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CRITICAL REVIEW OF LITERATURE
ON FORMATION AND PREVENTION OF SCALE

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FOREWORD

This is the twenty-fifth 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 reports submitted by W. L. Badger and Associates, Inc., under Contract No. 01-001-99. 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.

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INTRODUCTION

Scale is defined by Webster as "a hard incrustation deposited on the inside of a vessel in which water is heated." In the narrower chemical engineering sense, true scale is defined (3) as a deposit formed by precipitation from solution of a substance which has a solubility that decreases with an increase in temperature. By this latter definition, the solubility of a scale-forming material is lowest at a heated surface and deposition will most likely occur on this surface. In an evaporator, the heated surface is that through which the heat required for evaporation is transmitted. A scale deposit will form an insulating blanket on this surface, which greatly impedes the flow of heat, causing a reduction in capacity or efficiency or both.

Scale formation has long been recognized as a problem, but the causes of its formation and means of prevention have not always been (and are not now) perfectly understood. This report is an attempt to correlate the data that is known regarding scale formation and its prevention. The mechanism of scale formation is described and possible means of prevention are listed. Attempts are made to explain the mode of action of the various scale prevention techniques that have been successful in some industries. This permits assessing the possibility of using these same methods in sea water evaporators. The critical factors that have sometimes been overlooked in scale research are described and the fields in which further research is needed are outlined.

This report is based primarily on a comprehensive survey of literature published since 1930 and unclassified reports put out by various research organizations and governmental laboratories. Both the literature survey and the current review have been performed under Contract No. 14-01-001-99 with the Office of Saline Water of the United States Department of the Interior. The literature review resulted in the preparation of some 900 abstract cards, which are on file at the Office of Saline Water.

Many research reports on the purification of sea water have not been specific as to the source or composition of the raw material used, and, in addition, there is a great variety of terms used to express sea water concentration. The Appendix describes the various terms used in expressing sea water concentration, and presents curves summarizing the known or estimated properties of sea water concentrates.

I. MECHANISM OF SCALE FORMATION

Early theories* of scale formation held that it was due to impingement of solid particles on the heat transfer surfaces. These particles then adhered to the surfaces and gradually built up to form a continuous coating. The actual formation of the particles that eventually became scale was thus assumed to occur in the bulk of the liquid. Such explanations are still sometimes found in current literature (29). Subsequent research has disproved these theories for the most common occurrences of scale formation, but some instances of deposits formed by this mechanism do occur. In these instances, solids suspended in the solution settle out at points of low velocity or at times when fluid circulation is poor or absent.

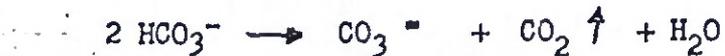
The current theory of scale formation (49) gained widespread acceptance about 1925 (6, 21, 47, 51, 59, 60, 98, 99, 122). If a solution saturated with a substance having a solubility that decreases with an increase in temperature is heated, the solution becomes supersaturated. This solution will tend to deposit crystals and the tendency will be greatest at the point of highest temperature. If heat is transferred to the liquid through a metal wall, the thin film of liquid in contact with the wall will be at a higher temperature than the bulk of the liquid. Therefore, crystals will deposit in that part of the film nearest the wall and will adhere to the wall as scale.

The initial formation of crystals from a clear solution (nucleation) takes place with considerable difficulty. Carefully filtered solutions can be taken to concentrations much higher than the equilibrium value without forming crystals (74). However, any solid contaminants, such as crystals already deposited, dust, or even the walls of the container, greatly reduce the concentration that can be reached. In other words, if a substance is to deposit from solution, it would much rather deposit on existing solid than form new crystals. The atomic structure of crystals of the material being deposited naturally form the most favorable environment, but almost any solid will promote precipitation. This is another reason for the adherence of scale deposits to the heating surfaces. The first trace of scale usually has nothing but the metal walls on which to deposit. Subsequent deposition then takes place preferentially on the scale already formed.

