SALINE WATER CONVERSION BY FLASH DISTILLATION PROCESSES

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CHAPTER I

INTRODUCTION

General

The possibilities of converting saline water to potable water have recently gained widespread interest although the idea is not new.

Man has been trying for centuries to obtain fresh water from the sea. Since early times man has been intrigued with the possibilities attendant on simple, economical processes for ever-going needs for personal, industrial, or agricultural uses.

Sea water desalination dates back to at least as far as the sixteenth century. In 1593, an English sea captain, Sir Richard Hawkins, (1) wrote:

> Although our fresh water supply has failed us many days....yet with an invention I had in my skippe I easily drew out of the water of the sea sufficient quantities of fresh water to sustain my people with little expense of fewell; for with foure billets I stilled a hogshead of water, and therewith dressed the meat for the sick and the whole. The water so distilled we found to be wholesome and nourishing.

And, then others experimented and observed, "that with a heat sufficient for distillation, salt will not rise in vapor, and that salt water distilled is fresh." (2)

But, information on the experiences and experiments of Hawkins and others was not adequately spread abroad among mariners for many years. As a result of personal experiments, Thomas Jefferson expressely recommended that knowledge about sea water distillation be made available to all mariners in the first scientific document published by the United States Government in 1791. However, the recommendation was not adopted and ships continued to run short of water in a field of plenty until nearly sixty years later evaporators started to get some recognition for sea water distillation. It was with the arrival of steam power that sea water conversion slowly began to be adopted for maritime purposes. Through the nineth century controversies raged about the potability of distilled water. This discouraged its universal acceptance. It was not until World War II, when ships were forced to operate for long periods on sea and armed forces had to become self-sufficient on deserts, that real attention was turned toward the conversion of sea water. Thus, technological developments for sea water distillers have been completely directed toward marine and military fields. Only rarely was saline water conversion ever resorted to for civilian applications, except for fields with a high-purity requirement, such as for boiler feed water or pharmaceutical water. Recently both independent researchers and industrial developers have become aware of the demand for civilian application in the United States and abroad.

Purpose and Scope of the Saline Water Conversion

The experience of the Department of the Interior over the past years has shown one vital fact--water problems touch all states of the United States. The water requirements, in terms of quality and quantity, vary from area to area, ranging from shortage to excess. New sources are required in the areas where an inadequate rainfall exists. These new sources are also necessary where the drought comes during the growth of crops.

On the other hand, industrial growth usually depends upon the quality and quantity of water. In some cases, industries have been forced to move or to change to an operation that requires less water because of the lack of adequate water in those regions. The coastal cities, which have been more developed than inland cities, are investigating the possibilities of economical and adequate water supplies because they recognize that the growing population and developing industries require more water. At the same time, the national consumption of fresh water is growing at an accelerating pace along with rapid increase in population, industry and agriculture.

Table I illustrates the water consumption in the United States in 1960 (3).

TABLE I

AMOUNT OF WATER USED IN THE UNITED STATES IN 1960

For Major Industries	= 150 BGD
For Irrigation	= 135 BGD
Other Uses (Household, Animal Watering, etc.)	= 30 BGD
Total Water Used	= 315 BGD
Population	= 180 million
Water Index = $315 \times 10^9/180 \times 10^6$	=1750 GPCPD

It is seen that at the present time the nation requires more than three hundred billion gallons of water daily; in only twenty years the requirement may exceed six hundred billion gallons per day.

While water shortage is not todays serious problem, it is obvious that it is and will be a vital problem for municipal, industrial, and perhaps for irrigation uses in both big coastal cities and in inland cities which are located in semiarid regions. Because it was estimated that the population of the United States will have about doubled by the year 2000, there is a serious question as to whether or not sufficient water resources can be made available readily from conventional fresh water sources (4). Existing water supplies will not be enough for future tremendous requirements. Perhaps re-use of water, with better treatment after use, will provide more usable water for municipal and industrial purposes, but it will not solve the problem entirely. For agricultural uses reduction of evaporation losses from fields and irrigation channels will be helpful, but again, it will not be a solution to the serious problem.

The average total precipitation is about four thousand three hundred billion gallons a day in the United States. Most of this evaporates from soil, snow and water surfaces and transpires from the leaves of the plants. About one-fourth of the precipitation is runoff and is sufficient for use. Thus, about seven per cent of the total precipitation, or thirty per cent of the overland flow, is consumed in the United States at the present time. It is extremely difficult to catch all of this amount of water to use in municipal, industrial, and irrigation purposes. On the other hand, rainfall in the United States varies from the lush abundance in the evergreen Pacific Northwest to the scarcity in the parched Southwest, and it also varies from season to season and from year to year. Unfortunately, the location of irrigable lands, population and industry in relation to places with heavy rainfall and stream flow are displaced. For example, Western United States refers to the seventeen states lying west of one hundred degree longitude and includes all of the desert and semiarid areas of the United States with the exception of Alaska and Hawaii.

According to S. B. Morris (5) the seventeen western states cover 61.5 per cent of the area of the United States with the exception of Alaska, but average runoff is only 27 per cent of the runoff of 48 states. Namely, the area has the least rainfall and lowest runoff.

Average values for runoff and water use and their distribution are illustrated in Table II (5).

TABLE II

A. AVERAGE RUNOFF AND ITS DISTRIBUTION IN THE U.S. IN 1950

Item		17 Western States	31 Eastern States	United* States
Area	- 10^6 acres	1,168	737	1,905
Runoff	- 10^6 acre-ft.	393	1,057	1,450
Runoff Depth	- in.	4.03	17.23	9.13
Irrigated Area	- 10^6 acres	22	+	22

B. AVERAGE WATER USE AND ITS DISTRIBUTION IN THE U.S. IN 1950

Item		17 Western States	31 Eastern States	United* States
Municipal and Industrial	- 10^6 acre-ft.	10	80	90
Irrigation	- 10^6 acre-ft.	90	+	90
Total	- 10^6 acre-ft.	100	80	180

* Excluding Alaska

+ Negligible

Thus, neither water nor the demand for it is evenly distributed with the low average runoff in the semiarid West in comparison to that in the humid East.

A questionnaire survey has been made of the fifty states and the

Canadian provinces by an AWWA Task Group to determine the present extent of public, brackish, raw-water sources as well as the opinions of the design review agencies regarding brackish-water treatment. The committee observed that of twenty thousand two hundred fifteen municipal water utilities in fifty states of the United States and five provinces of Canada, one thousand sixty six had raw water with total dissolved solids in the range of one thousand to three thousand ppm and thirty one had water with total dissolved solids of three thousand to ten thousand ppm (6). Those brackish water sources are being used at the present time by municipalities and industry. These values define the principal markets for desalination. These areas are scattered in the southwestern and north central parts of the United States, the Gulf of Mexico and Florida coasts, and the prairie provinces of Canada. In these areas desalinization is already necessary and must be used from now on.

It was recognized that the ocean water could be used to solve the future water problem. The ocean is the largest reservoir (3.7×10^{20} gallons or 3.7×10^{11}billion gallons) of the world (7). If the water from the world's supply of sea water, which covers more than seventy per cent of the earth's surface, were distributed among the present human inhabitants of the world, each persons share would be more than one hundred billion gallons, which is approximately one-third of the United States daily water requirement. Nature has given such tremendous resources of water, but natures timing of delivery, distribution and quality of it are imperfectly suited for human beings. Hence, the conversion of ocean water to fresh water is inevitable for tomorrow and it is a way to virtually unlimited new supplies and a way to supplement other sources.

Saline Water Conversion Research and Development Activities

In the United States, many groups and organizations both governmental and private are interested in saline water conversion research and development. The State of California has a sea water conversion project. Its research has been carried out by the University of California. Other federal agencies having particular interest in saline water conversion include the Department of Defense, the Atomic Energy Commission, and the Office of Emergency Planning (4).

The United States Government's work in this subject goes back to 1952 when Congress passed the Saline Water Act to provide for research and development of economical and practical methods of producing potable water from saline sources. The Act authorized $2,000,000 for a five year program. The Department of Interior, by the Office of Saline Water (OSW), carries out this program by means of federally financed contracts and grants, by research in federal laboratories, and by co-operating with private and governmental organizations. In 1955, the Act was improved by increasing the authorization to $10,000,000 and extending the program to 1963. Public Law 85-883, approved by President Eisenhower on September 2, 1958, added a new responsibility to the office and authorized $10,000,000 for the design, construction, and operation of five saline water conversion plants to demonstrate the reliability, engineering, and operating of sea or brackish water conversion processes (8).

The first demonstration plant, which is located at Freeport, Texas, produces 1 MGD of fresh water. The second plant is a multistage flash distillation type and is located at San Diego, California (now at Guantamamo

Naval Base in Cuba). It also has a capacity of 1 MGD. The third sea water conversion plant is at Webster, South Dakota, operates on brackish well water, and has a capacity of 0.25 MGD. The fourth one will be located at Wrightsville Beach, North Carolina. It will produce one to three MGD of potable water. The fifth demonstration plant will operate on a highly brackish water and will be located at Roswell, New Mexico. Its capacity will be 1 MGD (4).

In a special message to Congress on natural resources on February 23, 1961, the late President John F. Kennedy (7) stated that:

> No water resources program is of greater long-range importance - for relief not only of our shortages, but for arid nations the world over - than our efforts to find an effective and economical way to convert water from the world's greatest, cheapest natural sources - our oceans - into water fit for consumption in the home and by industry. Such a breakthrough would end bitter struggles between neighbors, states, and nations - and bring new hope for millions who live out their lives in dire shortage of usable water and all its physical and economical blessings.

Another law was enacted in September, 1961. It increased the research and development program by authorizing $75,000,000 for the next six years. The new law also provides for recommendations to Congress for additional demonstration plants.

There is world wide interest in this subject. There has been extensive development in Europe, particularily in the Netherlands, Great Britain, and France. There has been research and development activity in Australia, Germany, Israel, Italy, Japan, North and South Africa, and Russia (9).

Scientific and technical activities in saline water conversion range from basic research to commercial plants. Now, more than 25 MGD of potable water from saline sources is being produced in large plants in various parts of the world. Most of this is obtained from sea water by using several methods of distillation. The largest sea water distillation capacities are in Kuwait, on the Persian Gulf (6.25 MGD), and in Aruba and Curacao in the Caribbean (3 MGD), at Freeport, Texas, (1 MGD) and at San Diego, California, (U.S. Navy in Cuba) (1 MGD). Large electodialysis plants for brackish water are located at Bahrein in the Persian Gulf; Welkom, South Africa (3 MGD), and more recently Buckeye, Arizona and at Webster, South Dakota, (0.25 MGD) (4).

