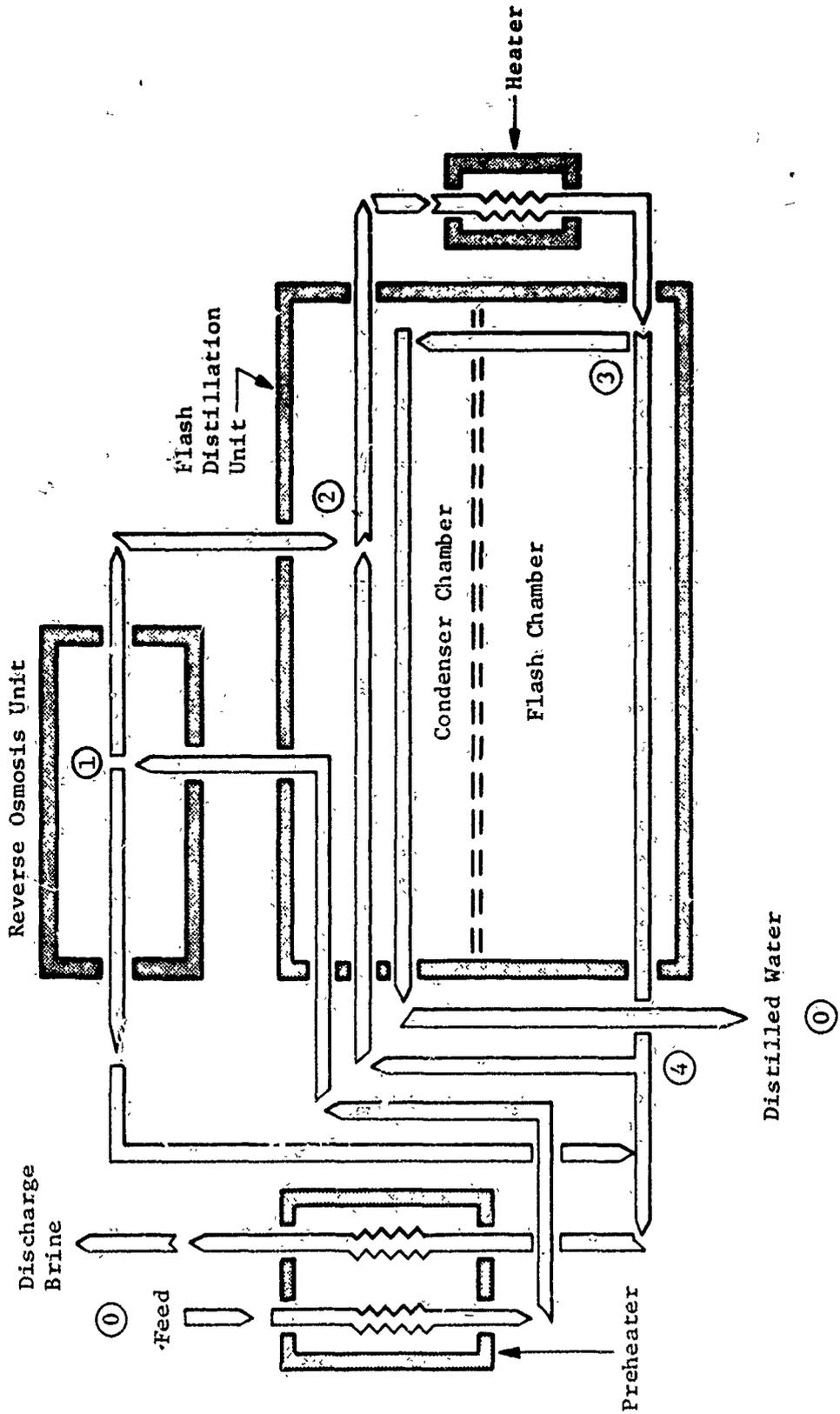


Figure 10. ROFD flow diagram.

and the flash distillation unit of the ROFD system. By this it is meant that the reverse osmosis unit must be able to supply enough partially desalted water to the flash still to replace the water drained off as pure water and as concentrated brine. And, the RO unit must remove a sufficient amount of the salts, in particular the scaling salts, so that scale will not be precipitated in the 350°F heater.