Not all scale is due primarily to substances having a solubility that decreases with an increase in temperature (inverse solubility). The two most important scale formers in sea water distillation are calcium carbonate (CaCO_3) and magnesium hydroxide (Mg(OH)_2). Although these materials

*The best review of past and present theories of scale formation, together with experimental data and photographs of scale growth is contained in reference 98.

do have inverse solubility curves (30, 60, 77, 90), their deposition is affected also by a chemical reaction. Carbon dioxide is present in sea water primarily as the bicarbonate ion. When sea water is heated or aerated, part of the carbon dioxide is driven off as gas and the remainder is transformed to carbonate. The reaction involved is as follows:



The carbonate reacts with calcium in the sea water to form calcium carbonate, which is relatively insoluble. The evolution of carbon dioxide is accelerated by an increase in temperature and by the presence of a surface. Therefore, the carbon dioxide is released primarily at the heating surface and this is the point at which the insoluble calcium carbonate is formed, as scale.

The carbonate ion can also be broken down by further evolution of carbon dioxide by the reaction:



The hydroxide ions may then react with magnesium ions to form a precipitate of magnesium hydroxide. Whether calcium carbonate or magnesium hydroxide is deposited depends primarily on the temperature. At sea water temperatures below 150-180°F., calcium carbonate predominates, while magnesium hydroxide is usually formed at higher temperatures (60, 76, 77).

A heated surface is not essential to scale formation. If a solution is supersaturated, it will have a tendency to form crystals. The tendency will be greatest at a heated surface, but any surface is better than none. One such case is in municipal water distribution systems. A water high in calcium bicarbonate will lose carbon dioxide when the pressure is reduced as the water is pumped out of the well. This will increase the concentration of carbonate ion and make the water supersaturated with respect to calcium carbonate. The calcium carbonate will then deposit on the walls of the pipelines, even though these walls are at the same temperature as the water (104, 118).

II. THE ROLE OF SUPERSATURATION

A saturated solution of any salt is a solution which will neither dissolve any more salt or precipitate salt when the solution and large crystals of that salt are intimately mixed for an applicable period of time. Solubility of a salt is the amount of that salt contained in a given quantity of saturated solution. The solubility varies with temperature and is also influenced by the presence of other salts in the solution. The solubility increases with an increase in temperature for most substances, such as common salt (NaCl), and these are said to have "normal solubility curves." If the solubility decreases with an increase in temperature, the salt is said to have an "inverted solubility curve" and will tend to form scale on being heated.

A supersaturated solution is one that contains more of the salt than it should hold when saturated. If such a solution were brought into contact with large crystals of the salt, some of the salt would separate out of the solution and deposit on the crystals. If sufficient time were allowed, enough material would deposit to bring the solution back to saturation. In order for any of the salt to deposit from solution, the solution must be supersaturated to some extent, no matter how slight (87).

Since a supersaturated solution contains more of the salt than it could normally hold, it follows that such a solution must be formed by some means other than merely mixing crystals of the salt with water. Supersaturation is usually generated by the following mechanisms:

1. Chemical reaction, such as the formation of carbonate from bicarbonate by the escape of carbon dioxide.
2. Removal of part of the solvent, such as evaporation of water from the solution.
3. Heating of a solution having an inverted solubility curve (or cooling of a solution having a normal solubility curve).
4. Addition of another salt that depresses the solubility of the salt in question. Also, it frequently happens that if two saturated solutions of a salt containing different amounts of a second salt are mixed, the solubility of the first salt in the mixture is less than the average of the solubilities in the original solutions. In this case, the mixture will be supersaturated.

All supersaturated solutions have a tendency to deposit the excess salt contained. Whether or not they actually deposit salt depends on the environment, the time allowed, and the degree of supersaturation (amount of salt contained in excess of the value at saturation).

The definition of an ordinary saturated solution specifies the presence of "large" crystals. This is because the tendency for salt to go into solution increases with a decrease in crystal size (87, 91). Thus, any number of "solubility curves" could be drawn if large crystals were excluded and the solubility at any temperature would be higher as the crystal size was reduced. A solution supersaturated in the ordinary sense might then be unsaturated with respect to sufficiently small crystals if these were the only ones present. The influence of crystal size is not appreciable with crystals larger than somewhere between 5 and 50 microns (0.00002 to 0.0002 inches) (87, 91, 119). Therefore, almost all industrial crystals are "large crystals." However, fine grinding can increase the solubility of gypsum as much as 20% (66).