CHAPTER II

THE COMPOSITION OF SALINE WATERS

Classification

The classification of natural salt waters is shown in Table III (12).

TABLE III

THE CLASSIFICATION OF SALINE WATERS

Description of Water	Dissolved Solids (ppm)
Slightly Brackish	1,000 - 3,000
Moderately Brackish	3,000 - 10,000
Highly Brackish	10,000 - 33,000
Sea Water	33,000 - 36,000
Brine	36,000 - Over

Formation and Composition of Ocean Water

The oceans contain about three per cent of sodium chloride and 0.5 per cent other salts, or a total of 3.5 per cent (by weight) of total salts. There are some differences of salinity in the oceans but the relative proportions of the main constituents are the same. Solar radiation evaporates the water of the ocean, but the salts do not evaporate since they are not volat

When the vapor reaches cold sections in the sky it condenses into visible water droplets which form clouds. Then, it returns to the earth and ocean in the form of precipitation such as rain, snow, sleet, hail, and freezing rain. Because oceans cover more than seventy per cent of the earths surface about three-fourths of the total precipitation falls into them. The rest of the precipitation falls on land and forms overlandflow surface runoff and ground water which ultimately finds its way to the ocean through pervious underground material. Ground water interacts with soil and rocks, and carries soluble minerals to the ocean. Surface waters also collect soluble and insoluble organic and inorganic materials and carry these to the ocean. Thus, all the evaporated water from the oceans returns to them (hydrologic cycle).

Geological evidence shows that there is no large change in the average composition of sea water during the hydrologic cycle (3).

Sea water has various kinds of elements, but most of them are in minor concentrations. The main elements in sea water are illustrated in Table IV (3).

The total salt concentration of saline water is expressed by means of salinity, which is equal to the sum of dry solids (in grams) per kilogram (1000 grams) of sea water, or the chlorinity, which is about the concentration of chloride ions. (They are expressed as parts per thousand.) In the open oceans the salinity lies between 33.6 and 36.8 part per thousand. In the Baltic Sea, surface salinity drops to three parts per thousand because precipitation and inflow are larger than evaporation. In the Red Sea, the salinity has risen to forty one part per thousand (3).

TABLE IV

MAIN CONSTITUENTS OF SEA WATER*

Sodium (Na^+)	10,561 ppm
Magnesium (Mg^{++})	1,272 ppm
Calcium (Ca^{++})	400 ppm
Potassium (K^+)	380 ppm
Chloride (Cl^-)	18,980 ppm
Sulfate ($SO_4^=$)	2,649 ppm
Bicarbonate (HCO_3^-)	142 ppm
Bromide (Br^-)	65 ppm
Other Solids	34 ppm
Total Dissolved Solids	34,483 ppm

*Chlorinity = 19.000, Salinity = 34.325

Not only oceans, but some large lakes such as the Dead Sea, the Great Salt Lake (Utah), and the Caspian Sea contain brine water. There are also many brackish groun waters in arid and semiarid regions.

Concentration of salts of these lakes is shown in Table V (3).

TABLE V

CONCENTRATION OF SALTS OF DIFFERENT LAKE WATERS

Salts	Dead Sea (100 yards below surface) ppm	Great Salt Lake, Utah ppm	Caspian Sea ppm
Sodium	32,000	67,300	3,200
Magnesium	35,700	5,600	773
Calcium	12,700	300	297
Potassium	6,400	3,400	70
Chloride	178,600	112,900	5,500
Sulfate	400	13,600	2,970
Carbonate	Trace	200	48
Bromide	5,200	Trace	-

CHAPTER III

SCALE FORMATION AND PREVENTION OF SCALE FORMATION

Scale Formation

The deposition of minerals in the heat transfer surfaces of sea water evaporators results in the production of scale. Calcium (Ca^{++}), magnesium (Mg^{++}), sulfate (SO_4^{--}), and bicarbonate (HCO_3^{-}) ions are troublesome in the distillation processes since they produce various insoluble deposits, such as calcium carbonate, magnesium hydroxide, and calcium salfate in the heat surfaces of the evaporator tubes. In the tubes, the presence of scale is highly objectionable because it reduces the heat conductivity of the tubes by reducing the diameter of the tubes, causes operation difficulties, and loss of efficiency of the unit except when the layer is extremely thin.

The scale is a serious problem at all temperature, particularily at temperatures in excess of 340°F (160°C).

When sea water is heated its scale-forming elements, such as Ca^{++}, Mg^{++}, HCO_3^{-}, and SO_4^{--}, become supersaturated. Scale materials will be deposited at the point of highest temperature. This point is the metal surface through which heat is passed, that is, evaporator tubes.

There are three main scale deposits which result from the following reactions (11).

$$2\ HCO_3^- \rightarrow CO_3^= + CO_2\uparrow + H_2O$$

$$Ca^{++} + CO_3^= \rightarrow CaCO_3\downarrow$$

$$H_2O + CO_3^= \rightarrow 2\ OH^- + CO_2\uparrow$$

$$(H_2O + CO_3^= \rightarrow OH^- + HCO_3^-)$$

$$Mg^{++} + 2\ OH^- \rightarrow Mg(OH)_2\downarrow$$

$$Ca^{++} + SO_4^= \rightarrow Ca\ SO_4\downarrow$$

Sea water contains bicarbonate ion which reacts with water on heating to form carbonate ion and carbon dioxide which tends to be evolved as a gas. The increased amount of carbonate ion present causes the super saturation of calcium carbonate which comes out of the solution. As the carbon dioxide is least soluble at the temperature of the hot metal surface, the calcium carbonate has its greatest supersaturation at the surface and deposits there.

As the sea water is heated further, the remaining carbonate ion reacts with water to form hydroxide ion which makes the solution supersaturated with respect to magnesium hydroxide. Magnesium hydroxide will have the greatest supersaturation at the temperature of the hot metal, where it also will deposit.

As the sea water is heated still higher, calcium sulfate will precipitate.

Thus, if the evaporation temperature is kept below 180°F (80°C), the predominant scale is calcium carbonate; between 180°F (80°C) and 250°F (120°C) the scale is magnesium hydroxide; and, above 250°F (120°C) calcium-sulfate scale appears in large quantities mixed with the magnesium hydroxide scale.

Prevention of Scale Formation

There are three major scales: calcium carbonate scale, which is called soft scale and easy to remove; magnesium hydroxide scale; and calcium sulfate scale, which is a relatively insoluble scale and difficult to remove. (Calcium-sulfate scale exists in three different crystal forms: anhydrate, hemihydrate, and gypsum). These chemical compounds are found in solid forms (pure or in mixture).

The rate of scale formation is related to the operating temperature, the rate of evaporation, the rate of brine circulation over the operating surface, the average brine concentration and the pH of the incoming sea water.

Since supersaturation of magnesium hydroxide and calcium sulfate increases with increasing temperature, the most important factor in scale prevention is the choice of the minimum possible operating temperature. (Magnesium hydroxide scale forms at higher temperatures than calcium carbonate scale, and the precipitation of magnesium hydroxide liberates acid and thus inhibits the precipitation of calcium carbonate.)

Standiford and Sinek (12) have stated the following facts as a rough indication of the temperature-concentration relation:

Below 185°F (85°C), sea water can be concentrated to four times normal strength without formation of sulfate scale.

At 252°F (122°C), the maximum allowable concentration factor is 1.7 to 2.0.

At 300°F (150°C), substantially no concentration can be done without rish of scale formation. These limits apply only to the case of the sulfate scale.

To reduce the scale formation on the tubes, a smooth transfer surface should be obtained because smooth surfaces do not provide nuclei for crystalization. Scale formation can also be reduced by decreasing the detention time in the units. This can be done by obtaining as high velocities of the brine as possible.

Hydroxide and carbonate-scale prevention, in distillation process, can be obtained by the control of pH, the seed recycling, the use of some additives, the ion-exchange resins, and contact stabilization methods.

1. pH Control

By suitably altering the concentration factor or the temperature of the sea water being distilled, either calcium carbonate or magnesium hydroxide can be made to be the main constituents of the scale. While other materials are deposited, these two can make up ninety eight per cent of the scale, and can be prevented from depositing by controlling the pH with acidic materials such as sulfuric acid, citric acid, and hydrochloric acid or with a salt such as ferric chloride which is either added as a chemical or is generated electrolytically by sacrificial iron electrodes in sea water (13). Thus, these chemicals reduce the pH, but extremely lowered pH causes corrosion.

The MANUAL OF BRITISH WATER ENGINEERING-PRACTICE (14) recommends the addition of calcium chloride and sodium bicarbonate with pH adjustment using sodium hydroxide or lime to prevent the scales. The quantities used are of the order of 45 ppm. calcium chloride, 70 ppm. sodium bicarbonate and lime or sodium hydroxide to give a pH value of 8.0 to 8.4 to eliminate corrosion.

2. Seed Recycling

Carbonate and hydroxide scales can be prevented by use of seed crystals of calcium carbonate and magnesium hydroxide suspended in the evaporating solution (at least up to 250°F (120°C). The concentration of seeds should be between 0.1 and 0.5 per cent by weight (15).

3. The Use of Additives

Mixtures of corn starch, soda, and disodiumphosphate have been used for scale prevention and found quite effective (16). Thus, a mixture of sodium tripolyphosphate and lignin sulfuric acid derivatives (Hagevap LP) is suitable for reducing scale formation in flash distillation of sea water. In this case, no scale deposition is obtained as long as the maximum brine temperature does not exceed 200°F (93°C), and at temperatures from 210°F (99°C) to 215°F (102°C) there is indication of scale from the increase in terminal temperature difference (TTD) (15).

4. Ion-Exchange Resins

The removal of calcium and magnesium ions by ion-exchange with polystyrene cation resins and the use of the waste brine as regenerant have also been investigated at the University of California and sixty seven per cent removal was achieved in a one-stage and seventy seven per cent in a two-stage process (15). Dow Chemical Company's Dowex 50W cation exchange resin was tested for removal of scale-forming constituents from sea water and it was found that it removed about fifty per cent of the calcium from sea water. This was a sufficient amount to prevent accumulation of sulfate scale (15).

5. Contact Stabilization

Supersaturated (evaporating) brine is withdrawn from the evaporator and is passed through a bed of crystals (sand) where precipitation occurs. It is then recirculated to the evaporator. In this method, the contact bed should be periodically cleaned (16).