In order to establish reasonable characteristics which the RO unit must have, the ROFD system has been modeled and analyzed. The flow diagram for the model is presented in Figure 10, and is described below, followed by the analysis of the system.

Cold seawater enters the system through a heat exchanger and is warmed by discard brine from both the RO and flash still units. The flow diagram shows it then passing through several low temperature stages of the flash still condenser chamber where it is further heated before entering the RO unit. The scheme shown would be used if the RO membranes are of the charged type which have optimum performance (water flux and salt rejection) when operated at 165°F. If use is made of open cellulose acetate membranes which perform better at lower temperatures, the seawater intake would be passed through fewer, or perhaps none, of the flash unit condenser stages. The partially purified product of the RO unit is pumped back into the flash still where it mixes with and dilutes the recirculating brine from the flash chamber. Scaling salt concentrations of the mixture must be low enough to preclude precipitation downstream in the 350°F heater. This mixed flow experiences a temperature rise as it moves through the high temperature stages of the condenser chamber. The temperature is further raised to 350°F in the heater. Upon leaving the heater, the flow is directed back into the flash chamber of the still and passes through the successive stages. Although flashing and recondensation of pure water occur in each stage, the model shows the sum from all stages as one product flow. An approximation to be made for the analysis is that 20 percent of the flow through the heater will be converted to pure water. Finally, part of the brine from the flash still is recirculated, and part is discarded through the intake heat exchanger.

The above model allows an analysis to be made of the system so that the capacity and salt rejection requirements of the RO unit may be established. The analysis is based on the law of conservation of mass. There are four positions within the system where either a single flow is split or two flows are merged. These four positions are numbered: ①, ②, ③, and ④, in Figure 10. Station ① designates anything exterior to the ROFD system. At each of these places, water in equals water out and salt in equals salt out. The only salt species of interest in this analysis are those which contribute to scale at 350°F, i.e., other  $\text{Ca}^{++}$  and the  $\text{SO}_4^{--}$  ions. So at each of the four junctions, conservation equations will be written for water, for  $\text{Ca}^{++}$  ions, and for  $\text{SO}_4^{--}$  ions. Additional equations will be required, however, so that as many equations as unknowns appear. For water, at ① :  $F_{01} - F_{10} - F_{12} = 0$

$$\text{at } \textcircled{2} : F_{12} + F_{42} - F_{23} = 0$$

$$\text{at } \textcircled{3} : F_{23} - F_{34} - F_{30} = 0$$

$$\text{at } \textcircled{4} : F_{34} - F_{42} - F_{40} = 0$$

Eight unknowns appear in these four equations. But other conditions can be established. Designate the pure water output of the system as  $W$ , so  $F_{30} = W$ . Since the product is 20 percent of the flow through the heater,  $F_{23} = 5W$ . Designate the input flow rate to the RO unit as  $N$ , i.e.,  $F_{01} = N$ . Only a portion of this is partially desalted and passed into the flash still. Let  $F_{12} = xF_{01} = xN$ , where  $0 < x < 1$ . Solving the entire system,

$$F_{01} = N$$

$$F_{10} = (1-x)N$$

$$F_{12} = xN$$

$$F_{23} = 5W$$

$$F_{34} = 4W$$

$$F_{30} = W$$

$$F_{42} = 5W - xN$$

$$F_{40} = xN - W$$

Next the mass balance equations for the ions are set up. Ion concentrations are designated by  $C_{mn}$ , with units of (weight of ion/weight of water)  $\times 10^{-6}$ . The rate of ion flow at a point is then given by the product ( $F_{mn}C_{mn} \times 10^{-6}$ ).

