UNITED STATES
DEPARTMENT OF THE INTERIOR

CORROSION OF METALS IN SEA WATER

OFFICE OF SALINE WATER
RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 46

For sale by the U.S. Department of Commerce, Business and Defense Services Administration,
Office of Technical Services, Washington 25, D. C.

UNITED STATES
DEPARTMENT OF THE INTERIOR

FRED A. SEATON, SECRETARY

FRED G. AANDAHL, ASSISTANT SECRETARY
FOR WATER AND POWER DEVELOPMENT

RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 46

CORROSION OF METALS IN SEA WATER

BY
Frederick W. Fink
BATTELLE MEMORIAL INSTITUTE
Columbus, Ohio

FOR

OFFICE OF SALINE WATER

A. L. MILLER, M.D., DIRECTOR

W. Sherman Gillam, Chief, Division of Research

E. A. Haglund, Physical Chemist

December 1960

FOREWORD

This is the forty-sixth of a series of reports designed to present accounts of progress on saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea or other saline water.

Except for minor editing, the data herein are as contained in the report submitted by Battelle Memorial Institute under Contract No. 14-01-001-182. The data and conclusions given in this report are essentially those of the Contractor and are not necessarily endorsed by the Department of the Interior

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
CORROSIVITY OF SALINE WATER.	2
The Nature of Corrosion	2
Corrosive Ions in Sea Water	3
Conductance and Salt Concentration.	4
Oxygen and Temperature.	4
Crevice and Pitting Attack.	11
Velocity.	16
Heat Transfer	16
Stress.	16
Galvanic Couples.	18
PROBLEMS ASSOCIATED WITH HEATING SEA WATER	18
PERFORMANCE OF METALS IN SALINE WATER.	22
Steel	22
Cast Iron	26
Wrought Iron.	26
Aluminum and Its Alloys	27
Copper.	28
Brasses and Bronzes	29
Cupro Nickels	31
Monel	34
Stainless Steels.	34
Titanium.	35
Special Alloys.	37
DISCUSSION, CONCLUSIONS, AND RECOMMENDATIONS	42
ACKNOWLEDGMENTS.	44
REFERENCES	46
BIBLIOGRAPHY	50

CORROSION OF METALS IN SEA WATER

by Frederick W. Fink

INTRODUCTION

Marine problems are of national importance. At the present time, the U. S. Government is stimulating interest in marine activities in many areas. Examples of problems receiving attention are shore erosion, harbor protection, sea-water intrusion of the fresh-water table, navigation, underwater transportation, oceanographic exploration, hydrofoil ships, nuclear-powered vessels, iceberg movements, seafood, pollution control, etc. One program which has gained national and international interest is that of the Office of Saline Water to develop methods of converting sea or brackish water to fresh water.

For highly saline waters, such as sea water and brines from salt wells, many today favor distillation processes as the most economical method of producing potable water. Processes which can make use of waste heat (often available at shore-based steam plants, at refineries, and at chemical plants) are particularly attractive.

Some of the thermal processes under investigation by the Office of Saline Water include conventional distillation, distillation using vapor-compression multi-stage flash evaporators, distillation with vapor reheat, distillation without the use of metallic heating surfaces, vapor compression using forced circulation, etc.

This increased activity in the utilization of sea water involves the use of a variety of equipment and focuses attention on the need for knowledge of the behavior of metals and other materials in marine service.

Before choosing metals or other materials of construction for distillation plants handling sea water, many factors have to be considered. Among these are the initial cost of materials, the efficiency of the materials in the intended design, the lifetime of these materials as influenced by corrosion and by other factors, and the amount of servicing required to keep the intended design operational.

The chemistry of sea water is complex and much more information needs to be developed. Many materials behave unpredictably in sea water, particularly when incorporated into actual designs. This report is concerned primarily with the corrosion behavior of metals and other materials in sea water, in diluted sea water, and in brackish waters. Corrosion and scaling problems as a result of heating saline waters are given particular attention.

Information presented was obtained from (1) a review of pertinent corrosion literature, (2) consultations with experts in

the field of corrosion, (3) reports of marine corrosion research, presented at meetings of The Sea Horse Institute (directed by The International Nickel Company) at Wrightsville Beach, North Carolina, (4) manufacturers' technical publications, and (5) Battelle's own marine experience.

CORROSIVITY OF SALINE WATER

The Nature of Corrosion

Aqueous corrosion is known to be electrochemical in nature. A simplified concept of the corrosion mechanism proposes anodic and cathodic areas on the metal surfaces. At the anodes, the atoms of the metal release electrons, become positively charged ions, and enter the solution. The electrons pass through the metal to the cathodic area where they discharge a positive ion, often hydrogen. Thus the process involves a flow of electrons through the metal and a flow of charged ions through the solution or electrolyte. The electrical currents which cause corrosion are modified by polarization at the electrodes, by the formation of passivating films, by scale formation, by local variations in concentration of soluble materials in the electrolyte, and by a number of other complicating effects.

The following paragraphs outline the major factors which influence corrosion reactions. Since their inter-relationship is quite complicated, it can be seen that no use of them can be considered solely in analyzing a given situation. However, they are discussed individually for clarity.

Natural sea water differs from synthetic sea water, from the corrosion standpoint, mainly because of the effects of the living organisms present in the ocean. For this reason, it is most desirable to use natural sea water in conducting corrosion experiments at normal temperatures. However, since the organisms are killed by heat in the distillation process, their effect is not important in corrosion at elevated temperatures.

Much useful information has been developed from work done in the laboratory with saline solutions made up to simulate sea water with respect to its inorganic constituents. Hache⁽¹⁾ has, for example, carried out some very interesting experiments concerning the corrosion of iron in sodium chloride solutions. Such experiments provide information which has a direct and useful bearing on natural sea-water corrosion problems.

Corrosive Ions in Sea Water

The chloride ion is probably the most deleterious ionic constituent occurring in sea water in large quantities. Its corrosive nature comes from the fact that it readily penetrates passive protective films and thus enhances the corrosion reactions.

In addition to chloride ions, the anions found to the greatest extent in sea water are sulfate, bromide, fluoride, and bicarbonate. Lyman and Abel⁽²⁾ list a typical analysis for the major constituents of a sample of North Pacific Ocean water. Their data, tabulated below, also include the major cations present.

<u>Cations</u>	<u>per cent</u>	<u>Anions</u>	<u>per cent</u>
Na ⁺	1.056	Cl ⁻	1.898
Mg ⁺⁺	0.127	SO ₄ ⁻⁻	0.265
Ca ⁺⁺	0.040	HCO ₃ ⁻	0.014
K ⁺	0.038	Br ⁻	0.0065
Sr ⁺⁺	0.001	F ⁻	0.0001
Sum:	1.262	Sum:	2.184

H₃BO₃(undissociated) .003

Grand Total: 3.449 per cent

Natural processes, operating both at the surface and at great depths, result in a continuous circulation of ocean water, so that the relative proportions of dissolved salts are virtually the same everywhere, although the total salt content (salinity) may show appreciable variations with geography.

The halogen ions, other than chloride, are present only in small amounts, and their corrosive effects in sea water are probably masked by the very high chloride content.

Other corrosion experience would suggest that the sulfate also contributes much less to the corrosion by sea water than the chloride.

The presence of bicarbonate ions in water can help promote corrosion attack on many metals.

It should be mentioned that the pH of sea water normally ranges from 7.5 to 8.2, indicating a slight excess of hydroxyl ions.

Conductance and Salt Concentration

Since corrosion is dependent on electrolytic processes, it is greatly influenced by the conductivity of the solution. Sea water is a good electrolyte, so it is not surprising that it is corrosive. Figure 1(3a) shows that the resistivity of sea water is relatively low at normal temperatures. However, it can also be seen that as the water is diluted (as might occur near rivers), the resistivity is markedly increased. Accordingly, the corrosion might be expected to be somewhat less in the vicinity of rivers. Actually, the effect of varying the salinity is inter-related with some of the other variables, as far as corrosion is concerned. For example, concentrating sea water (as in a multiple-effect distillation process) reduces the oxygen solubility. For steel and for the temperatures involved in a typical process, it is found that the rate of attack becomes less as the brine becomes more concentrated. The role of oxygen is discussed more completely later.

It is interesting to note that resistivity for sea water in the normal range of salinity is not greatly affected by temperature (see the lower curve in Figure 2). On the other hand, a solution of only 1.84 parts/thousand (0/00) salinity decreases almost one half in resistivity as the temperature is increased from 32 to 77 F.

Oxygen and Temperature

Of the environmental factors, oxygen ranks high in degree of importance. It affects corrosion reactions by depolarizing cathodic areas, by oxidizing ferrous compounds, and by changing cell potentials.

An increase in temperature normally can be expected to speed a chemical reaction so that corrosion could be expected to accelerate as the temperature is increased. Since oxygen content and temperature are related, the individual effect of each is difficult to differentiate.

According to Speller⁽⁴⁾, when steel is heated in ordinary water at a constant oxygen content the corrosion rate increases with temperature in the range 100 to 300 F. If the oxygen is allowed to reach its normal saturation level, the corrosion reaches a maximum at about 175 F and decreases with increasing temperature above that point because of the decrease in oxygen solubility. The oxygen level in sea water can vary from low to relatively high concentrations (0 to 12 ppm)^(3b). For example, photosynthesis in green plants in the water tends to increase the amount of oxygen in solution. Wave action and spray formation tends to maintain the water near the surface approximately saturated with oxygen. On the other hand, the activities of bacteria in polluted water may result in lower oxygen content and an increase in carbon dioxide and, at the same time, cause the presence of hydrogen sulfide. The surface water at the tropics, because of the elevated temperature, may have only half as much oxygen present as for Arctic waters.

FIGURE 1. CHANGE IN RESISTIVITY WITH SALINITY AT 59 F

Adapted from Reference 3a

FIGURE 2. CHANGE IN RESISTIVITY WITH TEMPERATURE AND SALINITY FOR SEA WATER

No systematic investigation has been made correlating corrosion with the oxygen content of sea water. However, several research workers have reported results in this area for steel in salt solutions and the general conclusions can probably be applied to sea water.

The corrosion behavior of iron and the oxygen solubility as a function of the salinity of the solution at 75 F, as reported by Hache⁽¹⁾, is illustrated in Figure 3. It is to be seen that sodium chloride does not affect the solubility of oxygen in water until a concentration of almost 10 g/liter (about 1 per cent) is reached. From that point on, the oxygen solubility decreases with increased salt content and approaches 1 ppm at 360 g NaCl/liter. The curves also show that a corresponding decrease in corrosion rate follows the decrease in oxygen content.

The oxygen solubility in chloride solutions and the corresponding corrosion rate of a steel coupon as studied in another laboratory⁽⁵⁾ are shown in Figure 4. It can be seen, as was just pointed out, that the dissolved oxygen content is significantly decreased by an increase in salinity. In general, the values are slightly lower than those presented in Figure 3.

The corrosion rate of steel (in this short-time test) reached a maximum in about 1 per cent of sodium chloride. This corresponds to the highest oxygen concentration studied. At higher salt contents, the reduced oxygen content of the solution resulted in a reduction in the rate of attack. This reduction varied directly with the oxygen content.

Figure 5 shows the effect of temperature on the corrosion of iron by air-saturated and partially deaerated solutions containing 30 g/liter of sodium chloride. As might be expected, the corrosion increased with an increase in temperature. At the lower temperature studied, the aerated solution contained about four times as much oxygen as the partially deaerated solution and was about three times as corrosive. At about 140 F in this open system, the oxygen contents were about the same and the corrosion rates were identical. A similar temperature dependence had been reported earlier by Palmaer⁽⁶⁾.

At ordinary temperatures, practical experience has shown that steel will resist saline waters if essentially all of the oxygen is removed. Not much quantitative information is available about the behavior of steel in saline waters at elevated temperatures free from oxygen. However, some related experience seems to be significant.