Calcium sulfate deposition can be controlled by keeping the concentration below the saturation value at any point in the system. It can also be controlled by use of calcium sulfate seed crystals suspended in the evaporating salt solution. Work in a long-tube vertical (LTV) pilot plant, Freeport, Texas, showed that the sludge recirculation method using a slurry of about one per cent calcium sulfate was effective in preventing scale up to 300°F (150°C) (15).

CHAPTER IV

CORROSION AND PROTECTION OF METALS IN SEA WATER

Formation of Corrosion

The corrosion of metals in sea water conversion plants is a very important problem because sea water is corrosive even under normal conditions. Water is corrosive to a solid when it tends to dissolve the solid. The solution of a solid mineral such as $CaCO_3$ is accompanied by its dispersion as positive and negative ions (cations and anions) in solution. The solution of a solid non-polar compound is accompanied by its dispersion as nonionized molecules in solution. Neither of these cases involves a transfer of electrons and there is not any flow of electricity.

In order for corrosion to take place, there must be water in contact with the metal, and the water must contain ions to form the electrolyte.

Metals are usually subject to electrochemical corrosion in sea water conversion operations. Sea water is corrosive because the solution is a good electrolyte; it contains ions which accelerate the attack on common metals; it contains dissolved oxygen (D.O.) that promotes the attack by reacting with nascent hydrogen formed at the cathode; and it contains a multitude of forms of organic life. Besides, many other factors contribute to the overall results known as corrosion.

Aqueous corrosion is electrochemical in nature and involves the passage of electric currents. The current enters the solution at local anodes and leaves the solution at cathodic areas on the metal. In the case of steel, ferrous ions enter the solution at the anode and hydrogen is deposited at the cathode. (The oxidation reaction by which a metal corrodes is an anodic reaction. The equivalent reduction is a cathodic reaction.) The following types of anodic reactions show the corrosion of metals (17).

a. Metallic element $\underset{\text{Red}}{\overset{\text{OX}}{\rightleftarrows}}$ cations + electrons

$(\underline{Fe} \rightleftarrows Fe^{++} + 2e^-$ (Anodic action)

$H_2 \rightleftarrows 2H^+ + 2e^-)$ (Cathodic action)

b. Anions + metal $\underset{\text{Red}}{\overset{\text{OX}}{\rightleftarrows}}$ compound + electrons

$(2\ OH^- + \underline{Fe} \rightleftarrows Fe(OH)_2 + 2e^-$

$Cl^- + \underline{Cu} \rightleftarrows CuCl + e^-)$

c. Compound I + metal $\underset{\text{Red}}{\overset{\text{OX}}{\rightleftarrows}}$ compound II + cations + electrons

$(\ H_2S + \underline{Zn} \rightleftarrows \underline{ZnS} + 2\ H^+ + 2\ e^-$

$H_2S^- + \underline{Fe} \rightleftarrows \underline{FeS} + H^+ + 2\ e^-$

$1/2\ O_2 + 2H_2) + \underline{Fe} \rightleftarrows \underline{Fe\ (OH)_3} + H^+ + e^-\ )$

The most important factors affecting corrosion are carbon dioxide

(CO_2), dissolved oxygen (D.O.), Temperature, pH of the sea water, cavitation, impingement (erosion-corrosion), composition of sea water, pollution with compounds not present in sea water, contact of dissimilar metals, and bio-fouling on the exposed metal surface.

1. Carbon Dioxide (CO_2)

Free carbon dioxide is found in sea water. The amount of carbon dioxide picked up by rain water from the atmosphere is very small and usually ranges from about 0.5 to 2.0 ppm (18). The free carbon dioxide content of oceans varies from surface to bottom. It is less on the surface than in the bottom of oceans. The reason for this is that process of decay at or near the bottom of the sea generates carbon dioxide, while in the upper layers, microscopic plants use up the carbon dioxide by photosynthesis and give out oxygen. In other cases, water at or near the surface gives up carbon dioxide as it becomes aerated by the atmosphere.

When carbon dioxide dissolves in sea water, it forms a weakly disassociated carbonic acid:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The presence of bicarbonate ions also decompose and release carbonic acid under the influence of heat:

$$2HCO_3^- + H_2O + \text{Heat} \rightarrow H_2CO_3 + O_2\uparrow$$

Water containing an acid, even one so weak as carbonic acid, reduces iron to the ferrous condition and produces hydrogen in accordance with the following reaction (18):

$$2\ Fe + 2\ H_2CO_3 \rightarrow 2\ Fe\ CO_3 + 2\ H_2\uparrow$$

The ferrous carbonate then reacts with the oxygen and water to form ferric hydroxide and then to release carbonic acid again as follows:

$$2\ Fe\ CO_3 + 5\ H_2O + 1/2\ O_2 \rightarrow 2\ Fe(OH)_3 + 2\ H_2CO_3$$

Thus, carbonic acid will attack more iron and it may cause severe pitting of the tubes. At a low pH value, carbon dioxide, of itself, is corrosive and an accelerating factor in dissolved-oxygen corrosion when oxygen is present (18). Hence, it is necessary to keep the carbon dioxide content of the steam as low as possible.

2. Dissolved Oxygen (D.O.)

Dissolved oxygen causes corrosion at ordinary temperatures. Previously, it was mentioned that carbon dioxide is an accelerating factor in dissolved-oxygen corrosion. Therefore sea water which contains, in addition to dissolved oxygen, a high content of carbon dioxide in relation to its alkalinity will be much more corrosive than a water which contains a low content of carbon dioxide in relation to its alkalinity. In other words, a water having a given dissolved oxygen content is much more corrosive if it has a low pH than if it has a high pH value.

Oxygen is an exceedingly active element which combines with a host of other materials. A solution of oxygen in sea water is extremely corrosive to iron, galvanized iron, steel, and brass (18). When iron enters solution as cations it combines with the anions of water to form ferrous hydroxides

$$Fe + 2\ H_2O \rightarrow Fe\ (OH)_2 + H_2\ .$$

The hydrogen released in this way then combines with the dissolved oxygen in the sea water to form hydrogen peroxide:

$$H_2 + O_2 \rightarrow H_2O_2$$

Then, the peroxide reacts with ferrous hydroxide to form ferric hydroxide (rust) which is insoluble (19)(20):

$$2\ Fe\ (OH)_2 + H_2O_2 \rightarrow 2\ Fe\ (OH)_3$$

Corrosion of metals results in the formation of tubercles of ferric hydroxide ($Fe(OH)_2$). This deposit is known as tuberculation and reduces the pipe cross section and increases the roughness of pipe in the treatment unit (21).

3. Temperature

More corrosion is obtained with an increase in the temperature of sea water due to decreased visosity and increased convection currents which promote the diffusion of oxygen through the metal surface film. In the range from 50°F (10°C) to 122°F (50°C), the corrosion increases at the rate of approximately five per cent per degree centigrade (19). If all of the D.O. stayed in solution, if protective film did not form, and if it is assumed that this reaction followed the general rule of roughly doubling in speed for each 18°F rise in temperature, corrosion would be about five hundred times as fast at 194°F as at 32°F. In practice, the greatest speed of corrosion in the heaters takes place at approximately 160° to 180°F (18). The rate of corrosion is affected by temperature because (1) the rate of chemical reaction increases with temperature, (2) the solubility of gases decreases with temperature increase, and (3) the solubility of most substances other than gases increases with temperature (20). Friend (22) states:

> Electrical or galvanic activity is due to irregular composition of the metal, to segregation, to contact with other similar and dissimilar metals, and so on, and which may be capable of slowly exerting an influence upon the corrosion of the iron at ordinary temperatures, becomes greatly enhanced as the temperature rises, so much so as to yield quite astonishing results.

4. pH of the Sea Water

Normally, the pH of sea water is between 7.50 and 8.25 (19). Corrosion is more rapid in acid than in alkaline solutions. That is, high concentrations of hydrogen ions, which menas low pH value (or a higher acidity of the water) tend to increase corrosion of metals. This promotes the deposition of atomic hydrogen as the metal ions go into solution in the sea water. Hydrogen-ion concentration (pH) also affects the conductivity of the electrolyte and solubility of the products of corrosion. Thus, the rate of corrosion can be controlled by the rate at which hydrogen deposited on the cathode area can be removed by oxidation and by the rate of release of bubbles of the gas (20). As previously indicated, at a low pH value of the condensate the carbon dioxide attacks the metal surfaces and accelerates the rate of the dissolved-oxygen corrosion. High pH values tend to retard it.

5. Cavitation

Water flowing at high velocity may be at sub-atmospheric pressure. It will then be turbulent and therefore subject to rapid changes of pressure. At instants of low pressure, very small vapor or gas bubbles may be released by the water, which collapse with implosive force the moment the pressure is again increased or the bubble moves to an area of higher pressure. Under a continual bombardment of these implosions, the surface undergoes fatigue failure and small particles are broken away (21). This damaging action of cavitation is known as pitting. Exposed active metal sites are rapidly attacked and cause corrosion by the sea water. This kind of corrosion usually occurs at the tips of the impeller blades of centrifugal pumps and at bends in pipes where high velocity flow reduces pressure to sub-atmospheric.

Cavitation is prevented by maintaining a positive pressure on the suction pipeline of the pump.

5. Impingement (Erosion-Corrosion)

If the critical velocity is exceeded, the protective film layers on metals are eroded away. It is not considered good practice to control rate of flow by throttling at the valve because this causes turbulance just beyond the valve. Thus, corrosion is promoted by the impingement of a high velocity of sea water on the tube metal surfaces. Usually inlet ends of condenser tubes are attacked by the excessive turbulance. The maximum velocity to prevent corrosion is low for copper (about 2 feet per second); higher for aluminum and aluminum bronzes; and highest for stainless steel, Hastelloy C, and titanium (19).

7. Composition of Sea Water

Since sea water contains chloride, sulfate, bicarbonate, bromide, and fluoride ions, it causes corrosion on metal surfaces. The chloride ion is the main culprit in causing corrosion. At the same pH, sulfate solutions are less corrosive than similar chloride solutions. The presence of bicarbonate ions in sea water due to dissolved carbon dioxide accelerates corrosion attack on a metal surface. Bromide and fluorides are extremely corrosive ions, but they are present in small quantities in sea water (15) (19).

8. Pollution With Compounds not Present in Sea Water

Organic content of sea water is another important factor in causing corrosion. Fouling of the surface by organic deposits can lead to severe pitting because of the concentration-cell effects.