$$\text{For } \text{SO}_4^{--}, \text{ at } \textcircled{1} : F_{01} C_{01}' - F_{10} C_{10}' - F_{12} C_{12}' = 0$$

$$\text{at } \textcircled{2} : F_{12} C_{12}' + F_{42} C_{42}' - F_{23} C_{23}' = 0$$

$$\text{at } \textcircled{3} : F_{23} C_{23}' - F_{34} C_{34}' - F_{30} C_{30}' = 0$$

$$\text{at } \textcircled{4} : F_{34} C_{34}' - F_{42} C_{42}' - F_{40} C_{40}' = 0$$

Again there are eight unknowns and four equations. Other valid conditions can be seen, however. The feed water to the RO unit is seawater with a concentration of  $\text{SO}_4^{--}$  of approximately 2650 ppm. So,  $C_{01}' = 2.65 \times 10^{-3}$ . The concentration of sulfate ions must be less in the product stream of the RO unit than in its feed stream. Let  $C_{12}' = p' C_{01}'$ , where  $p'$  is the passage rate for sulfate ions by the membrane. Obviously,  $0 < p' < 1$ , and the passage rate is related to the rejection rate by  $p' = (1 - r')$ . Another condition is established when it is observed that the system product water is pure, i.e.,  $C_{30} \approx 0$ . Finally, at  $\textcircled{4}$ , the simple splitting of stream  $\textcircled{3}$  to  $\textcircled{4}$  does not act to concentrate or dilute the

flow. Therefore,  $C_{34}' = C_{42}'$ . It is redundant to say  $C_{40}' = C_{34}'$ . Solving the final set of equations,

$$C_{01}' = 2.65 \times 10^{-3}$$

$$C_{10}' = (2.65 \times 10^{-3}) \left( \frac{1 - xp'}{1 - x} \right)$$

$$C_{12}' = (2.65 \times 10^{-3}) p'$$

$$C_{23}' = (2.65 \times 10^{-3}) p' \frac{4WxN}{5WxN - 5W^2}$$

$$C_{34}' = C_{42}' = C_{40}' = (2.65 \times 10^{-3}) p' \frac{5WxN}{5WxN - 5W^2}$$

$$C_{30}' = 0$$

The equations for the calcium ion are so similar to those for the sulfate ion that they will not be written out completely. One difference is that the passage rate of the membrane to the calcium ions may be different from that to the sulfate ion. For  $Ca^{++}$ , the passage rate is designated  $p''$ . The only other difference is that the concentration of calcium ions in seawater is 400 ppm, as opposed to the 2650 ppm for sulfate ions. So,

$$C_{01}'' = 4.00 \times 10^{-4}$$

$$C_{10}'' = (4.00 \times 10^{-4}) \left( \frac{1 - xp''}{1 - x} \right)$$

$$C_{12}'' = (4.00 \times 10^{-4}) p''$$

$$C_{23}'' = (4.00 \times 10^{-4}) p'' \frac{4WxN}{5WxN - 5W^2}$$

$$C_{34}'' = C_{42}'' = C_{40}'' = (4.00 \times 10^{-4}) p'' \frac{5WxN}{5WxN - 5W^2}$$

$$C_{30}'' = 0$$

It is seen at this point that if one establishes the pure water output of the system ( $W$ ) and knows the characteristics of the RO unit ( $x$ ,  $N$ ,  $p'$ , and  $p''$ ), then the water flow rate and concentrations of calcium and sulfate ions can be computed anywhere in the system. Of most interest is the flow through the heater, i.e., through path ② to ③. The concentration product,  $C_{23}'C_{23}''$ , must be kept below the scaling limit for 350°F. From Figure 9, it is deduced that the allowable scaling limit is approximately  $1.12 \times 10^{-7}$ . So,

$$1.12 \times 10^{-7} \geq C_{23}'C_{23}'' = (2.65 \times 10^{-3}) (4.00 \times 10^{-4}) p' p'' \times \left( \frac{4WxN}{5WxN - 5W^2} \right)^2$$

For computational purposes, assume that the ROFD system output (W) is  $10^6$  gpd. Assume also that the RO unit discharges ( $\times N$ ) =  $1.5 \times 10^6$  gpd to the flash still as partially purified make-up water. Further assume that the membrane rejects calcium and sulfate ions equally well, so that  $p' = p''$ . Solving the inequality,

$$p' \leq 0.134$$

or

$$r' = (1 - p') \geq 0.866$$

A membrane with a rejection of 90 percent would be more than adequate for use in the RO unit having a  $1.5 \times 10^6$  gpd output feeding a  $10^6$  gpd flash unit.