In certain oil-field secondary-recovery operations, brines (some containing the same salts as in sea water) are pumped to the surface and reintroduced at another point into the formation. Experience has shown that these brines, which may be at temperatures of 200 F or above, can be handled in steel equipment such as pumps, valves, piping, and other fittings. Satisfactory lifetime is experienced if no oxygen is allowed to mix with the brine solution in this closed system. Slight air leakage can be compensated for by using a chemical oxygen scavenger such as sodium sulfite. In some

FIGURE 3. VARIATION OF CORROSION OF IRON AS A FUNCTION OF THE SALINITY, $T = 75\text{ F}$
Adapted from Reference 1

FIGURE 4. CORROSION OF STEEL AND OXYGEN SOLUBILITY AT VARIOUS NaCl CONCENTRATIONS

Adapted from Reference 5

FIGURE 5. CORROSION OF IRON IN 3% NaCl SOLUTION SHOWING THE EFFECT OF TEMPERATURE AND AERATION

Adapted from Reference 1

cases, it is desirable to add a small amount of a corrosion inhibitor to the brine.

At The Sea Horse Institute, it has been observed that steel immersed in sea water at the 80 to 90 F summer temperatures corrodes at about 50 per cent faster rate than at the 40 to 45 F winter temperatures.

The effect of temperature on the corrosion of brass has been studied. For example, red brass and Naval brass are compared in a 10.8 per cent sodium chloride solution, see Figure 6⁽⁷⁾. Both materials show higher rates of attack with increase in temperature. The Naval brass (60Cu-39Zn-1Sn), which shows the highest rates of the two materials, is not presently considered a preferred metal of construction for saline waters. Although not given in the reference, one would expect dezincification attack on the Naval brass in heated chloride solutions.

Admiralty brass is a widely used metal in brackish water and sea water. It shows, in another experiment, greatly accelerated deposit attack as the temperature is increased (see Figure 7). A 3 per cent sodium chloride solution was used as the corrodent, and cotton wads were placed on the metal surface to simulate deposits.

It should be noted that the corrosion for the above metals is much different from that for steel in that there is no indication of a decrease in corrosion rate at elevated temperatures as oxygen is lost from solution.

Crevice and Pitting Attack

Perhaps the most common type of localized attack in sea water and in brackish water is pitting. Figure 8 gives an example of this severe form of corrosion. There are a variety of causes which promote pitting. Deposits of foreign matter may initiate pits. Steel, if covered with mill scale, may pit at breaks in the oxide coatings. Aluminum tends to pit at sites where heavy metal ions, such as copper, deposit and form local cathodes. Unhibited brasses may show a special form of local attack known as "plug-type dezincification"; this type of attack often is found under deposits of sand, cinders, or other obstructions. Localized corrosion of the metal surface often results from biofouling. For example, when a barnacle or mussel attaches itself to a plate of stainless steel in sea water, a differential aeration corrosion cell is formed. Intense local pitting results, which may lead to complete perforation in a relatively short time. In one case, a 0.75-inch-thick stainless steel plate was perforated beneath a barnacle base after immersion of 9 months in sea water.

FIGURE 6. CORROSION OF NAVAL AND RED BRASSES IN 10.8 PER CENT SODIUM CHLORIDE SOLUTION (249-DAY WATER-LINE TESTS)

Adopted from Reference 7

FIGURE 7. DEPOSIT CORROSION OF ADMIRALTY METAL IN 3 PER CENT SODIUM CHLORIDE SOLUTION

Adapted from Reference 7

19X

N-71539

**FIGURE 8. CROSS-SECTION AREA OF CONDENSER
TUBE SHOWING PITTING ATTACK**

Figure 9 illustrates how a differential aeration cell can be formed at crevices to which water and oxygen have restricted access.

Pitting sometimes has been found to be associated with the metallurgical factors or with the history of the fabrication of the metal. For example, tube-drawing lubricant residues on the metal surface may promote pitting attack on condenser tubes.

Each case of pitting attack usually requires special study to establish its cause. Both environmental factors and the surface condition of the metal surface can be involved in pitting. Usually, maintaining the flow of sea water within the recommended velocity range for the metal in question will reduce the tendency to pitting.

Marine fouling is likely to occur in all the oceans. In northern waters, fouling occurs only during the summer; in the tropics, it is practically continuous.

A variety of animals and plants, as well as colonies of micro-organisms, may deposit from natural sea water onto the metal surface. The life processes and decomposition products may contribute directly to attack on the metal. Fouling may obstruct flow in heat exchangers and pipes, leading to such corrosive effects as are caused by overheating or by impingement at local high-water velocities.

Some organisms enter a marine piping system in their larval stages, then anchor themselves to sites such as interior tube walls. If these larvae are allowed to grow, the local turbulence may result in severe corrosion. The organisms may be killed by flooding temporarily with fresh water, or by heating, or by use of toxic materials such as chlorine or sodium pentachlorophenol. Even when the organisms are killed, their decomposing bodies may clog the sea-water system and cause corrosion.

At velocities of 2 to 3 ft/second and above, metals are not apt to foul.

FIGURE 9. CONCENTRATION CELLS

Velocity

Oxygen-saturated sea water at the surface of the metal tends to increase the over-all corrosion reaction in most cases. However, in a few instances, oxygen is necessary to promote the formation of desired protective films. If a critical velocity of flowing sea water is exceeded, the protective film may be eroded away. For example, the inlet ends of condenser tubes are frequently attacked (see Figure 10). Jet tests have been devised for ranking the susceptibility of metals to such impingement attack. The maximum velocity for useful corrosion resistance is low for copper (2 to 3 ft/second); higher for aluminum, cupro nickels, and aluminum bronzes; relatively high for stainless steels and Hastelloy C; and highest for titanium (20 to 50 ft/second).

Cavitation is caused by the repeated pounding on the metal, resulting from the rapid collapse of vapor bubbles in the water. Where there is violent flow of the water, such as that of a ship propeller at high speeds, the pressure at some area on the metal surface may be reduced so that localized boiling forms bubbles of vapor. At another site, when these bubbles suddenly collapse, the resultant hammering may in time cause a layer at the surface to fail by repeated compression, allowing pieces of metal to flake off. The active metal exposed may, in turn, be rapidly attacked by exposure to the sea water. It has been found difficult to develop a laboratory test that will accurately simulate cavitation attack as it occurs in actual marine service.

Heat Transfer

With heat being transferred through the metal surface, there is a boundary film of sea water next to the metal surface which may be much hotter and, therefore, different in composition and behavior from the bulk solution. Scale, because of reduced solubility in this film, can be expected to deposit on the metal and interfere with the corrosion attack.

Stress

Some metals, particularly the stainless steels, are very susceptible to stress corrosion and corrosion fatigue in sea water. It is generally good practice to minimize surface tensile (residual or design) stresses in metals exposed to corrosive saline waters.

FIGURE 10. INLET IMPINGEMENT ATTACK DUE TO EXCESSIVE TURBULENCE

Galvanic Couples

When two metals of different potentials are galvanically coupled, the acceleration of the attack on the less noble metal of the two is observed frequently. It is well known that a small area of an anodic metal coupled to a large area of a second metal that is cathodic can be particularly dangerous. The reverse (namely, a small cathode coupled to an anode that is large in area), while not the most desirable situation, often proves satisfactory in service. A useful guide to help in predicting unfavorable combinations is the galvanic series of metals in sea water^(3c).

PROBLEMS ASSOCIATED WITH HEATING SEA WATER

As sea water is heated, a series of chemical changes take place which greatly alters its corrosivity to a metal such as steel. The discussion will first review briefly the scaling problem, then touch on other changes which affect corrosivity as sea water is heated.

When a heated metal surface is brought into contact with brackish water or with sea water, the calcium and magnesium compounds will tend to precipitate. As the mineral scale grows in thickness, it tends to insulate the metal from the water, thereby impeding the flow of heat. This, in turn, is often accompanied by an increase in the temperature of the metal. The marine distillation industry has been plagued for many years with the sea-water scaling problem, and many investigations have been conducted.

Research on the chemistry and the mechanism of scale formation has indicated that two conditions are important for the formation of sea-water scale:

1. The scale-forming constituents in the solution must be supersaturated. In the example just referred to, supersaturation tends to occur in the thin film of solution next to the surface of the hot metal. In laboratory demonstrations at Ann Arbor⁽⁸⁾, the W. L. Badger staff have shown that there is an induction period (sometimes of six or more hours) before the first scale nodule is precipitated from a supersaturated solution onto a cleaned copper surface.
2. Supersaturated constituents in solution need not have a metal surface for scale deposition. Suitably selected solids, suspended in solution, may also provide sites for nucleation of scale.

The formation and precipitation of the scaling deposits takes place primarily by the following simplified mechanism and is enhanced by the fact that the salts exhibit inverse solubility curves. First, it must be pointed out that the bicarbonate ion in the sea water is basically responsible for the low-temperature deposits (100 to 250 F). This is true because as the sea water is heated and evaporated, the bicarbonate ions break up into carbonate ions, water, and gaseous carbon dioxide. A certain amount of the carbon dioxide is continuously lost. A condition is soon reached on the heated surface where the solubility product for calcium carbonate is exceeded and a layer of this compound is formed. This reaction predominates in the temperature range of 140 to 180 F in an evaporator under dynamic conditions.

The second scaling constituent is formed because hydrolysis of the sodium carbonate in the sea water is continuously taking place. Heating promotes this reaction and thus an accumulation of sodium hydroxide or hydroxyl ions tends to occur. Soon there are sufficient hydroxyl ions present to combine with the magnesium ions already in solution and magnesium hydroxide is precipitated. Accordingly, heavy deposits of magnesium hydroxide are normally found at temperatures of 180 F and above. Figure 11 shows the relative amounts of magnesium hydroxide and calcium carbonate deposited at three temperatures⁽⁹⁾. It should be noted that a relatively constant amount of calcium sulfate was deposited at all temperatures.

When water temperatures (under pressure) of the order of 310 F to 325 F are reached, the scale becomes increasingly high in calcium sulfate because this material is less soluble at the elevated temperatures. Of the three types of deposit, the sulfate is the most difficult to remove. Until an effective scale treatment is developed for calcium sulfate, a maximum of about 300 F is suggested for sea-water distillation-plant designs.

Partridge and White⁽¹⁰⁾ studied calcium sulfate solubility in water. Apparently, hemihydrate is twice as soluble at about 290 F as anhydrite. As one increases the temperature of sea water, the scale is mainly gypsum at about 290 F, is hemihydrate at 315 F, and is anhydrite at about 330 F. Experience suggests that the gypsum is the least troublesome of the calcium sulfate scales to remove.

In a multi-effect evaporator, the sea water increases in salinity with each temperature increase. However, it has been found⁽⁸⁾ in the lower temperature ranges that calcium sulfate does not reach saturation until sea water has been concentrated several-fold. Thus, conditions can be found where distilled water can be produced and calcium sulfate deposition be held to a minimum.

Experiments have shown that adding acid or certain acid salts to the incoming sea water greatly reduces the tendency to form calcium carbonate scale and magnesium hydroxide scale. From a corrosion standpoint, it normally is desirable to have a protective thin film of scale form on the metal, especially if the scale is hard and impenetrable. Experience has shown that this mineral scale

FIGURE 11. SCALE COMPOSITION FROM BOILING SEA WATER

Adapted from Reference 9

affords considerable protection to metals, such as steel and cast iron, from the corrosive sea water.

The various methods for controlling scale formation from saline waters need to be examined from the corrosion viewpoint⁽¹¹⁾. These include such chemical treatments as (1) acid or acid salt additions to prevent calcium and magnesium compounds from forming, or (2) seeding to encourage the above compounds to form in solution away from the metal surfaces, or (3) the use of organic materials such as starch to cause a scale to form which is readily removed at scheduled intervals by mechanical means, such as thermal shock.

The addition of mineral acids (e.g., HCl) or of organic acids (e.g., citric) would be expected to be accompanied by an increase in the corrosivity of the saline water. An acid salt addition, such as ferric chloride⁽¹²⁾, or sodium bisulfate would also be expected to increase the corrosivity of sea water.

Seeding methods would not be expected to cause any marked increase in corrosion.