The pollution of sea water causes an unbalance of pH, changes the marine-organism concentration, decreases the dissolved oxygen, and/or changes the ionic balance of sea water. Sulfates, which accelerate corrosion of metals, are found in polluted sea water (19)(22).

9. Contact of Dissimilar Metals

Corrosion of metals may result from electrolytic action which is often caused by the galvanic action resulting when dissimilar metals are immersed in sea water. The rate of electrolysis depends upon the dissimilarity of the two metals coupled (23). When two metals of different potentials are galvanically coupled, the promotion of the attack can be observed frequently on the less noble metal (low in electrochemical series) of the two. A small area of an anodic metal coupled to a large area of a second metal which is cathodic can be dangerous. However, the reverse situation, that is, a small cathode coupled to an anode which is large in area, can be satisfactory in service (19).

10. Bio-Fouling on the Exposed Metal Surface

Certain living organisms in the sea water cause marine fouling on the exposed metal surface leading to corrosion of the equipment at sea water conversion plants. Some sorts of animals and plants, as well as colonies of micro-organisms, are deposited from sea water onto the metallic surfaces.

Fouling obstructs flow in pipes leading to such corrosive effects as are caused by overheating or impingement at local high-water velocities.

Some organisms enter a piping system in their larval phases and anchor themselves to the interior tube walls. If these are allowed to grow, turbulance may result in severe condition at those sites. Even when the organisms are killed by chlorination, by flooding temporarily with fresh water, by hot sea water, or by toxic materials such as sodium pentachlorophenol, their decomposing bodies can still clog the sea-water piping system and cause corrosion (15) (19).

Marine fouling is present in all the oceans, especially during the breeding period. Fouling happens only during the summer, in northern waters, but it is continuous in the Tropics (19).

Protection From Corrosion

The factors that cause corrosion are numerous and, for this reason, difficult to control. However, corrosion may not be eliminated completely, but the problem can be minimized or reduced in most cases by following these five steps: (1) careful processing in the manufacture of the metal which will be used in the unit, (2) cathodic protection, (3) protection of the surfaces by use of coatings, (4) control of the substances coming into contact with the metallic surfaces, and (5) selection of suitable materials for specific conditions.

The use of deaeration to remove oxygen from the solution is probably the most effective way of combating corrosion and will make possible the use of ordinary steel in sea water conversion plants (15). A thin egg-shell scale of calcium carbonate also protects the metals against an improperly deaerated feed water. At velocities of 2 to 3 fps or more, the metals usually are not apt to foul (19). For that reason, bio-fouling corrosion can be prevented by keeping the velocities higher than the above minimum limits.

A variety of protective coatings is available for steel in sea water service. In practice, compatible anti-fouling paint is applied over the corrosion-resistant primer coating system (19).

Steel can be protected by cathodic current supplied either from sacrificial anodes or an external direct current source. This method is effective for completely immersed steel. Aluminum also can be cathodically protected (19).

Corrosion prevention by the use of inhibitors usually is found to be expensive, but, if sea water is first deaerated, only a small amount of corrosion inhibitor would be needed to prevent attack on steel or copper-base alloys (19).

CHAPTER V

METALS USED IN SEA WATER

The metals most commonly used for equipment exposed to sea water are iron-based metals, aluminum and its alloys, copper-base alloys, monel, titanium and Hastelloy C.

Iron-Based Metals

1. Wrought-Iron

This metal is widely used in piping. Wrought iron appears to be more resistant than mild steel to general and localized corrosion by sea water. For the same initial cost a much thicker wall can be bought in a case iron pipe than for one of wrought iron. An older form of wrought iron which was made in England contained slag layers which were found in some corrosion environments to prevent pitting from progressing deeply into the metal. While these layers, when suitably oriented, provide a longer lifetime than the old form of iron, it does not follow that the modern fibrous form of wrought iron will outlast it in identical sea water service (19).

2. Cast Iron

Cast iron is attacked by sea water. If the layer of graphite left with corrosion product is dense and compact, corrosion can be stifled. If the graphite layer is porous, corrosion can be promoted by the galvanic action between the graphite and iron beneath. This makes the cast iron unsatisfactory in sea water equipment.

3. Steel

Steel has found considerable application in sea water, particularly as a structural material such as off-shore drilling towers, piling for piers, dock and sea walls, and in piping to handle sea water. It is the basic material of construction for sea-water conversion plants. Since steel is the least expensive of materials for construction, it provides a broad application for sea water service. Even if it may corrode in some parts of a plant, such as a distillation unit, its low cost may result in lower over-all cost. If proper steps are taken, such as the removal of all oxygen from sea water by use of deaeration or by use of other processes, it can be used to handle sea water below 250°F (120°C).

The rate of attack for immersed conditions is uniform in polluted sea water. General attack, when it occurs, is a linear function of time. It is often subject to pitting attack by sea water. The presence of mill scale on the steel increases the rate of pitting. This is a result of the mill scale serving as large cathodes to the small, bare anodic areas (19).

4. Stainless Steel

Stainless steel does not give good results in sea water unless used under carefully controlled conditions and in special circumstances. It can be used in heat exchanger service at much higher velocities than most metals. However, any points at which highstress and high chloride concentrations are present there is a possibility that stress-corrosion cracking can take place. If the temperature is raised this becomes much more severe.

Generally, stainless steel withstands polluted sea water and brackish water better than copper-base alloys.

In spite of that stainless steel pump impellers have been used in sea water service successfully. Stainless steel screens, because of the crevices involved where wires cross, are not recommended for use in sea water (19).

Aluminum and Aluminum Alloys

Aluminum can be used for sea water construction as a resistant material. Some experiments at Fort Belvoir, Virginia, proved that by proper corrosion control practices, aluminum can be employed in whole plants converting sea water to potable water. The incoming water must be free from all metallic ions, particularly copper or nickel. At such a plant copper base alloys must not be used and galvanic couples to other metals must be avoided. Aluminum-clad tubing has been used successfully to get longer lifetime in sea water. If properly selected, the covering acts as a sacrificial metal and the attack will not enter into the base metal until most of the cladding has been corroded by sea water because it is slightly anodic to the base alloys (15) (19). However, savings in weight and in losses due to corrosion are favorable compared with mild steel.

Copper Base Alloys

If the velocity of the feedwater exceeds 2 fps, ordinary copper tubes are erroded. But the following copper-base alloys have given good results in sea water service.

1. Admiralty Brass

Admiralty brass which is 70% Cu + 29% Zn + 1% Sn + inhibitor (such as arsenic), is widely used in the fabrication of condenser tubes. It is not so resistant as cupro-nickels, but its lower inital cost makes it available (19).

2. Aluminum Brass

76% Cu + 22% Zn + 2% Al, has also found wide use in sea water service. In this alloy the presence of aluminum increases the resistance to velocity and impingement (19).

3. High-Tin Bronze

90% Cu + 10% Sn has excellent lifetime in sea water as condenser tubes, but its high cost restricts the wider use of this resistant alloy.

4. Cupro-Nickels

They are considered the most useful material for sea water plants at the present time. The most widely used cupro-nickels are 90% Cu + 10% Ni, 80% Cu + 20% Ni, and 70% Cu + 30% Ni. The lower nickel content results in a cost advantage over the 70 Cu - 30 Ni alloy.

The first alloy with about 1.5% iron is the most widely used, but the second and third alloys may be preferred for more severe conditions (15).

Generally, cupro-nickels are accepted as the best alloy for condenser tubes and pumps (19).

Monel, Titanium, and Hastelloy C

Monel, titanium, and Hastelloy C have extensive use for handling sea water. Titanium particularly can be used at velocities of twenty to fifty feet per second. The three of them are very resistant to hot sea water, but they are so expensive that their wider use in sea water service is restricted except for special parts subjected to severe corrosion (15) (19).

Design Considerations

While selecting materials for sea water, heat exchangers, evaporator and pump service, some factors, such as cost, availability, efficiency, and corrosion resistance, should be considered. All metals which will be used in sea water service must be fabricated by well established methods. As the thermal conductivity of the alloys varies greatly, the designer should be interested in the over-all rate of heat transfer in service. Thin protective films on the heat transfer surface are to be preferred to heavy deposits of scale and corrosion products.

1. Heat Exchangers Using Cooling Water

The most troublesome area in a tube and shell-type heat exchanger is at the inlets of the tubes where impingement corrosion is caused by high-velocity turbulent flow. However, impingement attack at the inlet ends can be minimized by providing a suitable amount of cathodic current. While this current does not enter the tube ends to any great depth, it protects the first few inches. The current may be provided by sacrificial anodes made of iron, zinc, aluminum, or magnesium. Protective current can also be provided by using the iron heads or the water boxes as sacrificial anodes. These water boxes, when made of heavy steel or cast iron, provide galvanic protection to the tube ends and tube sheets as they corrode. But, if the iron heads or water boxes in a condenser are lined with a protective coating or with a metal such as Monel, the inlet tube ends do not get cathodic protection from the iron to copper alloy couple. Then, at the tube ends, impingement attack will be more severe (19). Thus, sacrificial anodes will be needed to reduce impingement corrosion at the inlets of the tubes by providing cathodic current.

2. Evaporators and Heat Exchangers for Handling Sea Water

Heat-transfer equipment must be made of corrosion resistant and good thermal conductive metals. But, it is difficult to find a metal which has these two properties.

Experience at the pilot plant of Wrightsville Beach, North Carolina, showed that:

> Evaporator tubes of aluminum, brass, admiralty brass, copper, and 90/10 cupro-nickel were almost completely resistant to corrosion and results with steel tubes were encouraging. The tubes were insulated electrically from the tube sheets in order to avoid galvanic action. Severe pitting occurred with aluminum tubes. (24)

Cupro-nickels and monel have been used successfully in evaporators, especially if sea water is handled at 200°F (93°C) or higher. Titanium is the most promising metal for a sea water exchanger from the corrosion viewpoint.

Fink (19) recommends that the heat-transfer surfaces of evaporators and the heat exchangers for handling hot sea water be made of 70/29.3 cupro-nickel with 0.7% iron.

3. Pumps

At low velocities, sea water has been handled successfully in pumps using casing made of cast iron containing a few per cent of nickel. At higher velocities, monel, bronze, and cupro-nickel are better than cast iron. Pump impellers are usually made of one of the bronzes and stainless steel. For pump shafts K monel gives excellent results in sea water services (19).

CHAPTER VI

FLASH DISTILLATION PROCESS

Classification

A simple classification of saline-water-conversion processes is based on (1) whether water or salt is removed, and (2) the nature of the second phase. This classification, which pertains to the actual process of separation, is illustrated in Table V (7).