#### COST ANALYSIS

Water production costs for the dual mode system are compared to those for other systems, namely the conventional 250°F MFD, the 350°F MFD with fluidized bed, and the 350°F MFD with an ion exchange desulfation of the feed water. Production costs are given in terms of cents/1000 gallons of pure water. Production costs naturally differ with the size of the purification unit, but they are only estimated here for an output of  $10^6$  gpd. No forecasts are given for the  $10^4$  and  $10^5$  gpd systems also of interest to the Navy, primarily because the main sources of economic data available come from OSW and are applicable only to systems of  $10^6$  gpd or more.

Cost information for 350°F MFD systems is very sparse. No published figures were found, but communications with producers and operators of distillation equipment led to a conclusion that capital equipment costs can be reduced 15 percent on a per-unit production basis when the heater temperature is raised from 250°F to 350°F.

Tabulated costs for the four systems undergoing comparison are presented in Tables 4 through 7. The format was taken from Reference 22. It is seen that the water production costs include capital costs of the primary and auxiliary systems, interest, and all operational and maintenance costs. Charts and equations necessary to estimate most costs are included in Reference 22. Desulfation costs are found in Reference 18. The interest rates, operating labor costs, land acquisition costs, etc., may in some cases be more accurate for civilian applications than for military systems, but the figures are applied consistently to all four cases so that a valid comparison between the cases can be obtained. It is assumed that the capital equipment is financed on a 30 year loan with 5-1/2 percent annual interest charge (Prime rate fluctuates with economic conditions, but was 5-1/2 percent at time of writing.). Land cost is taken as \$2000/acre. The building cost index

Table 4. Water Production Costs, ROFD System

Cost Elements	\$10 <sup>3</sup>		Annual Cost		Water Costs	
	RO	MFD	RO	MFD	¢/kgal	¢/kgal
<b>Capital Costs</b>						
1. Plant and Equipment	995	1,716	68,500	118,000	13.8	35.8
2. Feedwater Pretreatment	288	0	19,800	0	4.0	0
3. Feedwater Supply	0	268	0	18,400	0	5.6
4. Water Transmission	0	0	0	0	0	0
5. Brine Disposal	0	0	0	0	0	0
Subsystem Capital Costs	<u>1,283</u>	<u>1,984</u>	<u>88,300</u>	<u>136,400</u>	<u>17.8</u>	<u>41.4</u>
Total Capital Costs	<u>3,267</u>		<u>224,700</u>		<u>59.2</u>	
<b>Operation and Maintenance Costs</b>						
6. Operating and Maintenance Labor						
a. Plant and Equipment					7.5	32.2
b. Feedwater Pretreatment					5.8	0
c. Feedwater Supply					0	7.5
d. Water Transmission					0	0
e. Brine Disposal					0	0
Subsystem Operating and Maintenance Labor					<u>13.3</u>	<u>39.7</u>
Total Operating and Maintenance Labor					<u>53.0</u>	

(Continued)

Table 4. Water Production Costs, ROFD System (Continued)