Since the early days of steam boilers, a variety of organic materials have been tried in boilers to prevent scale formation. In more recent years, these compounds also have been tried in sea water. Some examples include starches, tannins, sodium alginate⁽¹³⁾. This type of addition probably has little influence on the corrosion attack of the metal by hot sea water.

Two proprietary treatments were mentioned in discussions of the scaling problem; one is called "Hagevap"⁽¹⁴⁾. This treatment costs about 2.7 cents per 1000 gallons of product when used at 3.8-ppm feed. The Hagevap treatment has been used on a land-based submerged-tube evaporator operating in the Persian Gulf; it has prevented scale formation during a year of operation. The boiling temperature of the sea water is limited to a maximum of about 200 F.

The feedwater treatment that has been adopted at Morro Bay, California, consists of various concentrations of Nalco Starch D-1357⁽¹⁵⁾. For the past two years, the above starch treatment has been modified by adding Nalco 71NA antifoaming agent. These chemicals are mixed with fresh water and fed into the makeup line to the first-effect shell by means of a proportioning pump. The cost of this chemical treatment is 2.5 cents per 1000 gallons of distillate.

According to a short news release⁽¹⁶⁾, Dow Chemical Company (at Freeport) proposes to control calcium sulfate scale by partial ion-exchange softening.

PERFORMANCE OF METALS IN SALINE WATER

Steel

Compared to other metals, steel is one of the least expensive material of construction and is the basic material of construction for many sea-water plants. Even though steel may be attacked in sea-water service as a distillation unit, its low initial cost may result in lower over-all costs if good design and good corrosion-control practices are followed.

The rate of attack for steel under immersed conditions in clean sea water at ambient temperatures is fairly uniform and averages about 5 mils per year. General attack, when it occurs, continues at a fairly uniform rate even with an accumulation of corrosion products or marine growth.

Often, however, steel is subject to pitting attack by sea water. The pitting attack on bare steel is frequently reported to be about 10 to 15 mils per year. The presence of mill scale on the steel — especially when it covers a large portion of the exposed area — significantly increases the rate of pitting, and penetrations of about 20 mils per year, or more, can be expected. This is a result of the mill scale serving as large cathodes to the small, bare anodic areas. Pitting attack often tapers off with continued exposure.

A recent paper⁽¹⁷⁾ gives the results of an 8-year exposure of structural steels to tropical sea water. It was found that small additions of copper to mild steel did not alter the corrosion rate. Steels containing 2 and 5 per cent nickel were definitely inferior to mild steel on the basis of both general and local attack. Steels containing 3 and 5 per cent chromium were more resistant than mild steel for the first three years, but then corroded significantly more than mild steel during the remaining five years. The amount of pitting also was greater for the chrome steels during the latter period. For complete immersion, mild steel is preferred. In other experiments⁽¹⁸⁾ conducted in the polluted waters of San Diego Harbor, California, the rate of pitting for mild steel was found to be as high as 60 mils per year.

Welded copper-bearing steel, 5/8 inch thick, is used for the shells of the evaporators in operation at the Morro Bay station of the Pacific Gas and Electric Company. These evaporators have a 228 F steam supply, and the brine temperature to the first stage is 190 F. In the vapor phase, the steel evaporator shells are showing corrosion where condensation occurs. The evaporator condenser shells show most corrosion where the third-effect vapor line enters. Condensation with oxygen and carbon dioxide takes place at this point. It is estimated that at the baffle the wastage was 10 to 15 per cent in about five years. Where the steel is brine covered, it is holding up well.

In connection with the pilot-plant operation of the Long-Tube Vertical Evaporator at Wrightsville Beach(19), tubes and test spools were exposed to temperatures up to 250 F and in sea-water brines up to four times normal salinity. Test-spool results of three selected runs are reported as follows:

Test-Spool Metal	Corrosion Rate, ipy					
	First Run (30 Days)		Third Run (* Days)		Fourth Run (64 Days)	
	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Steel	.027	.021	.062	.030	.057	.044
Cast iron	.016	.030	.016	.031	.021	.032

* On third run, results were calculated for 17 days' evaporating time for the vapor samples, and on 28.4 days for the liquid samples.

The exposed tube samples, for the most part, showed lower rates of attack than did the identical materials tested as spools. This was explained by the fact that the test spools were exposed under relatively stagnant conditions. They conclude with the following:

"The moderate amount of corrosion observed in the steel samples and steel tubes was encouraging to the point that steel cannot be discarded as a material of construction for heating surfaces in the LTV-type evaporator system. From the accumulated data and observation of the materials of construction used in the evaporator and tube equipment, it may be concluded that steel can be used as a material for the construction of the major portions of the evaporators, pumps, piping, and perhaps heating equipment. . .

"As a broad, general conclusion, it is highly probable that steel will turn out to be the best all-around material for economical operation. . ."

The report also states: "Of the less-expensive non-ferrous alloys, admiralty metal, copper, aluminum brass, and 90-10 cupro-nickel are entirely satisfactory on the basis of corrosion results."

Methods of Protection

Protective Coatings. When heat transfer through the metal is not involved, a protective coating often is the best method of preventing steel corrosion. The choice of a protective coating must be guided, among other factors, by the maximum intended water temperature. Steel has been protected by widely different protective coatings and linings, such as epoxy tar, vinyl, and rubber. Normally, some temperatures between 160 and 250 F would be considered a good safe maximum for the best of the organic-type coatings. Metal linings, such as Monel, also are used to protect steel. Concrete has been used in some special cases.

A variety of protective coatings is available for steel in sea-water service. For such applications as hulls of ships, normal practice is to apply compatible antifouling paint over the corrosion-resistant primer-coating system. Figure 12-b shows panels which have resisted fouling for a year or more, compared with adjacent panels where the experimental coating does not prevent fouling.

Cathodic Protection. Steel can be protected by cathodic current, supplied either from sacrificial anodes or from an external direct-current source. The method is effective for completely immersed steel (that is, for surfaces on structures below the low-tide level). Current consumption can be greatly reduced by applying a suitable paint system to the steel before it is immersed in sea water (see Figure 12-a). Such a paint system should be alkali resistant.

Current demands tend to increase with increasing sea-water velocity and temperature. Cathodic protection does not appear to be used in applications with hot sea water. Information is needed to establish the potential value of cathodic protection in sea-water installations at temperatures above, say, 100 F.

Scale Formation. One method of controlling the corrosion of steel is to allow scale to form from the water.

On the Gulf Coast, a steel heat exchanger in refinery service held up well under the following conditions. The process streams, to be cooled, varied from 300 to 600 F. The brackish-water temperature was 180 F. The good results were attributed to a protective mineral scale. Another unit operating with 120 F water did not form scale, and the rate of corrosion was considerably higher.

For sea water or for brackish water, the thickness of the protective scale must be carefully controlled to prevent restrictions to water flow and to heat transfer. Normally, the water is treated to prevent scale formation and to increase the efficiency of heat transfer. One type of treatment is to lower the pH with acid or with an acid salt such as ferric chloride. This, in turn, will make the sea water more corrosive to the steel.

N-70108

(a) Effect of Cathodic Protection on Paint Systems

N-70109

(b) Antifouling Paint Studies

FIGURE 12. EXPERIMENTS AT BATTELLE'S DAYTONA BEACH MARINE STATION

Deaeration. F. C. Standiford⁽²⁰⁾ has stated that by the use of a deaerator to remove the oxygen in the sea water, it will be possible to use steel up to 250 F. Others believe that slightly lower temperatures (e.g., 220 F) will be the maximum serviceable temperature. This method is by far the most practical way of reducing seawater attack. After treating the incoming sea water in a deaerator, oxygen scavengers such as sodium sulfite or hydrazine⁽²¹⁾ may be used. The maximum temperature at which this combined treatment will provide effective reduction in the rate of corrosion to steel is not yet known.

Other. Recent British experience⁽²²⁾, using boiler water to which sea water had been added, suggests that corrosion resistance can be improved by first chromizing the boiler tubes. No pitting was observed on these tubes. Unfortunately, some of the chromized tubes showed failures such as splits on being expanded into the tube sheets. The British also found some evidence that the degree of pitting is decreased by increasing the copper content of seamless tubes to about 0.2 per cent.

Another observation by the British authors is the danger of corrosion of steel equipment used in saline waters during shut-down periods. During continuous operation, attended equipment can be better controlled than when left unattended during idle periods. If chloride-containing water is allowed to remain in a boiler, there is a high risk of pitting attack. There are many methods already worked out for the preservation of steel equipment during idle periods.

Cast Iron

Many years of service have been obtained from heavy-walled cast iron pipe and cast iron equipment in sea-water service. Initially, the iron phase in cast iron is readily attacked at rates similar to mild steel. Normally, the layer of graphite left with the corrosion product is dense and compact, and the corrosion tends to be stifled. However, if this residual layer is porous, further corrosion may be accelerated by the galvanic action between the graphite layer and the iron beneath. The attack then approaches a rate similar to that found for the pitting of mild steel.

Wrought Iron

Wrought iron has found considerable application in marine-based structures and in piping. While wrought iron, according to some sources, appears to be more resistant than mild steel to general and localized corrosion by sea water, there is no general acceptance of this material by operators of marine plants. Advantage is sometimes taken of its directional physical properties where corrosion resistance also is needed. It should be mentioned that for the same initial cost a much thicker wall can be purchased in a cast

iron or a steel pipe than for one of wrought iron. Until directly comparable engineering data are developed in the economic use of wrought iron versus steel or cast iron in sea-water plants, many experienced marine operators hesitate to specify wrought iron in place of other less-expensive ferrous materials.

It should be pointed out that an older form of wrought iron, as produced in England, contained slag layers. These layers, when suitably oriented, were found in some corrosion environments to prevent pitting attack from progressing deep into the metal. While this behavior accounts for the longer lifetime of the ancient form of the material, it does not follow (according to marine specialists) that the modern fibrous form of wrought iron will greatly outlast steel in identical sea-water service.

British wrought-iron boiler tubes⁽²³⁾ have given exceptionally long life in marine fire-tube boilers. These boilers use water to which sea water is intentionally added. A complex magnesium and calcium silicate scale is believed responsible for the long lifetime. The silicate is derived, in part, from the slag.

Aluminum and Its Alloys

In marine service, aluminum has already had considerable success in environments involving atmospheric exposure, such as the superstructure of ships of all sizes. It also is being used in structures and assemblies immersed in sea water.

For aluminum and its alloys, oxygen is found to be essential in sea water for good corrosion behavior. Apparently, without oxygen to repair breaks in the protective oxide film, the metal is attacked rapidly. Other variables which affect the performance of aluminum must be considered also. For example, aluminum alloys are susceptible to pitting. Often the pits are very deep; however, the corrosion usually slows down with time. Pitting can be caused by deposits and by heavy metal ions such as copper plating out from solution and forming local cathodes.

Pitting and localized attack can be minimized by cladding the aluminum alloy with the proper grade of aluminum or aluminum-zinc alloy. The objective is to select a cladding that is slightly anodic to the base metal in sea water. Experience has shown that the attack will not penetrate into the base metal until most of the cladding has been consumed by corrosion. It is of interest to note that the aluminum usually chosen for cladding is both more corrosion resistant and slightly anodic to the base alloy. The fact that a metal is more anodic than an adjacent one in the galvanic series for sea water does not necessarily imply it will corrode at a higher rate when exposed uncoupled.

Alloys such as 3003 (1.2Mn), 5056 (5Mg), or 6061 (1.0Si-0.6Si) are known to be more resistant to sea water than the copper-bearing alloys such as 2024 (4.3Cu).

Galvanic corrosion often is the cause of failure in aluminum alloy designs. Aluminum, for sea-water service, gives best results if it is not coupled to other metals.

Aluminum can be cathodically protected, but caution must be employed. If there is too much alkali developed as a result of too high a cathodic current, the aluminum will be attacked.

Aluminum can be employed in hot sea water as a resistant material of construction. Experiments by the U. S. Army, Engineering Research and Development Laboratories, and by investigators at other sites, indicate that, with proper corrosion-control practices, aluminum can be used for the construction of an entire plant to process sea water. The sea water entering the plant should be free of all metallic ions, especially copper or nickel. It is essential, in such a plant, that no copper-base alloys be used at all, and that galvanic couples to most other metals be avoided.