TABLE VI

A CLASSIFICATION OF SEPARATION PROCESSES

Constituent Removed from Saline Water	Phase to Which Transported	Process
Water	Vapor	Distillation
Water	Liquid	Solvent Extraction Reverse Osmosis
Water	Solid	Freezing Hydrate Adsorption
Salt	Liquid	Electrodialysis Osmionic Thermal Diffusion
Salt	Solid	Ion Exchange Adsorption on Carbon Electrodes

Grouping of Distillation Processes

Distillation processes are grouped in eight sub-groups which are flash distillation (evaporation); boiling type submerged-tube heating surface; boiling type long-tube, vertical evaporation (LTV); forced circulation vapor compression flash evaporation; rotating-surface evaporator; wiped-surface evaporator, vapor-reheat process; and heat transfer using an immiscible liquid.

History of Flash Distillation

The distillation process is the oldest of all methods known by which potable water has been obtained from sea water. Sea water distillation dates back to the sixteenth century when sea captain Sir Richard Hawkins and others on experimenting found that with a sufficient heat for distillation salt does not rise in vapor, and that the salt water distilled is drinkable.

Flash distillation, which is a variation of the conventional distillation methods, is the most promising process among all others at the present time. It is the only one which is commercially exploited on a large scale (25). Its first application to sea water distillation was during World War II. The first large scale, multistage flash units were installed at Kuwait in 1958. Now, there are several plants on shipboard, submarines, and in land-based installations where it has been used successfully.

The rapid expansion of the sea water distillation by the flash evaporation process can be explained by the general level of prosperity after the second world war. This particularly applies to the oil industry which has expanded a great deal since the end of the war. Where oil resources have been developed in arid areas of the world, use has been made of the sea water distillation process to provide the necessary potable water required by the personnel of the oil companies. The Sheikdom of Kuwait is the best example of this as prior to the development of Kuwait's oil resources, this small country depended on a few brackish water wells for its water supply. By 1960, the Kuwait Oil Company had a production capacity of 1.1 MGD, and the Kuwait Government had increased the capacity of their plant to 6.25 MGD (14).

This rapid change was brought about by the introduction of the multistage flash evaporator. It has lower manufacturing cost compared to the conventional types. This fact, combined with the larger size of the unit which can be constructed, has appreciably affected a reduction in capital cost. These have been reduced to approximately one-half for a 1 MGD installation (14). For that reason, at the present time, the flash distillation method is the most widely used method. For instance, in recent years, multistage flash-type plants have provided more total sea water conversion capacity than any of the other distillation types and other types of sea water conversion units (26).

As a result, at the present time, in large capacity plants, multistage flash distillation is the most economical process.

Besides Kuwait, other large land-based multistage flash units are located in Bermuda; Bahama Islands; Virgin Islands (0.25 MGD - 26 stages); San Diego, California, (1 MGD - 36 stages, 1962, since taken to Cuba); Isle of Guernsey in the British Channel (0.5 MGD - 40 stages); and Venezuela (15).

Principle of Flash-Type Distillation

In conventional distillation methods, heating of saline water and boiling are performed in the same vessel.

The flash distillation method unit does not boil the saline water on the heating surface, but raises the incoming water temperature while maintaining a slight pressure on it. Then, the heated sea water is passed through one or more than one series of flash chambers in which the pressure is reduced step by step to low vacuum. While the pressure is reduced, a portion of the sea water flashes into vapor. The vapor subsequently condenses and serves to heat the incoming sea water. This condensed water is the potable water product.

Flash distillation process is grouped into two parts, (1) singlestage flash distillation process, and (2) multistage flash distillation process.

The schematic principle of the singlestage flash distillation process is illustrated in Figure 1.

1. Singlestage Flash Distillation Process

As it is seen in Figure 1-a, the basic plant consists of a saline water vessel or container in which the flashing process occurs, a heater, a condenser, pumps, vent (vacuum pump), valves, and other auxiliary equipment for maintaining the proper pressure inside the flash chamber.

Sea water (or saline water) is pumped into the tubes which are in the vapor space of the flash chamber where the sea water is preheated from 68°F (20°C) to 140°F (60°C). It is then introduced into the heater

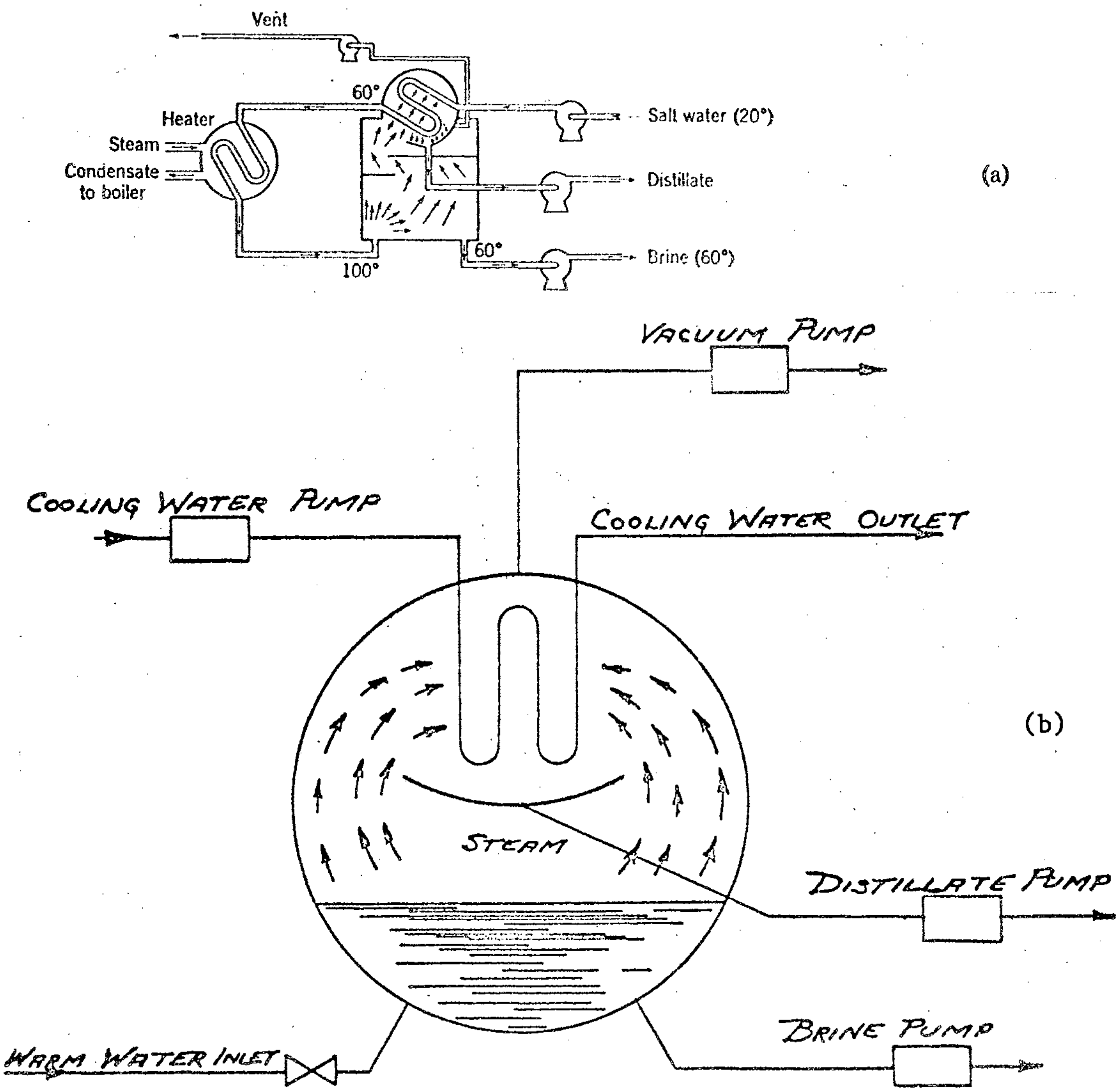

Figure 1 Schematic Principle of Single Stage Flash Distillation Process (3) (25)

which consist of several tubes which are externally heated by steam. Sea water temperature is raised from 140°F (60°C) to 212°F (100°C) in the heater. Here, the pressure is kept over 1 atmosphere, and thus, at 212°F (100°C) boiling of sea water does not occur. Then, the sea water is passed through the flash chamber which is under reduced pressure. Here some portion of the sea water vaporizes. The vapors are then condensed by the tubes carrying incoming cold sea water. Thus, distilled sea water, which is in the form of potable water, is pumped into storage tanks or the distribution main and the brine (concentrated sea water) flows by gravity or is pumped out of the unit.

The discharged brine temperature at the discharge end of the flash chamber depends upon the amount of the vapor flash off in the chamber. For example, if it is desired to distil 7.1% of the incoming sea water, it is necessary to make it cool to 140°F (60°C) in the chamber. Hence, the water-vapor pressure prevailing in the flash chamber must be that corresponding to the sea water at the same temperature (68°F) (3). The pressure around the tubes is kept lower than the bottom of the chamber for maintaining the vapor circulation.

There is another type of flash distillation process which is shown in Figure 1-b. (25). In this system, cooling water is used separately, instead of incoming warm sea water, in the flash chamber. Obviously, the latter system is less economical than the previous one.

2. Multistage Flash Distillation Process

2a. Multistage Flash Distillation Using Fossil Fuels

The schematic principle of the process is shown in Figure 2.