7. Other Operation and Maintenance Costs		
a. Payroll Extras (15% of 6a)	1.1	4.8
b. General and Administrative Overhead (30% of 6a + 7a)	2.6	11.1
c. Supplies and Maintenance Materials	2.0	2.6
d. Membrane Assembly or Replacement Tubing	10.0	4.2
e. Chemicals	3.0	1.0
f. Fuel or steam	0	24.2
g. Electric Power		
Plant and Equipment	11.0	9.0
Feedwater Supply	0	2.1
Water Transmission	0	0
Subsystem Other Operation and Maintenance Costs	29.7	59.0
Total Other Operation and Maintenance Costs	88.7	
Subsystem Operation and Maintenance Costs	43.0	105.3
Total Operation and Maintenance Costs	141.7	
Subsystem Water Costs	60.8	146.7
Total Water Cost (Total Capital Plus O&M Costs)	200.9	

Table 5. Water Production Costs, Conventional 250°F MFD System

Cost Elements	\$10 <sup>3</sup>	Annual Cost \$	Water Costs ¢/kgal
<b>Capital Costs</b>			
1. Plant and Equipment	1,768	135,500	41.0
2. Feedwater Pretreatment	n.r.	n.r.	n.r.
3. Feedwater Supply	268	18,400	5.6
4. Water Transmission	0	0	0
5. Brine Disposal	0	0	0
<b>Total Capital Costs</b>	<b>2,236</b>	<b>153,900</b>	<b>46.6</b>
<b>Operation and Maintenance Costs</b>			
6. Operating and Maintenance Labor			
a. Plant and Equipment			42.9
b. Feedwater Pretreatment			n.r.
c. Feedwater Supply			7.5
d. Water Transmission			0
e. Brine Disposal			0
<b>Total Operating and Maintenance Labor</b>			<b>50.4</b>

(Continued)

Table 5. Water Production Costs, Conventional 2500F MFD System  
(Continued)

7. Other Operation and Maintenance Costs	
a. Payroll Extras (15% of 6a)	6.4
b. General and Administrative Overhead (30% of 6a + 7a)	14.8
c. Supplies and Maintenance Materials	3.0
d. Membrane assembly or Replacement Tubing	4.7
e. Chemicals	3.0
f. Fuel or Steam	24.2
g. Electric Power	9.0
Plant Equipment	2.1
Feedwater Supply	0
Water Transmission	
Total Other Operation and Maintenance Costs	<u>67.2</u>
Total Operation and Maintenance Costs	<u>117.6</u>
Total Water Cost (Total Capital Plus O&M Costs)	<u>164.2</u>

n.r. - none required

Table 6. Water Production Costs, 350°F MFD System with Desulfation of Feedwater

<u>Cost Elements</u>	<u>\$103.</u>	<u>Annual Cost \$</u>	<u>Water Costs c/kgal</u>
<b>Capital Costs</b>			
1. Plant and Equipment	1,716	118,000	35.8
2. Feedwater Pretreatment	3,362	231,000	70.0
3. Feedwater Supply	0	0	0
4. Water Transmission	0	0	0
5. Brine Disposal	0	0	0
<b>Total Capital Costs</b>	<b>5,078</b>	<b>349,000</b>	<b>105.8</b>
<b>Operation and Maintenance Costs</b>			
6. Operating and Maintenance Labor			32.2
a. Plant and Equipment			27.4
b. Feedwater Pretreatment			0
c. Feedwater Supply			0
d. Water Transmission			0
e. Brine Disposal			0
<b>Total Operating and Maintenance Labor</b>			<b>59.6</b>

(Continued)

Table 6. Water Production Costs, 350°F MFD System with Desulfation of Feedwater  
(Continued)

7.	Other Operation and Maintenance Costs	
a.	Payroll Extras (15% of 6a)	4.8
b.	General and Administrative Overhead (30% of 6a + 7a)	11.1
c.	Supplies and Maintenance Materials	2.6
d.	Membrane Assembly or Replacement Tubing	4.2
e.	Chemicals	1.0
f.	Fuel or Steam	24.2
g.	Electric Power	
	Plant and Equipment	9.0
	Feedwater Supply	0
	Water Transmission	0
h.	Feedwater pretreatment	<u>141.0</u>
	Total Other Operation and Maintenance Costs	<u>197.9</u>
8.	Credit from Sale of By-products	<u>(108.1)</u>
	Total Operation and Maintenance Costs	<u>89.4</u>
	Total Water Cost (Total Capital Plus O&M Costs)	<u>255.2</u>