In an aluminum-constructed distillation unit, local attack may occur at crevices such as those formed by a flange with a gasket. Recommended practice is to place such joints in the vapor phase, where differential aeration cells will not be operative.

As with aluminum in sea water at ambient temperatures, best results are obtained if aluminum-clad alloy construction is used. There are reports of aluminum clad heat exchangers giving up to 10 years of service in sea water under favorable conditions.

Another example of the successful application of aluminum is in tankers. Steel-pipe heating coils, normally used at the bottom of oil compartments in ship tankers, suffer corrosion resulting from the alternating conveyance of sea water and crude oil of high sulfur content. In England, recent use has been made of aluminum-alloy heating coils. These are reported⁽²⁴⁾ to give equal or better results in all respects to a mild-steel steam system. Aluminum has higher rates of heat transfer and also there is a saving in weight and freedom from corrosion. The cost of the aluminum-alloy installation is said to be only slightly more than that for mild steel. It should be pointed out that aluminum is resistant to sulfur-contaminated crude as well as to sulfides and to sea water.

Copper

Experimentors studying distillation processes, in which a very low thermal gradient and good conductivity across the metal wall are required for success, would like to use copper^(25,26,27). Unfortunately, the corrosion resistance to sea water does not appear favorable. In the rotor type of still, for example, the high velocity of sea water over the copper surfaces needed for efficient heat transfer also tends to promote rapid attack. Protective sea scale cannot be permitted because the reduced conductivity would adversely affect the design criteria.

Ordinary copper is not recommended for sea-water plants if the water velocities are much greater than, say, 2 ft/second. It remains to be demonstrated whether copper can be employed in contact with completely deaerated sea water at much higher velocities.

Experiments using a copper rotor with completely deaerated and heated sea water will soon be in progress at the Richmond Marine Laboratory of the University of California. Staff members at this site believe that copper may be a useful material of construction for hot sea water under these carefully controlled conditions.

Brasses and Bronzes

There is a wide range of copper-base alloys that have given good service in sea water. Admiralty brass (70Cu-29Zn-1Sn) plus a small addition of arsenic, has found wide use as condenser tubes in marine-based plants using sea water for cooling purposes. While it is not so resistant as the cupro nickels, it often seems to be preferred because of the lower initial cost.

Another alloy that is widely used in cooling-water service is aluminum brass (76Cu-22Zn-2Al). The aluminum content improves the resistance to velocity and impingement. This alloy, however, seems to be more susceptible to pitting than some of the other copper alloys in stagnant sea water.

Silicon bronze is suitable for shell material, but not suitable for tube sheets subject to high velocity.

According to information received from the Tin Research Institute⁽²⁸⁾, tin-bronze condenser tubes (e.g., 90Cu-10Sn) are made to a limited extent in England. They are used only for special duty, namely, when the cooling water contains sufficient entrained sand and thus making erosion a serious cause of metal loss, or when the water is acid. Undoubtedly, their cost has restricted the wider use of these resistant alloys.

Research is in progress at the British Nonferrous Metals Research Association with brasses containing more than 4 per cent tin and with the zinc set at a maximum to provide for a single-phase alloy. In the laboratory test, these brasses have given good promise in polluted waters and in resisting impingement attack—the corrosion being uniform. These alloys were first mentioned publicly in a discussion by H. S. Campbell⁽²⁹⁾.

When either aluminum brass (76Cu-22Zn-2Al) or Admiralty brass (70Cu-29Zn-1Sn) are used as condenser tube materials, an inhibitor such as arsenic should be added to the metal to prevent dezincification. It is known that there is a greater tendency to dezincification with increased temperature.

In the tabulation below⁽⁷⁾, the inhibition of dezincification by arsenic in brasses is shown. These tests were conducted in corrosive well water at 176 F for 120 days. Although not given in

the reference, in all likelihood the water is contaminated with chlorides. It is predicted that tests in hot sea water would show a similar benefit for arsenic as an inhibitor.

<u>Alloy</u>	<u>Weight Loss, ipy</u>	<u>Depth of Dezincification, ipy</u>
Aluminum brass	.0024	0.46 ^(a)
Arsenical aluminum brass	.0024	Slight trace
Admiralty brass	.0030	0.15 ^(a)
Arsenical Admiralty brass	.0030	Trace

(a) Plug type.

The Standard Oil Company of New Jersey⁽³⁰⁾ has studied the problem of the effect of metal temperature on the rate of attack in sea water. In one experiment, Admiralty brass single-tube heat exchangers were made up and operated at metal temperatures up to 200 F. The incoming sea water was maintained at either 110 or 120 F. The experiment ran about 100 days. After the test, a comparison of the surface appearance of the Admiralty tubes was made by metallographic sectioning. Very little difference in the depth of attack was found with increase in temperature. There was a slight tendency for the surface roughness to increase with temperature.

Many refinery operators are of the opinion that corrosion failures of brass condenser tubes are more frequent during the hot season of the year. At some sites, warm-weather conditions coincide with longer production runs, higher plant through-put, higher salinity, higher cooling-water velocities, as well as warmer water supply for cooling purposes. In view of these variables, some corrosion specialists are not fully convinced that the greater frequency of failures in warm weather can be ascribed solely to temperature.

In condenser-tube service, if the water velocity is too low, air bubbles tend to form in the tubes as the water is being heated. These air (or gas) bubbles have been reported to initiate pitting. Once started, the pitting continues long after the bubbles disappear. This is just another example of the indirect effect of higher temperatures on corrosion.

Bruce⁽¹⁵⁾ reports that aluminum-brass tubes (1-inch OD, 16 BWG) are holding up well after five years in sea-water evaporator service in the Morro Bay, California, installation. These tubes are being used with rolled Naval brass tube sheets and with bronze floating-head covers.

Dual construction, using copper-base alloys in contact with stainless steel has been found unsatisfactory for sea-water service⁽³¹⁾. In this use, the copper provides a large cathode, which

greatly increases the rate of attack of anodic sites on the stainless steel.

Cupro Nickels

At the present time, most marine operators agree that the cupro nickels are among the most useful materials of construction for sea-water plants. Since World War II, the use of a 90Cu-10Ni alloy modified with about 1.5Fe has become well established. The lower nickel content results in a cost advantage over the 70Cu-30Ni alloy. Alloys containing 70Cu-30Ni or 80Cu-20Ni, each with added iron, are preferred by some designers to withstand more severe conditions. The cupro nickels are widely accepted as the best available alloys for condenser tubes.

For service in erosive conditions, a special copper-nickel alloy (30Ni-2Fe-2Mn) is useful and is normally preferred to bronze. In brackish waters, Admiralty brass is generally used if the total dissolved-solids content is below 2000 ppm. At higher dissolved-solids content, aluminum brass or the cupro nickels are favored. Cupro-nickel alloys are preferred to brasses in polluted waters. A useful survey of British practice is provided by P. T. Gilbert⁽³²⁾.

For service at higher temperatures, the copper-nickel alloys are much preferred over other copper base alloys.

Sea water, heated under pressure to 325 F, was allowed to contact three grades of cupro-nickel alloys for 54 days at a velocity of 0.5 ft/second. The results⁽³³⁾, shown below, indicate that these materials are resistant to sea water at this temperature.

Cupro-Nickel Alloy	Composition, per cent ^(a)					Depth of Corrosion, ipy
	Cu	Ni	Fe	Zn	Mn	
90-10	89.06	9.84	0.71	0.20	0.19	0.0010 ^(b)
90-10	87.85	10.07	1.7	(c)	0.24	0.0015 ^(b)
70-30	68.61	30.32	0.48	0	0.51	0.0006 ^(b)

(a) Method of determination not reported by supplier.

(b) No pitting.

(c) Not reported.

Dynamic corrosion tests at 550 F have been conducted by Lancaster⁽³⁴⁾ in natural sea water. Specimens were rotated at a peripheral velocity of 10 ft/second while under a bending stress of one-third the tensile strength of the material. In these studies, it was found that the copper-nickel alloys were unsatisfactory because of excessive weight losses from erosion.

Tests were conducted⁽³⁵⁾ at the U. S. Naval Engineering Experiment Station, Annapolis, Maryland, on the performance of materials in high-temperature sea water, as follows:

Flat specimens, 2 to 2-1/4 inch long by 5/8 inch wide, were prepared from stock, 1/8 and 1/16 inch thick, and placed in electrically heated pressure vessels lined with 18-8 stainless steel. The vessels were filled with 1800 ml sea water, and sealed after the air had been expelled.

The corrosion of eight specimens of 70-30 and 90-10 copper-nickel alloys was slight after 14 days in natural sea water at 450 F under pressure; the surface etching was visible only with the aid of a binocular microscope. Corrosion rates, calculated from the weight losses, were only 0.14 to 0.27 mils penetration per year.

Four specimens of 70-30 alloy containing 0.46Fe and two samples of 90-10 alloy containing 1.79Fe lost 0.27 to 0.29 mg/cm².

For handling hot sea water, there has been some favorable experience with cupro-nickel pumps.

Cupro-nickel tubes of 70-30 and tube sheets of 90-10 are holding up well in evaporator service at the Morro Bay plant, Unit No. 2⁽¹⁵⁾. This service, however, is not considered severe enough to justify the expense of using cupro nickel.

From the viewpoint of corrosion in hot saline water, a helpful article was written by Turnbull⁽³⁶⁾. Corrosion experiments were conducted in a four-effect evaporator. Experience has shown that 90-10 cupro-nickel heat exchanger tubes, at both high and low iron levels, and at velocities of 4 to 5 ft/second, failed in less than two years by corrosion in hot, neutral, sodium chloride brines. These brines contained sodium, calcium, and magnesium chlorides and suspended crystals of calcium sulfate and sodium chloride.

A plot of the results of copper and copper-nickel alloys is given in Figure 13. Between 100 and 180 F, there is a slight increase in the rate of attack. At the upper end of the temperature range, from 180 to 225 F, there is a tendency for the rates to increase more rapidly. Also of interest is the difference in rate of attack between copper and Monel. With alloys of increasing nickel content, there is a very significant tendency for improved resistance to corrosion.

FIGURE 13. CORROSION OF COPPER-NICKEL ALLOYS AFTER EXPOSURE TO NEUTRAL SALT BRINE FOR 185 DAYS IN A FOUR-EFFECT EVAPORATOR

Adapted from Reference 36

Monel

Extensive use has been found for Monel in handling sea water. It has given excellent service in heat exchangers, piping, sheathing to protect steel at the half-tide zone, valves, pump impellers, and fittings in general.

Monel shafts, such as the harder K Monel, are resistant to corrosion fatigue in sea-water service. Marine operators, in general, consider Monel to be one of the best all-around metals for handling sea water.

For distillation units and other hot sea-water applications, Monel can be expected to have a higher order of resistance than cupro nickels. For example, Monel has been used in fabricating distillation units. In one type⁽⁹⁾, a Monel heat exchanger "basket" can be made to flex in order that the sea-water scale will drop off, thus restoring thermal efficiency. This service is considered much too severe for most metals.

Limited studies have been conducted on Monel in natural sea water at temperatures of 350 and 690 F^(34, 37). Although some of these tests were of short duration, Monel showed a rather heavy deposit of corrosion products. In view of this, it would appear that temperatures of 350 F are beyond the useful range for Monel.

Stainless Steels

In special circumstances, under carefully controlled conditions, some grades of stainless steel have given good service in sea water. Most authorities, however, strongly recommend caution in the use of stainless steel for service in sea water.

In heat exchanger service, stainless steels can be used at much higher velocities than for most common metals. Nevertheless, there is the ever-present possibility that stress-corrosion cracking may take place. This becomes much more likely as the metal temperature is raised. Any site at which both high stress and high chloride concentrations occur are particularly prone to this type of failure.

Stainless steel also is susceptible to crevice corrosion and deposit attack. Differential aeration cells, formed between stagnant and well-aerated areas on the metal surface, may promote rapid attack.

In general, Type 316, which contains molybdenum, is more resistant to the initiation of pits. However, once a pit is started, the rate of penetration may be of the same order as for molybdenum-free grades.