As crystal size is reduced and degree of supersaturation is increased, the chances of spontaneous nucleation are enhanced. Occasionally random motion of ions of the salt in solution will bring enough together at one time to form an aggregate as large as the crystal size that would be in equilibrium with that solution. Smaller aggregates will tend to break up faster than they are formed, but if a larger one is formed, it will tend to grow and relieve the supersaturation. The formation of a large aggregate is more difficult than the formation of a small aggregate, since more molecules must be in very close proximity at the same time. Therefore, the chances of spontaneous nucleation increase as the supersaturation is increased, since smaller crystals are stable with respect to such a solution.

Spontaneous nucleation is a function of the time of contact, since it depends on accidental collision of sufficient molecules at one time to form an aggregate large enough to be stable. Theoretically, a solution having an infinitesimal degree of supersaturation would undergo spontaneous nucleation if maintained in this state for a long-enough period. Practically, however, an appreciable degree of supersaturation is needed to promote spontaneous nucleation in a reasonable time period. The experiment of Table I (61) is typical of results obtained. In this case, supersaturation was achieved by cooling salol, and the degree of supersaturation is measured by the difference between the melting point and the nucleating temperature. The samples were contained in sealed glass ampoules and the number of ampoules that had undergone spontaneous nucleation in a finite time was measured. This data indicates the probability relationship involved. The longer the time, the greater the chance of nucleation.

Once nucleation does occur (the chance formation of one aggregate large enough to continue growth), it is followed immediately by a shower of nuclei in the solution. This apparently is an ordering effect of the original nucleus, orienting the molecules remaining in the solution so that the chances of forming a suitable aggregate are greatly improved. This can be seen by dropping a seed crystal into a highly supersaturated solution (129). In view of this effect, it is obvious that the chances of spontaneous nucleation increase in proportion to the volume of the solution. Thus, degrees of supersaturation attainable in the laboratory cannot be reached in large commercial equipment.

TABLE I

Spontaneous Nucleation of Sälööl.
(Melting Point - 42-43°C)

Number of sealed ampoules out of a total of 70 that crystallized after holding at indicated temperatures.

<u>Hours</u>	<u>36.5°C</u>	<u>32.3°C</u>	<u>28.8°C</u>
0.5		16	
1		19	
5	18	29	56
20	24	30	63
43		34	
67		40	
100		44	
125	27		
140		49	
165		50	
214	29	52	
236		55	
260		57	
305	33		
453	35		

The results in a practical system are considerably different in magnitude from those indicated by Table I. Agitation, the presence of foreign material, dust, and the walls of the container all influence the degree of supersaturation attainable. Shock (134) and agitation (129) also increase the chances of spontaneous formation of nuclei. Foreign material such as dust or crystals of another material can also act as nuclei. The effectiveness of another material as a nucleating agent depends on the spacing of the atoms in its crystal lattice. The nearer this spacing is to the spacing of the atoms in a crystal of the material being precipitated, the more effective it will be. Thus, some materials are better promoters of crystallization of a given salt than others. In general, best nucleation results will be achieved if the crystallographic data of the foreign material and the salt to be precipitated agree within 15% (127). Table II shows how various materials affect the crystallization of sodium nitrate (136). Crystals or a surface of a foreign material of a given size may be thought of as corresponding to smaller nuclei of the precipitating material.

TABLE II

Nucleation of Sodium Nitrate on Foreign Seeds
(Solutions initially saturated at 80°C)

<u>Crystal</u>	<u>Degrees Subcooled</u>
None	60.0
Selenite	17.7
Orthoclase	14.1
Barytes	12.5
Albite	11.7
Muscovite	11.2
Calcite	7.8

III. SITE OF PRECIPITATION

In the evaporation of a scaling liquor, there is a continuous input of the scaling ingredient with the feed liquor. Assuming that there is no blowdown (or insufficient blowdown to carry away all of the scaling ingredient in solution), the scaling ingredient must precipitate. In a continuous process, such as sea water evaporation, the scaling ingredient must precipitate as fast as it is entering with the feed. Since some supersaturation is required for precipitation to take place, it follows that the boiling liquid will always be supersaturated. The higher the degree of supersaturation, the faster the material will deposit in a given area of solid surface. Conversely, the larger the surface, the less the degree of supersaturation required to deposit material at the required rate.

The driving force for precipitation might be termed the "effective supersaturation," which would be the difference between the actual concentration and the concentration required to initiate crystallization on whatever surface was present. Thus, the driving force would be different for precipitation from the same solution on different substances; highest for deposition on large crystals of the scaling ingredient; lower for small crystals, foreign seeds, and metal surfaces. By providing a large area of "large" crystals (over 10 microns) of the scaling ingredient, a relatively low effective supersaturation with respect to that surface would be required to deposit solid at the required rate. The resulting solution concentration might then be so low that there would be no effective supersaturation with respect to other surfaces.