Table 7. Water Production Costs, with Fluidized Bed Heater

<u>Cost Elements</u>	<u>\$103</u>	<u>Annual Cost</u>	<u>Water Costs</u>
		<u>\$</u>	<u>c/kgal</u>
<b>Capital Costs</b>			
1. Plant and Equipment	1,716	118,000	35.8
2. Feedwater Pretreatment	n.r.		n.r.
3. Feedwater Supply	268	18,400	5.6
4. Water Transmission	0	0	0
5. Brine Disposal	0	0	0
<b>Total Capital Costs</b>	<b>1,984</b>	<b>136,400</b>	<b>41.4</b>
<b>Operation and Maintenance Costs</b>			
6. Operating and Maintenance Labor			
a. Plant and equipment			36.4
b. Feedwater Pretreatment			n.r.
c. Feedwater Supply			7.5
d. Water Transmission			0
e. Brine Disposal			0
<b>Total Operating and Maintenance Labor</b>			<b>43.9</b>

(Continued)

Table 7. Water Production Costs, with Fluidized Bed Heater  
(Continued)

7. Other Operation and Maintenance Costs	
a. Payroll Extras (15% of 6a)	5.5
b. General and Administrative Overhead (30% of 6a + 7a)	12.8
c. Supplies and Maintenance Materials	2.6
d. Membrane Assembly or Replacement Tubing	4.2
e. Chemicals	1.0
f. Fuel or Steam	24.2
g. Electric Power	
Plant and Equipment	9.0
Feedwater Supply	2.1
Water Transmission	0
Total Other Operation and Maintenance Costs	<u>61.4</u>
Total Operation and Maintenance Costs	<u>105.3</u>
Total Water Cost (Total Capital Plus O&M Costs)	<u>146.7</u>

n.r. - None required

and labor cost index are taken at approximate 1971 values of 990 and 3.78, respectively. The cost of producing steam is taken as 25¢/10<sup>6</sup> Btu. Electrical power cost is assumed to be 1¢/kwhr. The desalination units are presumed to be located adjacent to the ocean and to the product storage tanks so that there is no cost for water transmission and brine disposal. Reduced operational and maintenance costs are foreseen for 350°F MFD plants due to less acid addition, smaller plant sizes, and sharing of duties with subsystems. This is reflected in a 25 percent decrease in labor costs for the 350°F MFD systems with feed water pretreatment by RO or desulfation units, and a 15 percent decrease in labor costs for the fluidized bed system.

Results of computations show the conventional 10<sup>6</sup> gpd MFD system to produce water at a cost of 164.2¢/kgal. The product of the ROFD system, however, costs approximately 201¢/kgal. The higher cost of ROFD water results from the fact that two practically independent units must be purchased and maintained. The same is true with the system which utilizes desulfation pretreatment. Product water of that system costs just over 255¢/kgal. Even though desulfation is not economically attractive for the 10<sup>6</sup> gpd plants, in the enormous systems of 50 × 10<sup>6</sup> gpd or more planned to supply fresh water to the civilian population the desulfation costs decrease to the point that this is the method being currently pursued by OSW.

Table 7 itemizes and totals the cost of water production using a 350°F MFD system with a fluidized bed heat exchanger rather than a conventional heater to raise the feed water temperature to the desired level. It is predicted that water costs will be less with this system than for any other system considered, even 10 percent less than the conventional 250°F MFD product. Savings result from the forecast 15 percent reductions in capital and labor costs.

## CONCLUSIONS

The primary objective of this study was to determine the feasibility of the ROFD system. A secondary objective was to predict costs of water production with the ROFD system and with competitive systems. It is concluded that the ROFD system appears to be technically feasible but not economically feasible.