Since the process side in a heat exchanger may demand stainless steel, as in the case of a marine-based chemical plant that

has been forced to use sea water for cooling purposes, it is necessary to consider measures for obtaining optimum service. First, the cooling water should be free from solids which could deposit on the tubes. Next, the velocity should not be allowed to drop much below 5 ft/second. Crevice areas and stagnant areas should be minimized or eliminated by design. Finally, residual and service stresses should be held to the lowest possible levels. Under such carefully controlled conditions, stainless steel could give good service.

Stainless steel pump impellers are giving excellent service in sea water. The same may be said for stainless steel ship propellers now in use on some coastal vessels. In all cases, it is essential that the stainless steel items not be left in stagnant sea water for long periods between runs.

Stainless steel generally withstands polluted sea water and polluted brackish water better than do the copper-base alloys. At a West Coast power plant, substituting an austenitic stainless screen for silicon-bronze trash racks has resulted in at least four times the service life. Normally, stainless steel screens are not recommended for use in sea water because of the crevices involved (where the wires cross each other). This alteration of the usual corrosion mechanism presumably is related to the hydrogen sulfide content of the polluted sea water and needs further study.

Titanium

Unlike other metals, titanium normally does not pit, is not susceptible to stress corrosion, is free from local corrosion under fouling organisms, is free from impingement and cavitation attack at velocities which attack copper-base alloys, and is not susceptible to sulfide attack in contaminated sea water. Experiments with water velocities at 20 to 50 ft/second show no attack on titanium.

Titanium and its alloys are said to be less susceptible to mineral scaling in sea water than most other metals. (The corrosion products on a metal, such as steel, probably help to anchor sea-scale deposits.) Even though the thermal conductivity is low, the over-all efficiency, taking full advantage of the very high velocities permitted, can be greater than presently used material in sea-water applications involving high rates of heat transfer.

Titanium cannot be coupled⁽³⁸⁾ to most other metals in sea water, because of the greatly increased rate of attack on the other metal in the system (see Figure 14). If the ratio of the "other metal" to titanium is 1:10, steel—instead of corroding at 5 mils per year—corrodes at the rate of 28.5 inches per year.

The effect is greatly reduced or eliminated if the ratio of the other metal to titanium is 10:1 (see right-hand side of Figure 14).

At extremely high sea-water temperatures, titanium shows little or no attack. A surface-protective film appears to be formed as indicated by discoloration. There is no indication of local attack

FIGURE 14. BEHAVIOR OF METAL-TO-TITANIUM GALVANIC COUPLES FOR 2500 HOURS IN AERATED SEA WATER

Adapted from Reference 38

such as pitting on titanium after exposure to sea water at temperatures of up to 690 F⁽³⁷⁾. On the basis of these data, it was concluded that titanium is the preferred material of construction for such extreme service conditions.

Special Alloys

Hastelloy C compares favorably with titanium in its resistance to attack in sea water at both low and high temperatures. Little or no attack has been observed at temperatures up to 690 F⁽³⁷⁾.

At the present time, Hastelloy C is being used by Freeport Sulfur at the hottest points in their system used to heat sea water to 325 F under pressure for the Frasch process. It is understood that service performance has been very satisfactory.

Inconel is another nickel-base alloy which exhibits good resistance to sea water. Sea-water fog tests on stressed specimens exposed over the temperature range 125 to 400 F have failed to indicate any susceptibility to stress cracking⁽³⁹⁾. Under similar conditions, Type 304 stainless steel rapidly cracked.

In other tests⁽³³⁾, Inconel has shown promise of being resistant to sea water at 550 F.

Tables 1 through 3 summarize the application and performance of metals in hot sea-water service.

TABLE 1. SELECTED MATERIALS FOR POSSIBLE SERVICE IN HOT SALINE WATERS

Material	Hot Salt Brine (a)		Hot Sea Water			
	(e.g., Evaporators)		(Dynamic Tests), Penetration Depth, ipy			
	Behavior (e)	Remarks	At 325 F (b) (54 Days)	At 350 F (c) (30 Days)	At 550 F (c) (15 Days)	At 690 F (d) (145 Hr)
Copper (f)	NF	Velocity and aeration increases attack	-	-	-	-
Admiralty Brass (f)	NF		-	-	-	-
Aluminum Brass (f)	NF		-	-	-	-
90Cu-10Ni-0.5Fe	-	For neutral or alkaline brines	0.0010	-	-	-
90Cu-10Ni-1.5Fe (f)	E		0.0015	0.121 (g)	NF	-
70Cu-30Ni-0.5Fe (f)	E		0.0006	0.019 (g)	NF	-
Nickel	E	Most favored	-	-	-	-
Monel (f)	E		-	0.031 (g)	-	.015
Inconel	G, P		-	0.00018 (h)	-	-
AISI 304	G	NF in stagnant conditions	-	0.103 (i)	NF	-
AISI 347	G		-	0.0001 (i)	NF	-
AISI 316	G		-	0.00005 (i)	NF	-
Carpenter 20	G	NF in stagnant	-	WG (i)	NF	-
Hastelloy C	E	All temps, and pH 2.5 to 12.0	-	WG, E	E	.0015
Titanium	-	Should be excellent	-	WG, E	E	WG, E
Aluminum	P, NF	Some alloys may be good	-	-	-	-
Cast Iron	G	Brine should be kept deaerated	-	-	-	-
Ni-Resist	G		-	-	-	-
Steel	G		-	-	-	-

Footnotes to Table 1:

- (a) Sodium chloride brine. See Reference 40; also some information taken from correspondence with specialists in leading salt companies.
- (b) See tabulation on page 31 of this report for details of the test.
- (c) See Reference 34.
- (d) See Reference 37.
- (e) Nomenclature: E = excellent, G = good, P = pitting attack, NF = not favored,
- = no information, WG = weight gain.
- (f) Brines with hydrogen sulfide present will attack these materials.
- (g) Considerable corrosion products.
- (h) Slight contact corrosion.
- (i) Susceptible to stress-corrosion cracking if test period is extended.

TABLE 2. MATERIALS USED IN HOT SEA-WATER COMPONENTS

Item	Material	Remarks
Centrifugal Pump	70Cu-30Ni-0.5Fe	Used for casing and impeller
Ditto	90Cu-10Ni-1.5Fe	Ditto
"	Monel	"
"	Carpenter 20	"
"	Bronze	Used in hot brackish water
"	Type 316 Stainless	Excellent for impeller
"	Type 316 Stainless	Shaft failed by stress corrosion
Valve	M Bronze ^(a)	Valve body must be insulated from steel piping; good at 190 F
<u>Evaporators, Heaters, and Other Heat Exchangers; Steel Shell; 190 F (Sea Water Plus Carbon Dioxide)</u>		
Tubing	76Cu-22Zn-2Al	Poor service
"	90Cu-10Al	Poor service; cracks found in tubing
"	Admiralty + As	Failed in 3-1/2 years
"	90Cu-10Ni-1.5Fe	Very good performance
Tubing ^(b)	76Cu-22Zn-2Al + As	Brines up to 220 F and 57,000 ppm chloride
Tubing Sheet ^(b)	Aluminum Bronze + Fe	
Shell	Steel	Good performance reported in some cases; sea scale protective
Shell	90Cu-10Ni-0.5Fe	Considered excellent; largely eliminates galvanic couple, as with steel shell

(a) Porosity in casting successfully corrected by impregnating with phenol-formaldehyde resin.

(b) Proposed construction.

TABLE 3. MATERIALS OF CONSTRUCTION, DISTILLATION UNITS
AT MORRO BAY, CALIFORNIA

Item	Material Used	
	Unit Number 1	Unit Number 2
Evaporators:		
Shell	Cu-bearing steel	Cu-bearing steel
First-effect tubes ^(a)	Al brass and As	70Cu-30Ni-0.5Fe
Floating head	Cast bronze SB 61	Cast bronze SB 61
Tube sheets	Rolled Naval brass	90Cu-10Ni-1.5Fe
Support plates	Rolled Naval brass	Rolled Naval brass
Vapor separator	Steel plate	Steel plate
Condensers:		
Shell	Steel plate	Steel plate
Water box and cover	Cast iron	Cast iron
Baffles	Steel plate	Rolled Naval brass
Tube sheets	Rolled Naval brass	Rolled Naval brass
Tube supports	Steel plate	Rolled Naval brass
Tubes ^(b)	Al brass and As	70Cu-30Ni
Hot well	Steel plate	Steel plate
Drain Coolers:		
Shell	Seamless steel pipe	Seamless steel pipe
Shell cover, channel	Cast iron	Cast bronze SB 61
Tube sheets	Rolled Naval brass	Rolled Naval brass
Baffles	Steel	Steel
Tubes	Al brass	Al brass

(a) 1-inch OD, 16 BWG.

(b) 0.75-inch OD, 18 BWG.

DISCUSSION, CONCLUSIONS, AND RECOMMENDATIONS

The selection of suitable metals to construct the plants is of prime importance to the success of the distillation programs of the Office of Saline Water.

For the corrosion of metals in sea water at elevated temperatures there is, unfortunately, a paucity of good experimental data. Even less information seems to be available on the actual performance of metals in hot sea-water service. Some of the same variables that affect corrosion at ordinary temperatures are believed to influence the corrosion behavior in heated saline waters.

Various examples have been given in natural and in salt water, indicating that the rate of attack is increased by raising the temperature.

The several types of attack associated with higher velocity (such as erosion-corrosion, impingement, and cavitation) probably also would operate in hot sea water, but not necessarily to the same degree. The chemical characteristics of the sea water or brackish water also must be studied in order to establish the effect of heating on the corrosion.

In general, higher temperatures are associated with more local attack such as pitting. If scale or deposits interfere with heat flow, local hot spots may develop. Bubbles of gas, forming at local sites, may promote corrosion pitting.

Slowly formed protective films on metal surfaces in contact with sea water at ambient temperatures may be quite different from those that occur in hot sea water.

In sea water, each metal and each type of environment must be considered individually. To isolate the effect of temperature, the sea water must be maintained in a state of equilibrium as it is heated. It will be necessary to treat it by chemical additions and to pressurize the system. For example, if the presence of the dissolved oxygen and carbon dioxide is desired in hot sea water for an experiment, the pressure of the system will have to be increased and an oxygen/carbon dioxide atmosphere provided. Otherwise, these gases will leave the solution as it is heated, reducing the corrosivity of the water to metals such as steel. As already explained, if the carbon dioxide leaves the solution, scale will precipitate, which, if formed on the metal, prevents corrosive attack.

Information in the report suggests that steel can be used economically in plants employing completely deaerated sea water or brackish water up to 220 to 250 F. It is possible, by a suitable chemical treatment combined with deaeration, that steel could be used at a somewhat higher range of temperatures.

Aluminum-clad aluminum alloys also show promise for hot sea water where it is not convenient nor desirable to employ deaeration. The upper limits for aluminum appear to be lower than for steel. More precise information is needed to establish how much oxygen is necessary to promote the formation and repair of the protective oxide film in hot sea water.

Copper is not considered as being satisfactory for hot sea-water service. However, if it can be demonstrated that corrosion resistance to saline waters is improved by complete deaeration, this may revive interest in the use of copper in distillation units using a high velocity of flow, such as the several types of rotating stills.

For copper alloys, the order of merit in hot sea water is not clearly established. The upper temperature limit needs to be established, for each of the main copper-base alloys, below which the alloy can be expected to have useful service life.

Metals such as Monel, Inconel, Hastelloy C, and titanium may have application for special components in a hot sea-water system, in spite of their moderately high cost. A design study of a high-capacity plant using sea water should be made to establish the economics of using these materials if the initial investment is amortized over, say, 30 years.

This study of available information has emphasized the fact that (1) corrosion data for saline waters are very widely scattered, (2) much of the information on hot sea water concerns scale control with little attention given to the corrosion problem, (3) basic information for metals in hot brackish water and sea water needs to be developed, particularly for carbon steel, copper, copper alloys, and aluminum.