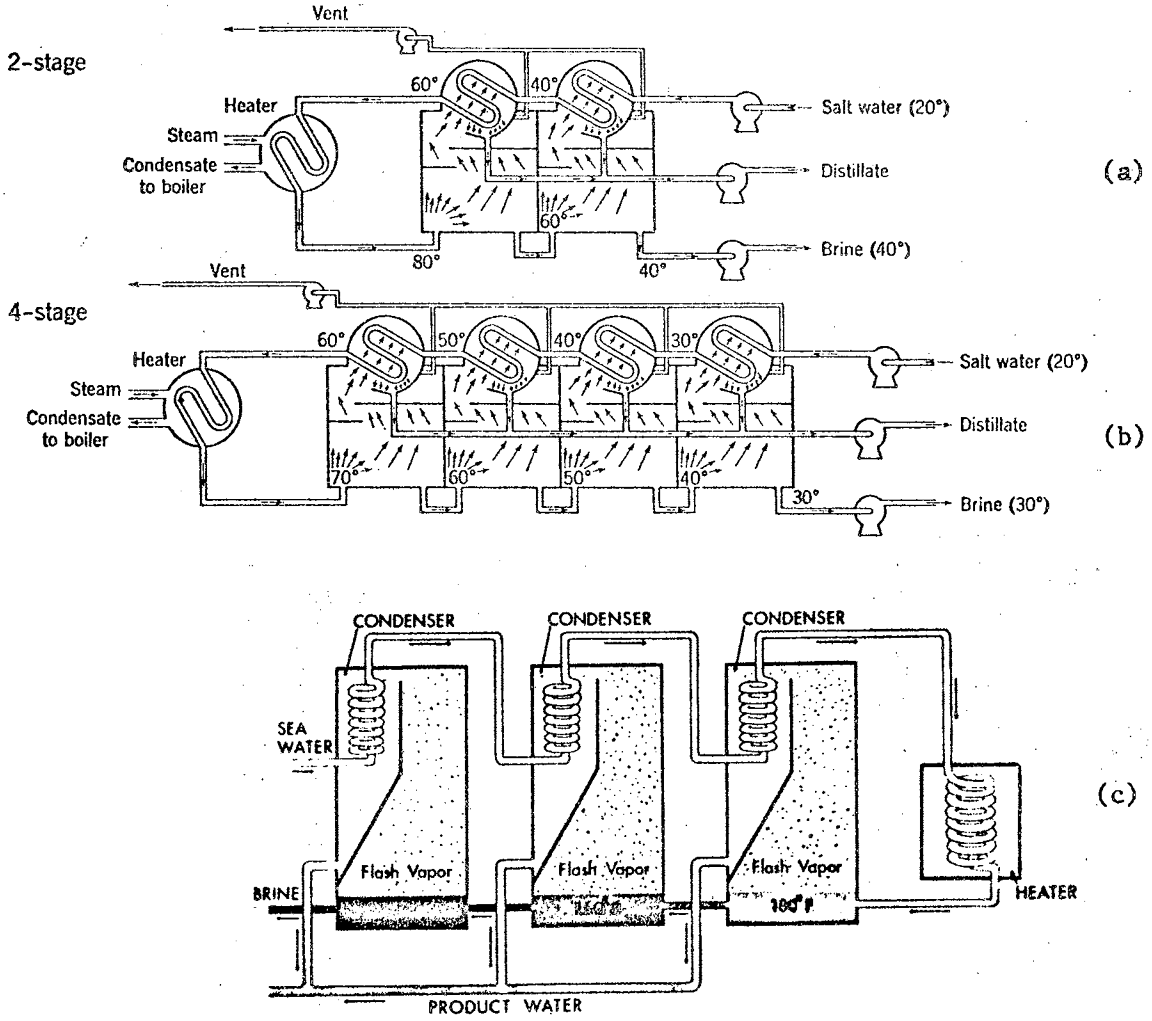

Figure 2 Schematic Principle of Multistage Flash Distillation (3)(27)

The multistage flash distillation process is the arrangement of two or more flash chambers side by side. Thus, it is possible to produce more distilled water per unit of heating steam by carrying out the flashing in multistage.

In this process, sea water is heated in tubes and then is passed through a series of flash chambers in which the pressure is reduced step by step to a low vacuum. As the pressure is decreased, a portion of the sea water flashes into the vapor phase. After that vapor is condensed into potable water and serves to heat the incoming sea water.

Sea water is pumped into the lowest temperature stage condenser. From this stage it is passed in series through the higher stages. Then it is introduced into the heater where its temperature is raised to a maximum. After leaving the heater, it enters into the highest pressure and temperature stage where a part of the steam evaporates. From this first stage, the remaining brine is passed through the second stage which is at a lower pressure and temperature. In the second stage another part of the steam vaporizes. Thus, this process is repeated through the following stages.

From the final (or the lower pressure and temperature) stage, the brine is discharged by gravity or pump, whichever is sufficient, and the condensed vapor (distilled water or product water) is pumped to the storage tank or distribution system.

In the multistage flash distillation process, most of the heat is recirculated in the chambers, hence economy improves with number of stages.

A two-stage flash distillation unit producing the same amount of potable water as the single stage is illustrated in Figure 2a. In the two flash chambers, the evaporating sea-water temperature is 140°F (60°C) and 104°F (40°C). The incoming sea water is heated to 68°F (20°C) in each unit. In this unit, less heat is required in the heater in which the temperature of the sea water is raised from 140°F (60°C) to 176°F (80°C), instead of 212°F (100°C) as in the single-stage unit. The amount of evaporated water in each unit is one-half of the corresponding amount in the single-stage unit. In a two-stage flash distillation unit, less heat is lost with the discharge brine because the brine is discharged at 104°F (40°C) instead of 140°F (60°C) as in the single-stage unit.

Similarly, in a four-stage distillation unit (Figure 2b) where the brine is pumped out at 86°F (30°C), the amount of heating steam required is one-fourth of the amount in the single-stage unit because the heater raises the temperature of the sea water 50°F (10°C) in each unit.

In fact, in practice, heat transfer is not as perfect as assumed. Hence, sea water in the tubes leaves all stages colder than the condensing distillate.

2b. Multistage Flash Distillation Using Nuclear Energy (Uranium Fission)

Using nuclear energy to operate multistage flash distillation unit can result in the most economical production of potable water from sea water.

The schematic principle of such a plant is illustrated in Figure 3.

In this plant the incoming sea water is pumped through the tubes in the deaerator. The deaerated sea water is mixed in the deaerator with the slightly concentrated brine. These two combined streams are pumped through the stages as the flow line shows in Figure 3a. Some portion of

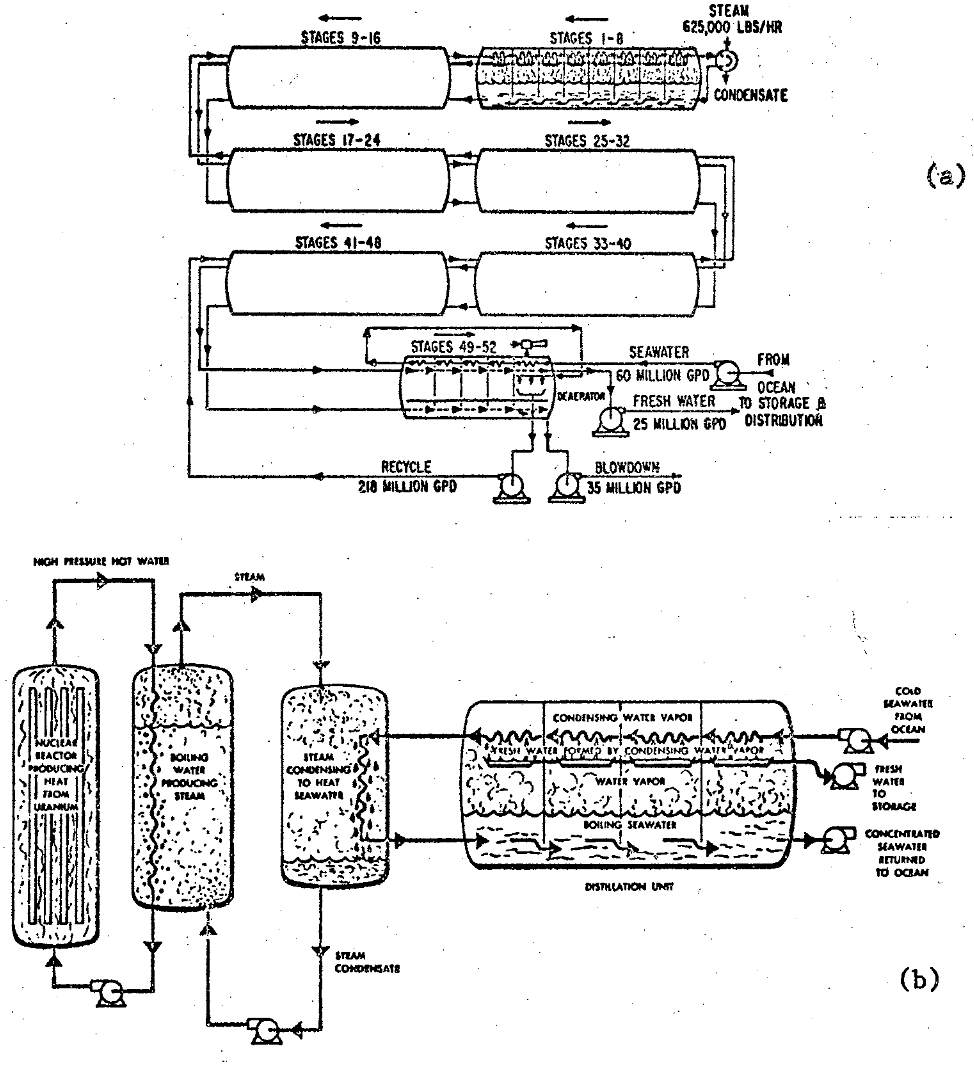

Figure 3 Schematic Principle of Multistage Flash Disstillation Using Nuclear Energy (28)

the water flashes from the brine solution in each stage as described previously. It condenses on the tubes of the evaporator. Finally, the condensed water and the brine reach the last stage (lowest pressure and temperature stage). Then, the condensed water is pumped from the system into the storage tank or distribution main. The excess brine is discharged to the ocean as blowdown. The remaining brine, which is required to be recycled, and the deaerated sea water are mixed and recycled through the system.

To remove the inerts from the plant an ejector system is put at the lowest pressure point (which is the deaerator) in the system.

2c. Multistage Flash Evaporation Utilizing Solar Energy

In the application of solar energy to saline water conversion, the combination of a solar heat collector with a process which is capable of energy re-use can be more economical than conventional distillation processes. The multistage flash distillation process can utilize the relatively low temperature saline water produced in a flat-plate solar heat collector more efficiently than most other conversion processes. A combination plant with 20 stages was designed under the Office of Saline Water to produce annually 345 X 10^7 gallons (9.425 MGD) of water when collecting about 4 trillion BTU of heat. Location of the plant will be in Southern California (29).

The schematic general flow diagram of multistage flash distillation process and the solar heat collector is shown in Figure 4.

The process conditions shown are typical for operation with a brine temperature of 104°F, as would be the case during May, June, and July.