The projected costs of producing water in various types of plants, each of 10<sup>6</sup> gpd capacity, are:

350°F MFD with fluidized bed	147¢/kgal
250°F MFD conventional system	164¢/kgal
350°F ROFD system	201¢/kgal
350°F MFD with desulfation	255¢/kgal

The ROFD system is not economically feasible since its product is more expensive than water from conventional distillation equipment. The

fluidized bed system produces water at less cost than the conventional system.

The ROFD system does not have other redeeming features. It is more complicated than conventional stills. Operating and maintenance personnel would be required to be familiar with two different subsystems. Logistical demands of two subsystems would be greater than supply for only one.

Problems of personnel training and increased logistical demands would be more severe for mobile desalination systems with outputs in the range  $10^4$  -  $10^5$  gpd. Permanent systems in the  $10^6$  gpd class could be operated by civilian personnel under contract. The necessary specialized training could be given, and adequate incentives offered, to retain the skilled personnel. Desalination systems with outputs in the nominal range of  $10^4$  and  $10^5$  gpd will be operated by military personnel, however. Due to the temporary nature of military assignments and the demand for versatility from military personnel, it is not reasonable to expect as high a degree of proficiency from military operators as from civilian operators.

For the above reasons, to inject the more complicated and costly ROFD system into the Navy inventory is not recommended.

Development of 350°F MFD plants with fluidized beds should be pursued for Navy use. Based on projected capital and labor cost savings, water production costs are roughly 10 percent less than with conventional systems. The fluidized bed system is so similar to the conventional MFD that no more intensive training will be required than is now given to operating personnel.

A systematic development program will include:

- (a) analysis of the flow through the plant
- (b) design, fabrication, and testing of a fluidized bed under simulated installed conditions,
- (c) design and fabrication of the 350°F flash plant, and,
- (d) testing the plant-heat exchanger combination.

The designer must consider military criteria of portability and intermittent use for the  $10^4$  -  $10^5$  gpd systems. Eventually, consideration should be given to operating the systems with available waste heat for increased economy.

## REFERENCES

1. Naval Civil Engineering Laboratory. Technical Note N-1054: Twenty years of progress in seawater desalination at NCEL, by Allan S. Hodgson. Port Hueneme, California, September 1969.
2. \_\_\_\_\_. Technical Note N-1075: Test and evaluation of 2,500 GPD seawater reverse osmosis unit, by Allan S. Hodgson and D. Pal. Port Hueneme, California, January 1970.
3. \_\_\_\_\_. Technical Note to be published: Test and evaluation of an 80,000 GPD reverse osmosis seawater desalination plant mounted on an ammi pontoon, by C. K. Smith.
4. University of California, Los Angeles, Department of Engineering. Report Number 66-7: Cellulose acetate membranes as a means of removing scale forming ions of natural saline waters, by D. L. Erickson. Los Angeles, California, January 1966.
5. C. Milstead. Gulf General Atomic Incorporated (telephone conversation), San Diego, California, October 1971.
6. Health Service. Publication Number 956: Public Health services drinking water standards, revised 1962. US Government Printing Office, Washington, DC.
7. K. S. Spiegler. Salt water purification. New York. John Wiley & Sons, 1962, pp. 10-11, 18-33, 40.
8. US Department of the Interior, Office of Saline Water: The A-B-Seas of desalting. US Government Printing Office, Washington, DC.
9. General Electric Company, Internal Paper of Direct Energy Conversion Programs: Research on reverse osmosis membranes for purification of wash water at sterilization temperatures (165°F), by Joseph M. Amore, John F. Enos, and Anthony B. LaConti. Lynn, Massachusetts. Undated.
10. A. B. LaConti. General Electric Company (telephone conversation), Lynn, Massachusetts, October 1971.
11. Ralph C. Roe, and Donald F. Othmer. "Controlled flash evaporation," Mechanical Engineering, vol. 93, no. 5, May 1971, pp. 27-32.
12. W. L. Badger, Chemical engineering handbook, 3rd edition. McGraw-Hill Publishing Co., New York, 1950, p. 518.
13. W. F. Langelier, D. H. Caldwell, and W. B. Lawrence. "Scale Control in seawater distillation equipment," Ind. Eng. Chem., vol. 42, 1950, p. 126.