It is indicated that three types of corrosion programs should be inaugurated to develop the information needed for efficient design and use of metals in sea-water plants, namely:

1. A basic research program to investigate the mechanism of corrosion for carbon steel, copper, aluminum, and a few selected alloys in heated saline water. The hot water would be controlled so that the individual corrosion effects of temperature, salinity, oxygen, velocity, pH, etc., could be established for each important metal. This research would have the objective of indicating the range of usefulness for each variable. It would guide the planning of engineering studies for a specific plant.
2. A coordinated program of corrosion testing in hot sea water. In this program steel, aluminum, copper alloys, etc., would be evaluated in hot sea water under conditions in which factors such as heat transfer, scaling, and velocity were controlled to slightly more severe conditions than those required in proposed service in new distillation plants. One objective of this program would be to obtain critically needed data to

assist designers in making (a) suitable corrosion allowance and (b) provision for corrosion control. This program would help in the planning and construction of distillation plants that are to last 20 years or longer.

3. The third corrosion program that would be helpful is to collect information now being developed at a variety of brackish and sea-water plants in many parts of the world and correlate the data. Actual service information, where proper records of inspections and evaluations are kept, is also of great value in the planning of new construction. Troublesome points, if recognized and understood from a study of present design failures, could be avoided or kept to a minimum.

ACKNOWLEDGMENTS

The author appreciates the assistance of his co-workers at Battelle in gathering material for this report, in particular C. L. Peterson, W. K. Boyd, and P. D. Miller for their contribution and J. C. Vargo for preparing the drawings.

Space and time, unfortunately, do not permit the author to mention all the numerous company representatives who kindly provided helpful literature and information. The author wishes to thank those personally visited, in the following list, for their assistance in discussing the problem.

<u>Company or Agency</u>	<u>Person(s) Contacted</u>
Aluminum Company of America New Kensington, Pennsylvania	Mr. Ralph L. Horst
American Chemical Society, Div. of Water and Waste Chemistry, Symposium on Saline Water Conversion	Dr. W. S. Gillam, Messrs. J. J. Strobel and E. A. Cadwallader
Arabian-American Oil Company New York City	Mr. Alex Allessandria
Cities Service Refining Corp ⁿ Lake Charles, Louisiana	Messrs. J. J. Picarazzi, George Barnes, Herbert A. Robinson, and Richard O. Norris
Dow Company Freeport, Texas	Messrs. W. D. Brooks, W. F. McIlhenny, V. B. Volkening, D. W. Pennington, E. Ludwig, D. A. Ballard, C. M. Shigley, S. Stoval, R. A. Freeman, and J. Hart
Freeport Sulfur New Orleans, Louisiana	Mr. B. A. Axelrad

Humble Oil Research Laboratory
Baytown, Texas

Maxim Marine Laboratory
Waterford, Connecticut

Office of Saline Water
Washington, D. C.

Pacific Gas & Electric Company
San Francisco, California

Sea Horse Institute
Wrightsville, Beach, N.C.

Shell Development Corporation
Emeryville, California

Southern California Edison Co.
Mandalay, California

Standard Oil Co. of California
Richmond, California

The Texas Company
Beacon, New York

Union Carbide Chemicals Company
Texas City, Texas

Union Research Center
Union Oil Co. of California
Brea, California

U. S. Army Engineers
Fort Belvoir, Virginia

U. S. Naval Engineering Experiment Station
Annapolis, Maryland

U. S. Navy Department
Bureau of Ships
Washington, D. C.

U. S. Steel Corporation
Monroeville, Pennsylvania

University of California
Sea Water Conversion Lab
Richmond, California

Messrs. E. Q. Camp, R. V. Commeaux,
Edward Winegartner, and M. A.
Moseman

Mr. Bruce M. Watson

Dr. W. S. Gillam and Mr. E. A.
Cadwallader

Messrs. V. F. Estcourt and Elmer
Johnson

Dr. T. P. May, Messrs. David
Anderson, Victor Taylor, William
Dawson, et al.

Dr. Aaron Wachter

Messrs. R. E. Whistler and E. F.
Bladholm (arranged by Tom Hotchkiss)

Dr. H. P. Zeh, Messrs. J. R.
Cunningham, R. L. Piehl, and J. P.
Arbizzani

Mr. William S. Quimby

Messrs. William G. Ashbaugh and
L. Miller Rogers

Messrs. Loren Neff and Max Ellis

Mr. Richard J. Gainey

Messrs. W. Lee Williams, Frank
Clark, A. J. Ristaino, John L.
Basil, and Jack Bauman

Mr. Charles Tuley, Herman S. Preiser,
and George Serkin

Dr. E. H. Phelps, Messrs. R. C.
Bowden, Jr., R. L. Christian, R. J.
Schmitt, C. H. Muller, and S. K.
Coburn

Prof. Everett D. Howe and Mr. John
T. Chambers

REFERENCES

- (1) A. Hache, "Contribution a l'Étude de la Corrosion de l'Acier en Solutions Saline" (in French), Institut de Recherches de la Sidérugie, Series A, No. 138 (April, 1956); also, Revue de Métallurgie, No. 1, pp 76-80 (1956).
- (2) John Lymand and Robert B. Abel, "Chemical Aspects of Physical Oceanography", J. Chemical Education, Vol 35, pp 113-115 (March, 1958).
- (3) The Corrosion Handbook, edited by Herbert H. Uhlig, John Wiley & Sons, Inc., New York City; Chapman & Hall, Limited, London (1948).
 - (a) Ibid, p 1115, Table 6.
 - (b) Ibid, p 1116, Table 7.
 - (c) Ibid, p 416.
- (4) Frank N. Speller, Corrosion - Causes and Prevention, McGraw-Hill Book Company, Inc., New York City (1951), p 169.
- (5) E. Schaschl and G. A. Marsh, "Concentration Cells and Aqueous Corrosion", presented at NACE 16th Annual Conference in Dallas, Texas, March 14-18, 1960.
- (6) W. Palmaer, "Sur la variation de la vitesse de formation de la rouille en fonction de la temperature", (in French), J. de la lutte comtra la corrosion, pp 18-24 (November, 1938).
- (7) Bridgeport Brass Company, Condenser and Heat Exchanger Tube Handbook (1954), pp 76, 80, 81.
- (8) W. L. Badger and Associates, Inc., "Critical Review of Literature on Formation and Prevention of Scale", U. S. Department of the Interior, Office of Saline Water, Research and Development Progress Report No. 25 (July, 1959).
- (9) W. R. Williamson and J. C. Stewart, "A New Look at Sea Water Distillation", Society of Naval Architects and Marine Engineers (February, 1958).
- (10) E. P. Partridge and A. H. White, "Mechanism of Formation of Calcium Sulfate Boiler Scale", Industrial and Engineering Chemistry, Vol 21, No. 9, pp 834-838 (1929).
- (11) Ulick R. Evans, The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications, St. Martins Press, Inc., New York City (1960), pp 164-165.

- (12) H. Hillier, "Sea-Water Evaporation: Scale Prevention by Ferric Chloride Addition", Chemical Trade Journal and Chemical Engineer, pp 306-311 (February 6, 1953).
- (13) H. Hillier, "Scale Formation in Sea-Water Distilling Plants", The Engineer, pp 208-209 (February 6, 1953); also, pp 255-256 (February 13, 1953).
- (14) Hagan Chemicals and Controls, Inc., Pittsburgh, Pennsylvania.
- (15) Albert W. Bruce, "Five Years Experience Making Fresh Water From Sea Water at the Morro Bay Power Plant", Colloquim on The Desalting of Water at the California Institute of Technology, Pasadena, California (May 5-6, 1960).
- (16) C&EN News, p 19 (July 20, 1959).
- (17) B. W. Forgeson, C. R. Southwell, and A. L. Axlexander, "Corrosion of Metals in Tropical Environments: Part 3, Underwater Corrosion of Ten Structural Steels", Corrosion, Vol 16, pp 105t-114t (March, 1960).
- (18) M. H. Peterson and L. J. Waldron, "An Investigation of the Corrosion Rate of Mild Steel in San Diego Harbor", NACE 16th Annual Conference in Dallas, Texas, March 14-18, 1960.
- (19) W. L. Badger and Associates, Inc., "Operation of Pilot Plant LTV Evaporator at Wrightsville Beach, North Carolina", Office of Saline Water, Research and Development Progress Report No. 26, p 92 (December, 1959).
- (20) F. C. Standiford, Jr., "Evaporation of Sea Water in Long-Tube-Vertical Evaporators", ACS Symposium on Saline Water Conversion, presented at Cleveland, Ohio, April 14, 1960; to be published by the American Chemical Society in Advances in Chemistry, in 1960.
- (21) Axelrad and Brogdon, "Heating of Saline Water and Mining of Sulfur Therewith", U. S. Patent 2,756,035, Column 6 (July 24, 1956).
- (22) G. Butler and H. C. K. Ison, "The Corrosion of Welded or Coated Mild Steel and of Wrought-Iron Boiler Tubes in Highly Saline Water", North East Coast Institution of Engineers and Shipbuilders, Transactions, Vol 76, Part 3, Figure 3, p 114 (January, 1960).
- (23) Ibid, pp 95-130; Discussion, Part 5, pp 13-17 (March, 1960).
- (24) T. J. Peake, "The Use of Aluminum in the Petroleum Industry", Proceedings of the Fourth World Petroleum Congress, Section Vii/B; Reprint No. 5, "Heating Coils for Ship Tankers" (1955).
- (25) R. L. Clark, K. J. Nabavian, L. A. Bronley, "Heat of Mixing and Boiling Point Elevation of Sea Water", Symposium on Saline Water Conversion, American Chemical Society, 137th National Meeting, April 5-14, 1960.

- (26) K. C. D. Hickman, "Centrifugal Boiler-Compression Still", Industrial and Engineering Chemistry, Vol 49, No. 5, p 786 (1957).
- (27) J. A. Eibling, W. L. Buckel(Part I); K. C. D. Hickman, W. H. Hogan(Part II), "Progress Report on Centrifugal Barrier Vapor-Compression Distillation", American Chemical Society, Symposium on Saline Water Conversion, 137th National Meeting, April 5-14, 1960.
- (28) S. C. Britton, Tin Research Institute, England; private communication dated April 14, 1960.
- (29) H. S. Campbell, "Some Factors Affecting the Performance of Condenser and Heat Exchanger Tubes", Chemistry & Industry, pp 1424-1425 (November 1, 1958).
- (30) Private discussions at Engineering Research Laboratories in April of 1960.
- (31) G. Newcombe, "The Effect of Composition and Structural Condition on the Resistance of 18-2 Chrome-Nickel Steels to Electrochemical Attack", Metallurgia, Vol 61, pp 107-112 (March, 1960).
- (32) P. T. Gilbert, "Some Factors Affecting the Performance of Condenser and Heat Exchanger Tubes", Chemistry & Industry, Discussion, pp 888-895 (July 11, 1959).
- (33) W. C. Stewart and F. L. LaQue, "Corrosion Resisting Characteristics of Iron Modified 90:10 Cupro-Nickel Alloy", Corrosion, Vol 8, No. 8, pp 259-277 (1952).
- (34) C. J. Lancaster, "Testing of Various Materials in High-Temperature Waters", E.E.S. Report 040028D, U. S. Naval Engineering Station, Annapolis, Maryland (November 30, 1953).
- (35) C. J. Lancaster, "Report on Performance of Materials Tested in High-Temperature Sea Water", E.E.S. Report 4A(13)966870, U. S. Naval Engineering Experiment Station, Annapolis, Maryland (September, 1951).
- (36) J. M. Turnbull, "Salt Refinery Corrosion Caused By Varying Evaporator Conditions", Corrosion, Vol 16, pp 11-16 (July, 1960).
- (37) G. L. Laserson, B. Minushkin, L. S. Goldring, and K. M. Held, "Extraction of Fresh Water in the Supercritical State", Nuclear Development Associates, Inc., Report NDA 32-2 to the Office of Saline Water (July 31, 1954).
- (38) J. B. Cotton and B. P. Downing, "Corrosion Resistance of Titanium to Sea Water", Institute of Marine Engineers, Vol 69, No. 8, pp 311-319 (1957).