The incoming sea water is pumped into the tubes of the 20-stage evaporator plant. It is graduatlly heated from 57°F to 132°F as a result of the vapor condensing on the outside of the tubes. Thus, it leaves the first stage at 132°F and is discharged into a concrete lined and covered channel system. Here the sea water is allowed to flow by gravity

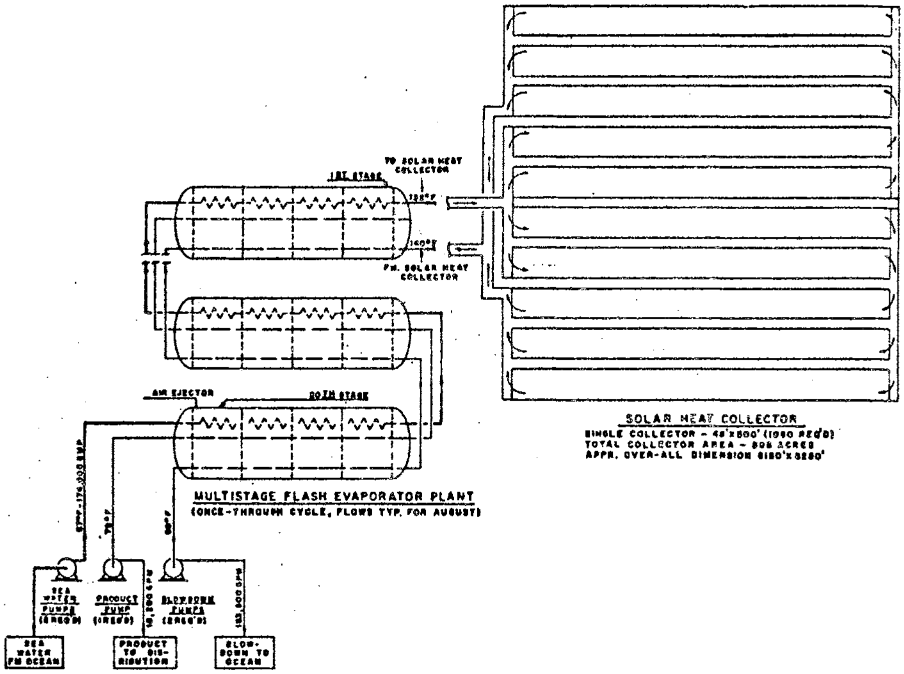

Figure 4 Schematic Principle of Multistage Flash Distillation Utilizing Solar Energy (29)

through the solar heat collector. There is travels about two miles in thirty two hours. The sea water is returned to the evaporator at 140°F during August and introduced into the shell side of the first stage which is under a low vacuum. Here the flashing process starts and ends at the lowest temperature stage which is the last stage (twentieth stage). In this system 164,000 gpm out of 174,000 gpm are returned to the ocean as blowdown and the remaining part, which is 10,000 gpm, is the product which is pumped from the system to the distribution main or storage tank (29).

The solar heat collector is made of plastic material the economy of which is greater when operating at lower temperatures. If the operation is above 150°F, brine temperature requires the addition of chemicals for scale control.

Comparisons of Fossil Fuels, Nuclear and Solar Energy

1. Fossil Fuels

The three important conventional fuels are coal, petroleum derivatives, and natural gas.

The heat value of coal reserves of the United States is 3.1×10^{18} Btu, and of the world reserve is 21.0×10^{18} Btu.

The heat value of oil and gas reserves of the United States is 0.9×10^{18} Btu, and of the world reserve is 6.2×10^{18} Btu (30).

Thus, the total fossil fuel reserve of the United States is 4.0×10^{18} Btu. Current rate of consumption is about 3.6×10^{16} Btu per year (30). If the increase in consumption of fuels is considered, it can be concluded that the period of grace is a century.

Bearing in mind the necessity of low-cost energy and rising population with increasing per capita energy use, Putnam (31) sees the critical dates for the United States emerging approximately as follows:

1. Peak production of all United States coal may be reached before 1990.
2. Peak production of oil and gas sometime around 1961
3. New low-cost sources of energy should be on hand by 1975 or earlier if the risk of seriously increased unit costs of energy in the United States is to be avoided.

On the other hand, in the southwestern United States the cheapest source of high temperature heat energy has been found for many years in the burning of natural gas.

The construction of transcontinental pipelines since World War II has tapped immense markets in distant states where much higher prices can be charged. Also, availability of cheap heat has attracted much new industry into the natural gas producing regions. These factors have greatly increased the demand for natural gas and have caused its price to go up. For example, the selling price of natural gas at the wells in Texas has more than doubled in three years and is still rising rapidly (32). Hence, reduction in the future cost of water can not be expected for a fossil-fueled boiler plant designed to produce potable water from the ocean.

For these two main reasons, it is not practical to use conventional fuels for converting sea water to potable water.

Combination With Other Plants

The costs for sea water distillation could be reduced by utilizing waste heat from electric generating stations.

In some medium-size towns, the municipal electric plant burns diesel fuel and the exhaust gases are thrown away at a rather high temperature. In this case, some useful energy is going to waste, but only a moderate amount of the water can be produced from combination with such a power plant. Here, the comparison analysis is based on a very large plant (say fifty million gallons per day) to serve large population areas. The people associated with the largest existing electric generating stations believe that any saving made in the cost of heat supplied to the sea water will actually be canceled out because the electricity produced in this plant will be more expensive than that produced by a plant designed for the most efficient output of electric power (32).

2. Nuclear Energy

Nuclear material (uranium and thorium) is a major and largely untapped source of energy. Economically recoverable world sources of uranium and thorium are presently estimated to be 25 X 10^6 and 10^6 tons, respectively. These would yield an energy input of 575 X 10^{18} Btu (30). Then, the potential supply of energy in economically recoverable uranium and thorium is more than twenty times greater than that from fossil fuels. The known reserved of uranium and thorium throughout the world are sufficient to supply the necessary energy for some five hundred years. Further, there is a tremendous quantity of uranium and thorium in deposits of too low a grade to be usable now. For example, the average granite contains about four grams of uranium per ton. If this could be extracted in some economical fashion and used in a nuclear-power reactor, each ton of granite would then produce as much energy as fifty tons of coal (30).

At present it will be possible to produce heat or power economically at quite large installations. Thus, it is clear that nuclear energy is one of the most sufficient sources of energy for use in large sea water conversion plants.

3. Solar Energy

Another major and largely untapped source of energy is sunlight. About 3200 X 10^{18} Btu of solar energy reaches the earth's surface per year. This amounts to about thirty two thousand times as much energy as the entire human race is currently using. But there are some serious shortcomings to solar energy which inhibits its full utilization.

a. Solar energy reaches the earth in the form of electromagnetic radiation. Visible light accounts for nearly half; a very small amount is in the invisible ultraviolet end, and the remaining one-half is in the heat or infra-red rays.

b. The sun's energy is available only intermittently. At night and under conditions of cloudiness the available energy falls to about zero. Thus, there is the problem of storage to make available a source of energy that can be tapped continuously.

c. The energy is at a low potential. The sun's surface has a temperature of about 9900°F (5500°C), but it is 93 X 10^6 miles away. The heat input to the earth from the sun at the outer edge of the atmosphere is about two small calories per square centimeter per minute. On the average, only about two-thirds of that reaches the surface of the earth because of absorption by the atmosphere (30). This energy is just about enough to keep mankind comfortable on a warm summer day. It does not have enough power to operate a steam engine. Namely, the sun's radiation as ordinarily received is not hot enough to be of much technical use. It must be focused by a lens or mirror so that the light from a large area is brought to bear on a small spot resulting in high temperatures. However, all attempts so far to utilize focused high-temperature solar heat have run into such large equipment costs for mirrors, boilers, etc., that it becomes more expensive than other energy sources (32). Hence, one of the basic problems in the use of solar energy is the devising of ways and means of reconcentrating it.

d. Collectors of solar energy have to be large. It requires about one acre for five thousand gallons per day (32). That is, in order to produce a potable-water output of ten million gallons per day, about two thousand acres (about three square miles) of actual area will be needed.

e. It cannot be transported cheaply very far from the collection point.

f. Finally, another problem particular to arid regions deals with the havoc which may be wrought by sand and dust storms on miles of plastics exposed near the ground. Flying particles will cover the plastics with minute scratches that greatly reduces their transparency (32). It is also hard to find plastics which do not discolor under continued exposure to sunlight. Discolored plastics reduce the amount ot energy available from sunlight.

In short, less reduction in the future cost of water can be projected for a fossil-fueled boiled plant designed to produce water than for a nuclear steam generator to produce water because of the assumption that fossil fuels will continue to increase in price.

Solar energy seems to be best suited for use in areas of low energy demand, not in large sea water conversion plants.

Consequently, by all present indications, nuclear energy will be best suited to large sea water conversion plants.

Determination of the Size of the Unit

Determination of the size of the unit basically depends on design variables and heat transfer coefficient.

1. Design Variables

There are three design variables in the optimization of large-capacity plants. These variables are the terminal temperature difference (TTD), number of stages, and performance ratio.

1a. Terminal Temperature Differences (TTD)

The most important design variable is the stage terminal temperature difference in the optimization of the large-scale flash distillation system because this factor has the strongest influence on the condensor surface required in the evaporators and on the heat economy of the unit.

Figure 5 illustrated the relative water cost as a function of TTD

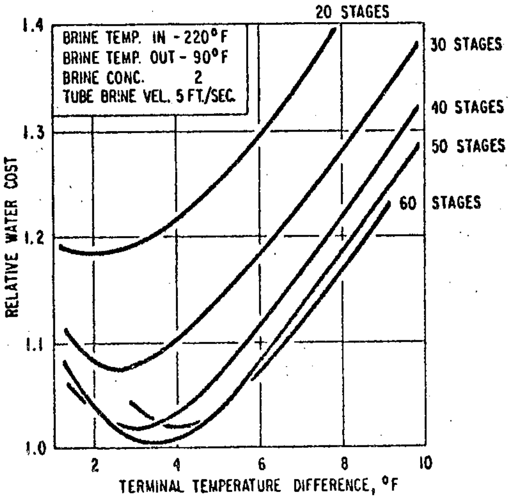

Figure 5 Relative Water Cost as a Function of TTD For Several Numbers of Stages (28)

1b. Number of Stages

The number of stages depends on the over-all temperature difference between the incoming sea water to the first stage and the blowdown to the ocean.

Theoretically, for a given TTD (Terminal Temperature Difference) the maximum number of stages can vary from one to infinity, but in practice this is not possible. As can be seen in Figure 6, for a brine temperature of 220°F, condenser tube velocity of five feet per second, blowdown temperature of 90°F, and brine concentration of twice sea water, a minimum water cost is obtained with a fifty stage plant operating with a terminal temperature difference of 4°F. Brice and Townsend's (28) studies show that the optimum number of stages for a flash distillation system is fifty two.