In an operating evaporator, conditions are not uniform throughout the solution. The temperature is always highest at the heating surface, since a temperature difference is required to force into the solution the heat that is needed for evaporation. With a scaling liquor, the solubility of the scaling ingredient will be lower in contact with the heating surface than it will be in the bulk of the solution. Thus, the effective supersaturation of the solution with respect to this hot surface will be greater than it is with respect to an unheated surface of the same material. The higher the difference in temperature between the metal wall and the bulk of the liquid, the higher the effective supersaturation. Thus, an increase in temperature difference will make it increasingly difficult to prevent formation of scale on the heating surface.

In most types of evaporators, the liquid in contact with the heating surface is allowed to boil. The formation of a vapor bubble results in an increase in concentration of the solution in the immediate vicinity of the bubble. Most of the vapor is supplied from the triple interface between the solution, the bubble, and the heating surface and the supersaturation is highest at this interface. The supersaturation reached will depend on the rate at which the film is swept away by agitation and replaced by fresh solution. If circulation is poor, precipitation of the scaling ingredient will occur as a ring around the place where the vapor bubble formed (98,106). Strong agitation, induced either by a pump or the

thermosyphon action of vapor evolution, will tend to reduce this tendency for local overconcentration. The tendency is completely eliminated in the submerged tube forced circulation evaporator. In this type, the heating surface is so far below the liquor level that hydrostatic head prevents boiling. Liquor is pumped from a vessel, through the heater, and back to the vessel where flash evolution of vapor occurs. Heat is put into the liquid as sensible heat and hence the temperature must rise as the liquid passes through the heater. This heating tends to increase the supersaturation of a scaling liquid, thus offsetting to some extent the advantages of the forced circulation evaporators.

In summary, if the blowdown cannot carry away all of the scaling ingredient in solution, some of it must precipitate. Precipitation will occur on some surface and, if scaling of the heating surface is to be prevented, some other surface must be provided to compete for the scale. Crystals of the scaling ingredient form the best competitor for the scale. To be most effective, they must offer the largest possible surface and must be in suspension in the boiling solution, since they will then be available at the point where supersaturation is generated. The tendency of the heating surface to scale will also be reduced by designing for operation at low temperature differences and good circulation past the heating surface.

Of course, once the heating surface starts to scale, it presents a surface of hot crystals to the solution, and hence this is the most favorable site for further deposition. Thus, it is easier to prevent scale accumulation on a clean surface than on a surface that is partially scaled (25,110). In general, once scale starts to form, it will continue to accumulate. The scaling rate can be reduced by providing a large surface of crystals in suspension to compete for the scale, but cannot be eliminated entirely. The only possible exception would be where the scale was removed mechanically as fast as it was forming.

IV. SCALING INVESTIGATIONS

Most of the work on the rate of scale formation has ignored the fact that the supply of scaling ingredient is frequently the limiting factor. Consider, for instance, a forced circulation evaporator operating at a fixed boiling point, fixed feed concentration, and fixed discharge concentration. In this type of evaporator, the heat-transfer coefficient does not vary appreciably with changes in temperature difference. Therefore, the evaporation rate, feed rate, and discharge rate are proportional to the temperature difference. The amount of potential scale that could form would be the amount entering with the feed less the amount that could be carried away in solution in the discharge liquor. Assuming all the potential scale actually deposited on the heating surface, the weight of scale formed in a given time interval would be proportional to the evaporator output and hence proportional to the temperature difference. Tests would therefore show that a 50% reduction in temperature difference would cut in half the rate of scale formation, as measured by thickness accumulated in a given time interval or by rate of decrease in the heat-transfer coefficient (13, 24). Actually, of course, just as much scale would form for a given output--it would just be spread over more heating surface.

In another case (11) synthetic sea water containing 0.125% CaSO_4 was concentrated to 50% of its initial volume. The concentration of CaSO_4 in the blowdown was therefore about 0.25%. However, the blowdown actually could have held almost twice as much CaSO_4 in solution. Thus, the amount of potential scale that could have formed was zero and nothing but the good results obtained could have been expected.