- (39) M. J. McGoff, "Stressed Inconel Piping in a Sea-Water Warm-Air Compartment", MSA Research Corporation, Callery, Pennsylvania, Technical Report 72 (April 14, 1960).
- (40) Dale W. Kaufmann, ACS Monograph No. 145, Reinhold Publishing Corporation, New York City (1960), p 485.

BIBLIOGRAPHY1960

- (1) Anon., "Results of Eight-Year Corrosion Tests Conducted by the U. S. Naval Research Laboratory on Ten Structural Steels and Wrought Irons", Engineering Service Department Report, A. M. Byers Company, Pittsburgh 22, Pennsylvania (1960).
- (2) Frank G. Bennett, "Saline Water Conversion, 1956058", NAA-SR-3737 (January, 1960); OTS, Department of Commerce, Washington 25, D.C., price, 50 cents.
- (3) Frederick W. Fink, "Metals in Chemical and Marine Applications", Journal of Metals, pp 146-147 (February, 1960).
- (4) J. H. Morgan, "Cavitation Damage and Cathodic Protection", Letters to The Editor, Chemistry and Industry, p 583 (May 21, 1960).
- (5) T. Howard Rogers, Marine Corrosion Handbook, McGraw-Hill Company of Canada Limited, New York, Toronto, London (1960).

1959

- (1) E. P. Anderson and T. P. May, "Hull Protection by Impressed Current", Marine Engineering/Log, Vol LXIV (January, 1959).
- (2) Anon., "Anti-Fouling and Corrosion Prevention Combined in New System", Corrosion Technology, pp 364-365 (December, 1959).
- (3) Anon., "Preliminary Design Study of an Optimum Nuclear Reactor-Saline Water Evaporator Process", Office of Saline Water, Research and Development Progress Report No. 34 (1959); OTS No. PB 161010.
- (4) A. Hache, L. Barriety, and J. Debyser, "Effect of Photosynthesis Upon the Corrosion of Steel in Sea Water" (in French), Corrosion et Anticorrosion, Vol 7, pp 56-61 (February, 1951); (in German), Werkstoffe u. Korrosion, Vol 10, pp 145-148 (March, 1959).
- (5) Everett D. Howe, "The Costs of Demineralizing Water", University of California, Sea Water Conversion Program, paper presented at the UNESCO-IRAN Symposium on Salinity Problems in the Arid Zones, Teheran, Iran, on October 11-15, 1958; Series No. 75, No. 12 (February 25, 1959).
- (6) F. Hudson, Marine and Power Engineers Meet in the United States, The Mond Nickel Company, Limited (Thames House, Millbank, London, S.W.1), reprinted from Foundry Trade Journal (April 30, 1959).
- (7) John H. Morgan, "The Internal Cathodic Protection of Large Steel Pipes Carrying Sea Water", Corrosion, Vol 15, No. 8, pp 417t-422t (1959).
- (8) M. H. Peterson, "A Review - Principles and Criteria for Cathodic Protection of Steel in Sea Water", Corrosion, Vol 15, No. 9, pp 483t-487t (1959).

- (9) J. C. Rowlands, "Stainless Steels and Related Alloys Versus Marine Environments", Corrosion Technology, Vol 6, pp 359-363 (December, 1959).
- (10) B. I. Smirnov, "Arc-Welding of Tube Conduits in Copper-Nickel Alloys" (in Russian), Svarochnoe Proizvodstvo (Welding Production), Vol 32, No. 1, pp 35-37 (1959); English translation of journal available from British Welding Research Association, 29 Park Crescent, London W. 1, England.
- (11) M. Thivin, "Sea Water Resistant Steels" (in French), Corrosion et Anti-corrosion, Vol 7, pp 195-202 (May, 1959).

1958

- (1) J. L. Basil and J. S. Whelen, "Sea Water Corrosion of Various Materials Tested in Seven 20-Tube Model Condensers", Naval Research Laboratory, U. S. Naval Engineering Experiment Station, E.E.S. Report No. 910027A (NS-643-078), 55 pp (March 21, 1958).
- (2) D. B. Brice, M. R. Dusbabek, and C. R. Townsend, "Study of the Applicability of Combining Nuclear Reactors With Saline Water Distillation Processes", Office of Saline Water, Research and Development Progress Report No. 19 (1958); OTS PB No. 161394.
- (3) B. F. Dodge and A. M. Eshaya, "Economic Evaluation Study of Distillation of Saline Water by Means of Forced-Circulation Vapor-Compression Distillation Equipment", Office of Saline Water, Research and Development Progress Report No. 21 (1958); OTS PB No. 161395.
- (4) S. Fukui and T. Hara, "Influence of Salt Concentration of Sea Water on Polarization Curves of Various Metals" (in Japanese), Corrosion Engineering, Vol 7, No. 5, pp 26-29 (September, 1958).
- (5) Griscom-Russell Company, "Research on and Analysis of Single-Effect Low-Temperature Flash Evaporation Process", Office of Saline Water, Research and Development Progress Report No. 18 (1958); OTS PB No. 161393.
- (6) R. L. Horst, "Aluminum Pile Casings", Aluminum Company of America, Sales Development Division, Chemical Section (April 15, 1958).
- (7) C. P. Larrabee, "Corrosion-Resistant Experimental Steels for Marine Applications", Corrosion, Vol 14, No. 11, pp 501t-504t (1958).
- (8) Y. Minami and H. Takada, "Corrosion-Fatigue of Mild Steel in Sea Water: Part I, The Influence of Cathodic Protection on the Corrosion-Fatigue", Transactions, Shipbuilding Association of Japan, No. 103, pp 165-170 (May, 1958).
- (9) U. S. Navy, Bureau of Ships, Military Specifications, "Anodes, Corrosion Preventive, Zinc: Plate, Slab, Disc and Rod Shaped", MIL-A-18001E (August 22, 1958).
- (10) U. S. Navy, Bureau of Ships, Military Specifications, "Plugs, Zinc Anode Retaining, Heat Exchanger, Cathodic Protection", MIL-P-19415 (SHIPS) (November 26, 1958).

1957

- (1) J. M. Abramcy, "The Effect of Different Factors on the Rate of Steel Corrosion by Periodic Wetting in Sea Water" (in° Russian), Bulletin, Acad. Sci. of the Azerbaidzhan. SSSR (Izvest. Amad. Naukmizerbaidzhan, 358), No. 8, pp 31-40 (August, 1957).
- (2) A. M. Byers Company, Pittsburgh 22, Pennsylvania, "A Structure Inspection of the Marine Yacht Harbor Piers, San Francisco, California, July 31 to August 2, 1957" (1957).
- (3) L. Barriety, J. Debyser, and A. Hache, "Changes in Sea-Water Characteristics in a Corrosion Testing Station" (in French), Corrosion et Anticorrosion, Vol 5, pp 51-57 (February, 1957).
- (4) V. H. Brogdon, "Process and Heating System for Providing Hot Water and Power for Sulfur Mining", U.S. Patent No. 2,781,635 (February 19, 1957).
- (5) Louis Caruso, "Selection of Tube Material Best Suited for Water Conditions", Phelps Dodge Copper Products Corporation, Elizabeth, New Jersey; paper, 18th Annual Water Conference, Engineers' Society of Western Pennsylvania, Pittsburgh, Pennsylvania (October 22, 1957).
- (6) K.C.D. Hickman, "Research Continuation of Badger-Hickman Centrifugal Distillation Testing on Unit Number 4", Office of Saline Water, Research and Development Progress Report No. 15 (March, 1957).
- (7) F. L. LaQue, "Theoretical Studies and Laboratory Techniques in Sea Water Corrosion Testing Evaluation", Corrosion, Vol 13, pp 303t-314t (May, 1957).
- (8) John Starr, "Protective Coatings Made From Sea Water", Materials & Methods, Vol 45, pp 188, 190, 192 (February, 1957).
- (9) U.S. Navy, Bureau of Ships, Military Specification, "Anodes, Corrosion Preventive, Zinc; Design of and Installation in Shipboard Condensers and Heat Exchangers", MIL-A-19521(SHIPS) 25 May, 1956; Amendment 1 (April 1, 1957).
- (10) U.S. Navy, Bureau of Ships, Military Specification, "Distillation Unit, Water, Thermocompression", MIL-D-16196C(SHIPS) (December 30, 1957).

1956

- (1) R. C. Adams, "Corrosion Problems of Naval Steam Power Plants", Proceedings, American Power Conference, Vol 18, pp 583-590 (1956).
- (2) B. A. Axelrad, "Sea Water Heating", U.S. Patent No. 2,756,207 (July 24, 1956).
- (3) B. A. Axelrad, et al., "Heating of Saline Water and Mining of Sulfur Therewith", U.S. Patent No. 2,756,035 (July 24, 1956).
- (4) B. A. Axelrad, et al., "Water Heating Processes for Sulfur Mining", U.S. Patent No. 2,756,208 (July 24, 1956).

- (5) V. H. Brogdon, "Heating Systems for Water Containing Dissolved Scale-Forming Solids", U.S. Patent No. 2,756,029 (July 24, 1956).
- (6) C. M. Cockrell, "Pressurized Heater for Producing Hot Process Water in Large Quantities from Scale-Forming Water", U.S. Patent No. 2,759,328 (August 21, 1956).
- (7) W. W. Cranmer, "Recent Navy Experience With Saran and Vinyl Coatings", Corrosion, Vol 12, pp 245t-246t (May, 1956).

1955

- (1) Aluminum Company of America, "Process Industries Applications of ALCOA Aluminum", p 75 (1955).
- (2) W. L. Badger and F. C. Standiford, "Engineering in Salt Manufacture", Chemical Engineering, Vol 62, Nos. 3 & 4, pp 173-177 and 180-183 (1955).
- (3) H. Barnes, "The Analysis of Sea Water; A Review", Analyst, Vol 80, No. 953, pp 573-592 (August, 1955).
- (4) Charles J. Fritts, "Corrosion Control on Offshore Drilling and Producing Equipment", Corrosion, Vol 11, pp 471t-476t (November, 1955).
- (5) J. Leicester, "Developments in Feed Water Treatments", Corrosion Prevention & Control, Vol 2, No. 5, pp 33-37 (1955).
- (6) T. J. Peake, "The Use of Aluminum in the Petroleum Industry", Proceedings of the Fourth World Petroleum Congress, Section VII/B, p 137 (1955).
- (7) A. D. Rust, "The Use of Sea Water in Industry", Southern Power & Industry, pp 50-52 (December, 1955).
- (8) A. N. Voripaieff, "Wrought Iron Beats Salt-Water Corrosion on Offshore Platform", Oil Gas Journal, Vol 54, No. 28, p 197 (1955); also Marine Engineer, Vol 60, No. 11, p 61 (1955).

1954

- (1) Anon., "Cast Monel Impeller", Materials & Methods, Vol 39, No. 3, p 114 (1954).
- (2) W. B. Brooks, "Sea Water as an Industrial Coolant: Part 1, Operating Conditions", Petroleum Refiner, Vol 33, No. 10, pp 127-130 (1954).
- (3) W. B. Brooks, "Seawater as an Industrial Coolant: Part 2, Equipment Experience", Petroleum Refiner, Vol 33, No. 11, pp 179-182 (1954).
- (4) P. T. Gilbert, "The Resistance to Failure of Condenser and Heat Exchanger Tubes in Marine Service", Transactions, Institute of Marine Engineers, Vol 66, pp 1-6; Discussion, pp 6-20 (January, 1954).
- (5) P. T. Gilbert and F. L. LaQue, "Jet Impingement Tests", Journal of the Electrochemical Society, Vol 101, pp 448-455 (September, 1954).

- (6) A. Hache and P. Deschamps, "Study of Sea Water Corrosivity" (in French), Corrosion et Anti-Corrosion, Vol 2, No. 4, pp 134-140 (July-August, 1954); also Publications, Institut de Recherches de la Siderurgie, Series A, No. 90, 7 pp (November, 1954).
- (7) J. W. Jenkins and J. B. Guerry, "Testing of Materials for Naval Ship-board Sea Water Carrying Systems - A Review", Journal of the American Society of Naval Engineers, Inc., Vol 66, No. 3 (August, 1954); published by The International Nickel Company, Inc., 67 Wall Street, New York 7, New York (1954).