1c. Performance Ratio (Heat Economy)

Performance ratio is the pounds of water produced per pound of steam condensed.

The relation of performance ratio, terminal temperature difference, and number of stages is illustrated in Figure 6 (28).

2. Heat Transfer Coefficient

While determining the size of the unit, the heat transfer rate across the heating tubes between the condensing steam and sea water is one of the most important factors because heat transfer rate determines the size and thus the cost of the equipment in which heat is transfered.

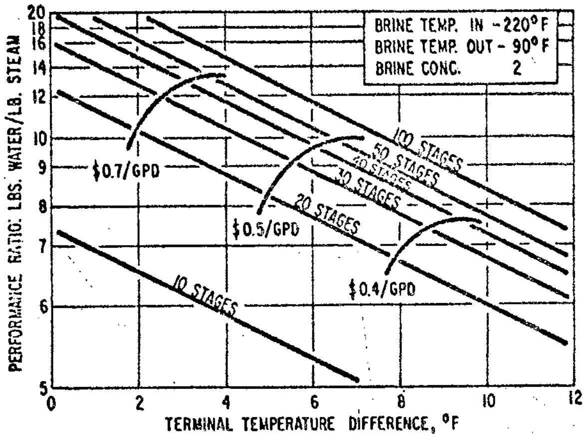

Figure 6 Relation of Design Variables (28)

The heat transfer coefficient of a uniform material is the thermal conductivity (Btu $ft^{-2}(F/in.^{-1})$ hr^{-1} divided by the thickness of the material. Thus, if the heat transfer coefficient is larger, a faster heat transfer is obtained and a smaller unit is needed to convert a given amount of sea water to potable water.

In the flash distillation process, scale formation on the tube material decreases the thermal conductivity of the material because the thermal conductivity of the scale is much smaller than the thermal conductivity of the material itself. However, this reduction in the rate of heat transfer in the tubes can be increased by increasing the velocity of the sea water up to the critical flow velocity. In this case it is necessary to be careful because if the critical flow velocity is exceeded, the protective film layers on the metals are eroded away.

Economic Comparisons

1. Desalted Water Cost

Water cost basically depends on the energy sources which are used in the heaters of the conversion plants.

1a. Product Water of Multistage Flash Evaporation Using Fossil Fuels

Using a method of figuring costs based on the OSW (Office of Saline Water) standardized procedure, S. F. Mulford's (25) cost estimation is between 65¢ and $1 per 1000 gallons in a 10 MGD plant. On a 0.1 MGD plant, the cost increases up to 75¢ to $1.15 per 1000 gallon of product water.

Mulford (25) also states that it can be reduced to 70¢ per 1000 gallons by using waste heat from some processes, such as the production of sulphurus and sulphuric acids from sulphur, by burning waste fuel which is the combustible products of a steam-electric power plant at higher than normal pressure.

However, at the present time, fossil fuels are the only applied source for large operations.

1b. Product Water of Multistage Flash Evaporation Using Nuclear Energy

D. B. Brice and C. R. Townsend's (28) studies show that a fifty two stage evaporator is the optimum multistage flash sea water conversion plant that can be combined with a three hundred seventy thermal megawatt (tmw) nuclear steam generator. Its nominal capacity would be fifty million gallons per day (MGD). In this plant, the estimated cost of potable water will be between 38¢ and 42¢ per 1000 gallons.

If the extent of improvements in heat transfer coefficients, in operation at higher temperatures as the result of improvements in scale control, in the possibility of using less expensive construction materials, and in decreasing the cost of steam in a nuclear steam generator is obtained within the next decade, the water cost can be reduced from the present level of about 38¢ per 1000 gallons to the range of 24¢ to 31¢ (28).

1c. Product Water of Multistage Flash Evaporation Utilizing Solar Energy

In this process, the estimated water cost is about $1.10 per 1000 gallons (29).

2. Present Domestic Water Production Cost

To compare the present and prospective production costs of desalted water with domestic water, it is necessary to review the usual costs of water production by municipalities.

Generally, municipal costs of water production rarely exceeds twenty five cents per one thousand gallons in the United States. Potable water production costs average three to twenty cents per one thousand gallons in the Los Angeles area. In the Baltimore area, the production cost of municipal water is about ten cents per one thousand gallons excluding filtration and distribution costs. In some places, the actual cost of potable water is about twenty cents per one thousand gallons including all aqueduct costs but excluding treatment (33).

Loebel (34) states:

> Surburban rates in Milwaukee, Norfolk, Oakland, and Oklahoma City range from 33 cents to 70 cents per thousand gallons, and these rates are going up. Much higher costs are experienced in suburban areas and towns.

In fact, these last costs include the costs of distribution and production. If twenty cents for storage and distribution is subtracted from these costs, municipal water production costs will be about thirteen cents to fifty cents per one thousand gallons in these suburban areas (34).

CHAPTER VII

SUMMARY AND CONCLUSION

The water problem is going to be a very important subject in the United States. By the year 2000, the population of the United States will have doubled. At the same time, the standard of living and national consumption of potable water will have risen along with an accompanying increase of industrial and agricultural activities. At the present time the nation requires more than three hundred billion gallons of water per day. In twenty years the requirement will be about six hundred billion gallons a day. There is a serious question as to whether that much can be made available readily from conventional potable water resources. Re-use, recharging, pollution correction, and conservation of water will solve the problem partially for a limited time, but not completely or forever.

The experience of the Department of the Interior over the past years has revealed the basic fact that the water problem touches all states of the United States. This problem varies from area to area and ranges from shortage to excess. Regardless of cause, as a nation the United States can no longer regard with indifference the increasing imbalance between the supply and demand for water by year.

In 1957, a study conducted by the United States Geological Survey revealed that in more than one thousand cities and communities, representing one-seventh of the nation's entire population, water shortages of varying degrees required their citizens to endure restricted use of water.

At the present time most water is inexpensive, but water is used in such tremendous quantities that it requires vast sums of money to provide the facilities to collect it and put it to beneficial use wherever it is needed. Water supplies nearest the point of demand were the first to be developed. When these sources becaome inadequate to meet growing demands, cities are forced to reach considerable distances to tap additional sources of supply at sites more expensive to develop.

This complex problem of providing adequate supplies of water is not limited to a few hot and arid areas of the South and Southwest, but also embraces regions in the humid East.

Thus, it is inevitable that new sources of potable water must be found. One answer to the growing problem is to tap the practically inexhaustible supplies of the oceans and the large brackish water reserves of inland areas. The remaining problem is how to get potable water from these sources at costs low enough for widespread use. The Department of the Interior through the Office of Saline Water is attempting to answer that question. A research and development program to find economical methods of producing potable water from sea and brackish waters was initiated in 1952, when Congress passed the Saline Water Act. Thus, the demonstration plant program has supplied much useful information about saline water conversion and captured the interest and imagination of the nation and the world.

Among the conventional sea water conversion processes the multistage flash distillation process is the most promising method because of cheaper construction and operation and higher average capacity.

In multistage flash distillation process, sea water is progressively heated and the introduced into a large chamber where pressure just below the boiling point of the hot brine is maintained. Water under low pressure will boil at relatively lower temperatures. Thus, when the brine enters this chamber, the reduced pressure immediately causes part of the water to flash or boil into vapor. The remaining brine is passed through a series of similar chambers at successively lower pressures where the flash process is repeated at progressively lower temperatures. The progressive heating of the sea-water feed is done by piping the incoming sea water through the flash chambers starting at the low temperature end. In each chamber the flashed steam condenses as it gives up its latent heat to the sea water. The warmer the water and the greater the reduction in pressure, the greater will be the evaporation. Thus, the condensed vapor is the product water. Final heating of the sea water before entering the first flash chamber takes place in a sea-water heater. The used energy sources in the heaters can be fossil fuels; waste heat, fuel or steam from various industrial operations; nuclear energy and/or solar energy, whichever is sufficient.

After fuel costs and capital costs, the important costs are those of maintenance and operation and in this regard the problem of scale and corrosion control have an important effect. The deposition of scale results from local supersaturation of a solution. Calcium sulfate may reach supersaturation through more temperature changes and thus produces scale on surfaces where liquid heating is taking place. Calcium carbonate and magnesium hydroxide may reach supersaturation slowly because of evaporation, heating, or the change of pH caused by gas evolution. Thus, the rate of scale depostion is related to the rate of evaporation, the pH of the feed water, the temperature, the average brine concentration, and the rate of brine circulation over the evaporating surface.

Scale can be prevented by contact stabilization, seed recycling, and the use of additives, the control of pH, and ion-exchange resins.

For economy in construction and operation of saline water conversion plants, particular attention must be paid to corrosion factors and metals to be used in the units. If the steel is protected by the use of coatings or is given cathodic protection, it can be used in many applications. If it does not conflict with other design factors, incoming sea water should be deaerated to control steel corrosion.

A large number of copper-base and nickel-base alloys have been used in sea water service successfully. Hastelloy C, Monel, titanium are very expensive but available for extremely corrosive situations.

Chlorination to residual of 0.5 ppm is widely used to prevent fouling of the monel or bronze in the screens, pipes, etc., but if the chlorination is not carefully controlled to low residual, it may increase the corrosion of metallic surfaces.

According to the saline-water conversion costs which are calculated by the Office of Saline Water in accordance with a rigid standard procedure which gives recognition to such items as engineering, maintenance and operation, depreciation, insurance, taxes, total plant investment, and amortization, cost is approximately $1.10 per 1000 gallons in a multistage flash evaporation plant which utilizes solar energy. It is about 65¢ to $1 per 1000 gallon in a 10 MGD size plant which uses fossil fuels, and the estimated cost of water is about 38¢ to 42¢ per 1000 gallons in a 50 MGD (52 stages) plant which uses nuclear energy.

These figures are above domestic water rates which are generally under 25¢. By 1972, the cost of desalted water can be reduced from the present level to the range of 24¢ to 31¢ if the extent of improvements that can be made in the next decade in heat transfer coefficients, in operation at higher temperatures as the result of improvements in scale prevention, and the possibility of using less expensive construction materials is obtained.

Thus, conversion costs are being reduced, but costs of potable water from natural sources are rising. In a number of places throughout the world, as in the Persian Gulf area and Aruba in the Caribbean, many millions of gallons of potable water for industrial and domestic uses are being obtained from the ocean every day. Thus, in the future, additional supplies of potable water will be available at prices low enough for widespread use.

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