14. W. F. Langelier. "Mechanism and control of scale formation in seawater distillation," Journal of American Water Works Association, vol. 46, 1954, p. 461.
15. J. R. Emmett. "Proceedings of society for water treatment and examination," vol. 6, 1957, p. 90.
16. W. L. Denman. "Maximum re-use of cooling water," Ind. Eng. Chem., vol. 53, no. 10, October 1961, pp. 817-822.
17. M. W. Kellogg Company, New York, New York, for Office of Saline Water. Contract Report CR-14-01-0001-291: Saline water conversion engineering data beds. Washington, DC, July 1965, pp. 14.11-14.14.
18. Mason-Rust report for Office of Saline Water, Contract Report CR-14-01-0001-2178: Evaluation of 75,000 gpd continuous ion exchange seawater desulfating pilot plant, Wrightsville Beach, North Carolina, by K. M. Garrison, and J. E. Gugeler. January 1971.
19. University of Michigan, Department of Engineering Research: Engineering Research Bulletin Number 15, by E. P. Partridge . 1930.
20. US Department of the Interior, Office of Saline Water: 1967 saline water conversion report. US Government Printing Office, Washington, DC, p. 264.
21. US Department of the Interior, Office of Saline Water: 1969-1970 saline water conversion report. US Government Printing Office, Washington, DC, pp. 392, 395.
22. Southwest Research Institute, for Office of Saline Water: Contract Report CR-14-01-0001-2260: Desalting cost calculating procedures, by W. Lawrence Prehn and Jerry L. McGaugh. February 1970.

## SYMBOLS

$c_p$ . . . . .	Constant pressure specific heat, $\frac{\text{Btu}}{\text{lb}_m - ^\circ\text{R}}$
$C_{\text{sub}}$ . . . . .	Concentration of substance identified by subscript, $\frac{\text{grams of substance}}{\text{grams of water}} \times 10^{-6}$
$C_{mn}, C_{mn}''$ . . . . .	Concentrations of $\text{SO}_4^{--}$ and $\text{Ca}^{++}$ ions, respectively, in the portion of the dual mode system between positions m and n (see Figure 10), $\frac{\text{grams of substance}}{\text{grams of water}} \times 10^{-6}$
$F_{mn}$ . . . . .	Water flowrate in the portion of the dual mode system between positions m and n (see Figure 10), $\frac{\text{gallons}}{\text{day}}$
$\Delta h$ . . . . .	Enthalpy change, $\frac{\text{Btu}}{\text{lb}_m}$
$K_1(T), K_2(T), K_3(T)$	Equilibrium constants, units vary
$M$ . . . . .	Mass, $\text{lb}_m$
$N$ . . . . .	Feed rate to RO unit, $\frac{\text{gallons}}{\text{day}}$
$p, p''$ . . . . .	Portion of $\text{SO}_4^{--}$ and $\text{Ca}^{++}$ ions respectively, passed by RO membranes, dimensionless
$r, r''$ . . . . .	Portion of $\text{SO}_4^{--}$ and $\text{Ca}^{++}$ ions respectively, rejected by RO membranes, $r = 1 - p$ , dimensionless
$S_{\text{sub}}(T)$ . . . . .	Solubility product of substance identified by subscript, units vary.
$\Delta T$ . . . . .	Temperature change, $^\circ\text{R}$
$x$ . . . . .	Portion of RO feed passed to become RO product, dimensionless

### Subscripts

$L$ . . . . .	Denotes liquid phase
$V$ . . . . .	Denotes vapor (gaseous) phase
$0, 1, 2, 3, 4$ . . . . .	Designates positions in the dual mode system (see Figure 10)

### Superscript

$*$ . . . . .	Designates value at solubility limit
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