1953

- (1) Anon., "Behavior of Light Metal Alloys Towards Sea Water" (in German), Aluminium, Vol 29, No. 5, pp 203-206 (1953).
- (2) Anon. "The Marine Corrosion Station of the I.S.M.L." (in Italian), Alluminio, Vol 22, No. 4, pp 424-426 (July, 1953).
- (3) British Cast Iron Research Association, "Behavior of Cast Iron in Sea Water: An Annotated Bibliography", Bulletin, Vol 12, No. 1, pp 8-14 (July, 1953).
- (4) V. J. Chir, F. H. Colenutt, and K. Turner. "Some Corrosion Problems Encountered in Mina-Al-Ah-Madi Refinery", Institute of Petroleum Review, Vol 7, pp 159-164 (May, 1953).
- (5) W. J. Danziger and O. A. Sundholm, "Protection of Heat Exchanger Channels and Covers From Corrosion by Salt Water", American Society of Mechanical Engineers, Preprint 52-A-145 (ASME Annual Meeting, November 30-December 5, 1952, New York City), 22 pp (1953).
- (6) F. L. Laque, "Results of Exposure of Steel, Ductile Iron, and Ductile Nickel Resist Bolts in Contact With Cast Iron to Flowing Sea Water at Harbor Island, North Carolina, for 907 Days (April 1951 to October 1953)", Harbor Island Project Report 3009.3, The International Nickel Company, Inc. (December 18, 1953).
- (7) C. P. Larrabee, "Corrosion Resistance of High-Strength Low-Alloy Steels as Influenced by Composition and Environment", Corrosion, Vol 9, No. 8, pp 259-271 (1953).
- (8) A. J. Maurin, "Rational Anti-Corrosion Measures - Corrosion of Condenser Tubes" (in French), Techniques et Applications Petrole, Vol 8, pp 2593-2596 (April, 1953).

1952

- (1) Anon., "Corrosion Resistance of Titanium", Westinghouse Engineer, Vol 12, pp 114-117 (July, 1952).
- (2) Anon., "Report on Wrought Iron for Salt Water Piping", U.S. Naval Engineering Experiment Station (Annapolis, Maryland), Report No. 4A(9) DT169 (April, 1952).
- (3) R. L. Davis and R. F. Heinzerling, "How Bahrain Petroleum Combats Sea-Water Corrosion at Persian Gulf Installations", Oil Gas Journal, Vol 51, No. 33, pp 264, 266, 268 (December 22, 1952).
- (4) K. M. Huston and R. B. Teel, "Some Observations of the Potentials of Stainless Steels in Flowing Sea Water", Corrosion, Vol 8, pp 251-256 (July, 1952).
- (5) C. J. Lancaster, "Performance of Materials Tested in High Temperature Sea Water: 'K' Monel Metal Chromium Plated", U.S. Naval Engineering Experiment Station (Annapolis, Maryland), Report No. 4A(15) 966870 (January, 1952).
- (6) National Association of Corrosion Engineers, "Corrosion - A Short Course", Symposium held at University of California, in cooperation with the National Association of Corrosion Engineers, February 4-8, 1952.
- (7) W. S. Patterson and A. W. Jones, "A Contribution to the Study of the Action of Certain Inhibitors Upon Corrosion in Chloride-Polluted Water", Journal of Applied Chemistry (London), Vol 2, No. 5, pp 273-280 (1952).
- (8) I. G. Slater, L. Kenworth, and R. May, "Corrosion and Related Problems in Sea-Water Cooling and Pipe Systems in H.M. Ships", Journal of the Institute of Metals, Vol 77, Part 4, pp 309-330 (1950); Corrosion, Vol 8, No. 12, pp 417-429 (December, 1952).
- (9) W. C. Stewart and F. L. LaQue, "Corrosion-Resisting Characteristics of Iron Modified 90:10 Cupro Nickel Alloy", Corrosion, Vol 8, No. 8, pp 259-277 (1952).
- (10) D. P. Thornton, Jr., "Dow Conquers Sea Water Corrosion", Petroleum Processing, Vol 7, No. 11, pp 1640-1643 (1952).

1951

- (1) G. L. Bailey, "Copper-Nickel-Iron Alloys Resistant to Sea-Water Corrosion", The Institute of Metals (4 Grosvenor Gardens, London SW 1); reprinted from Journal of the Institute of Metals, Vol 79, Part 5, pp 243-292 (1951).
- (2) G. Heinemann, "Problems of Industries Using Sea Water (as Cooling Medium)", Texas Journal Science, Vol 3, pp 311-341 (1951).

- (3) L. W. Johnson and E. J. Bradbury, "Corrosion-Resistant Materials in Marine Engineering", The Chartered Marine Engineer, Vol 2, No. 1, p 1 (1951); reprinted by The Mond Nickel Company, Limited.
- (4) C. M. Shigley, "Engineering Problems of Coastal Waters", The Texas Journal of Science, Vol 3, No. 1, pp 21-29 (March 30, 1951).
- (5) E. T. Wandered, "Aluminum Marine Pipe Line", Oil Gas Journal, Vol 50, No. 9, pp 58-76 (July 5, 1951).

1950

- (1) Anon., "On the Corrosion Resistant Properties of Ferritic and Pearlitic Ductile Iron", Nickel Topics, Vol 3, No. 9, p 8 (1950).
- (2) F. L. LaQue and J. F. Mason, Jr., "The Behavior of Iron Modified 70-30 Cupro-Nickel Alloy in Sea Water and in Some Petroleum Industry Environments", Proceedings 15th Mid-Year Meeting, American Petroleum Institute, Refining Division, Cleveland, Ohio (1950).
- (3) V. P. Volkening, "Corrosion of Steel Pipe by Chlorinated Sea Water at Various Velocities", Corrosion, Vol 6, p 123 (1950).

1949

- (1) H. E. Bethon, "Fouling of Marine-Type Heat Exchangers", Transactions, American Society of Mechanical Engineers, Vol 71, p 855 (1949).
- (2) W. Z. Friend, "Sea Water for Cooling", paper, AIChE Symposium on Water Problems of the Process Industries, New York City, 35 pp, November 17, 1949.
- (3) A. J. Gould, "Corrosion-Fatigue of Steel Under Asymmetric Stress in Sea Water", Journal Iron & Steel Institute, Vol 161, pp 11-16 (1949).
- (4) H. A. Humble, "The Cathodic Protection of Steel Piling in Sea Water", Corrosion, Vol 5, p 292 (1949).
- (5) I. G. Slater and N. L. Parr, "Marine Boiler Deterioration", Proceedings, Institute of Mechanical Engineers, Vol 160, No. 3, pp 341-358 (1949); Engineer, Vol 187, pp 158-161, 199-201 (February 11, 18, 1949); Corrosion, Vol 5, No. 12, pp 417-434 (1949).
- (6) D. Wyllie and G. C. N. Cheesman, "Sodium Nitrate as an Inhibitor Against the Attack of Sea Water on Steel: Part II, The Addition of Other Inhibitors to Nitrite", Journal, Society of Chemical Industry, Vol 68, pp 209-212 (July, 1949).

1948

- (1) W. F. Clapp, "Macro-organisms in Sea Water and Their Effect on Corrosion", Corrosion Handbook, Edited by H. H. Uhlig, John Wiley & Sons, Inc., New York City (1948), pp 433-441.
- (2) H. A. Humble, "Cathodic Protection of Steel in Sea Water With Magnesium Anodes", Corrosion, Vol 4, p 358 (1948).
- (3) F. L. LaQue, "Behavior of Metals and Alloys in Sea Water", Corrosion Handbook, Edited by H. H. Uhlig, John Wiley & Sons, Inc., New York City (1948), pp 383-429.
- (4) A. C. Redfield, "Characteristics of Sea Water", Corrosion Handbook, Edited by H. H. Uhlig, John Wiley & Sons, Inc., New York City (1948), pp 1111-1122.
- (5) G. W. Seagren, "Paints and Organic Coatings for Sea-Water Exposure", Corrosion Handbook, Edited by H. H. Uhlig, John Wiley & Sons, Inc., New York City (1948), pp 431-433.
- (6) G. H. Young, "Anti-fouling Measures", Corrosion Handbook, Edited by H. H. Uhlig, John Wiley & Sons, Inc., New York City (1948), pp 441-446.

1946

- (1) J. W. Cuthbertson, "The Resistance to Corrosion by Sea Water of Some α -Tin and α -Tin-Aluminum Bronzes", Journal of the Institute of Metals, Vol 72, pp 317-342 (1946).
- (2) F. Wormwell, "The Influence of Movement on the Corrosion of Metals in Salt Solutions and Natural Waters: Part I, Low-Speed Rotation of Mild Steel - Peripheral Velocities Below 100 ft/min", Journal of the Iron and Steel Institute, No. II, pp 219p-228p (1946).
- (3) E. H. Wyche, L. R. Voigt, and F. L. LaQue, "Corrosion in Crevices", Transactions, Electrochemical Society, Vol 89, pp 149-166 (1946).

1945

- (1) C. L. Bulow, "Corrosion and Bio-fouling of Copper-Base Alloys in Sea Water", Transactions of the Electrochemical Society, Vol 87, p 127 (1945).
- (2) P. Ffield, "Recommendations for Using Steel Piping in Salt Water Systems", Journal of American Society of Naval Engineers, Vol 57, No. 1 (1945).
- (3) F. L. LaQue and W. F. Clapp, "Relation Between Corrosion and Fouling of Copper-Nickel Alloys in Sea Water", Transactions of the Electrochemical Society, Vol 87, p 103 (1945).
- (4) A. W. Tracy and R. L. Hungerford, "The Effect of Iron Content of Cupro-Nickel on Its Corrosion Resistance in Sea Water", Proceedings of the American Society for Testing Materials, Vol 45, p 591 (1945).

1944

- (1) R. H. Brown and R. B. Mears, "Resistance of Aluminum-Base Alloys to Marine Exposure", Society of Naval Architects and Marine Engineers, Transactions, Vol 52, pp 91-113 (1944).

1943

- (1) J. W. Donaldson, "Corrosion by Sea-Water: A Review of Recent British and American Investigations", Metallurgia, pp 163-170 (August, 1943).

1941

- (1) F. L. LaQue, "Behavior of Nickel-Copper Alloys in Sea Water", Journal of American Society of Naval Engineers, Vol 53, No. 1, p 29 (1941).

1940

- (1) F. L. LaQue and G. L. Cox, "Some Observations of the Potentials of Metals and Alloys in Sea Water", Proceedings of the American Society for Testing Materials, Vol 40 (1940); distributed by The International Nickel Company, Inc., 67 Wall Street, New York, New York.
- (2) W. A. Wesley, "Controlling Factors in Galvanic Corrosion", Proceedings of the American Society for Testing Materials, Vol 40 (1940); distributed by The International Nickel Company, Inc., 67 Wall Street, New York, New York.

1939

- (1) J. L. Basil, "The Corrosion Resistance of Annealed and Hard 70:30 Copper-Nickel Alloy", Report No. B-640, U. S. Naval Engineering Experiment Station, Annapolis, Maryland (November 6, 1939).

1938

- (1) G. D. Bengough, U. R. Evans, T. P. Hoar, and F. Wormwell, "The Corrosion of Metals by Salt Solutions and Natural Waters: An Agreed Statement", Chemistry and Industry, Vol 57, No. 45, pp 1043-1047 (November 5, 1938).

1933

- (1) G. D. Bengough, "Corrosion of Metals in Salt Solutions and Seawater", Chemistry and Industry, Vol 52, No. 10, pp 195-210 (March 10, 1933); also, Vol 52, No. 11, pp 228-239 (March 17, 1933).

1925

- (1) W. H. Bassett and C. H. Davis, "Corrosion of Copper Alloys in Sea Water", Transactions, American Institute of Mining and Metallurgical Engineers, Vol 71, p 745 (1925).

FWF:ic

September 6, 1960