This same investigation used a very small, single-tube forced-circulation evaporator. Heat losses were so high that as much as 7,000 Btu had to be transferred through the heating surface to evaporate a pound of water. In a large plant, heat losses would be negligible and this same amount of heat would evaporate seven pounds of water. Thus, the input of scaling ingredient would be seven times as high in a large plant, per square foot of heating surface, as it was in this test. While the heat-transfer coefficient dropped 33% in a month under test conditions, the same decrease should occur in only 4 days in a full-scale plant.

In another investigation of sea water scaling rates (84), the sea water was recirculated through a heat exchanger where it was heated to high temperature. Since there was no fresh input of scaling ingredient, the only scale that could possibly form was that contained in the initial solution. The tests showed that the heaviest scale was formed at the highest temperature. Actually, if the test had continued long enough, all of the scale should have been found at the highest temperature. If the test had continued until equilibrium was reached, the sea water leaving the high temperature end of the heater would be saturated at this high temperature and would become unsaturated on cooling. When this

unsaturated solution was reintroduced in the low temperature end of the exchanger, it would dissolve any scale previously deposited therein and redeposit the scale at the high temperature end.

One of the most comprehensive and best studies of scale formation during evaporation of sea water (60) was conducted in such a manner as to yield a possible erroneous picture of scaling rates. A single-effect evaporator was used in these tests. The evaporator contained 3 steam coils, each heated by steam at a different pressure so as to show the effect of temperature difference on scaling rates. As would be expected, most of the scale was found on the coil operating at the highest temperature difference. However, no quantitative conclusions should be drawn from these tests, since all of the coils were competing for the same potential scale. Left unanswered was the question, How much scale would have been formed on the low temperature coil if the higher temperature coil had not been there to preferentially deposit the scale?

V. POTENTIAL SCALE

Two distinct types of scale prevention techniques are possible: those that reduce the amount of potential scale that could form for a given total product output, and those that reduce the percentage of potential scale that actually forms on the heating surfaces. Potential scale is usually considered to be the amount of scaling ingredient entering in solution in the feed less the amount that could be carried away in solution, at equilibrium, in the blowdown from that part of the system where conditions are most severe.

The application of this definition to sea water evaporation is rather difficult. The three major scale components of sea water are calcium carbonate, magnesium hydroxide, and calcium sulfate. The total amount of calcium carbonate plus magnesium hydroxide scale than can form is equivalent to the bicarbonate content of the initial sea water less the amount of carbonic acid gas (carbon dioxide) that is not lost during evaporation, or is lost and replaced by other acid (60, 77, 118). If the blowdown of any sea water evaporator were held long enough to reach equilibrium, practically all of the carbon dioxide would be lost. Therefore, in the absence of acid injection, the potential calcium carbonate plus magnesium hydroxide scale would be that entering with the feed sea water. Calcium sulfate scale can deposit three crystal forms--gypsum, hemihydrate, and anhydrite, each having a different solubility. Anhydrite would be the only phase stable at equilibrium, but the form usually encountered is hemihydrate (76, 77). The potential calcium sulfate scale can therefore have two definitions depending on the solid phase considered. The meta-stable hemihydrate phase is usually used unless otherwise specified.

Calcium sulfate does not reach saturation until sea water has been concentrated several fold. Therefore, it is possible to produce distilled water under conditions such that there is no potential calcium sulfate scale. However, as noted above, all the calcium carbonate plus magnesium hydroxide of the entering sea water can form scale. Therefore, the amount of this type of scale that can be formed for a given quantity of distillate will be reduced as the yield of distillate for a given value of sea water is increased. This is shown graphically in Figure I, taken from the data of Langelier (76, 77). This figure is based on untreated feed of normal sea water having a total alkalinity of 119.8 mg/liter and a calcium sulfate content of 1260 mg/liter.

Figure I shows that saturation with respect to calcium sulfate hemihydrate is reached at a concentration factor of 2.7 when the boiling temperature is 212°F. This is somewhat lower than Langelier, who gives a concentration factor of 3.1 at this temperature. The discrepancy is due to the choice of the original sea water from which the concentration factors were calculated. Figure I is based on initial sea water having a chlorinity of 19.381, for the reasons given in the Appendix. This is appreciably stronger than the sea water on which Langelier's data were based, so saturation with respect to hemihydrate is reached sooner.

POTENTIAL SCALE FROM NORMAL STRENGTH SEA WATER

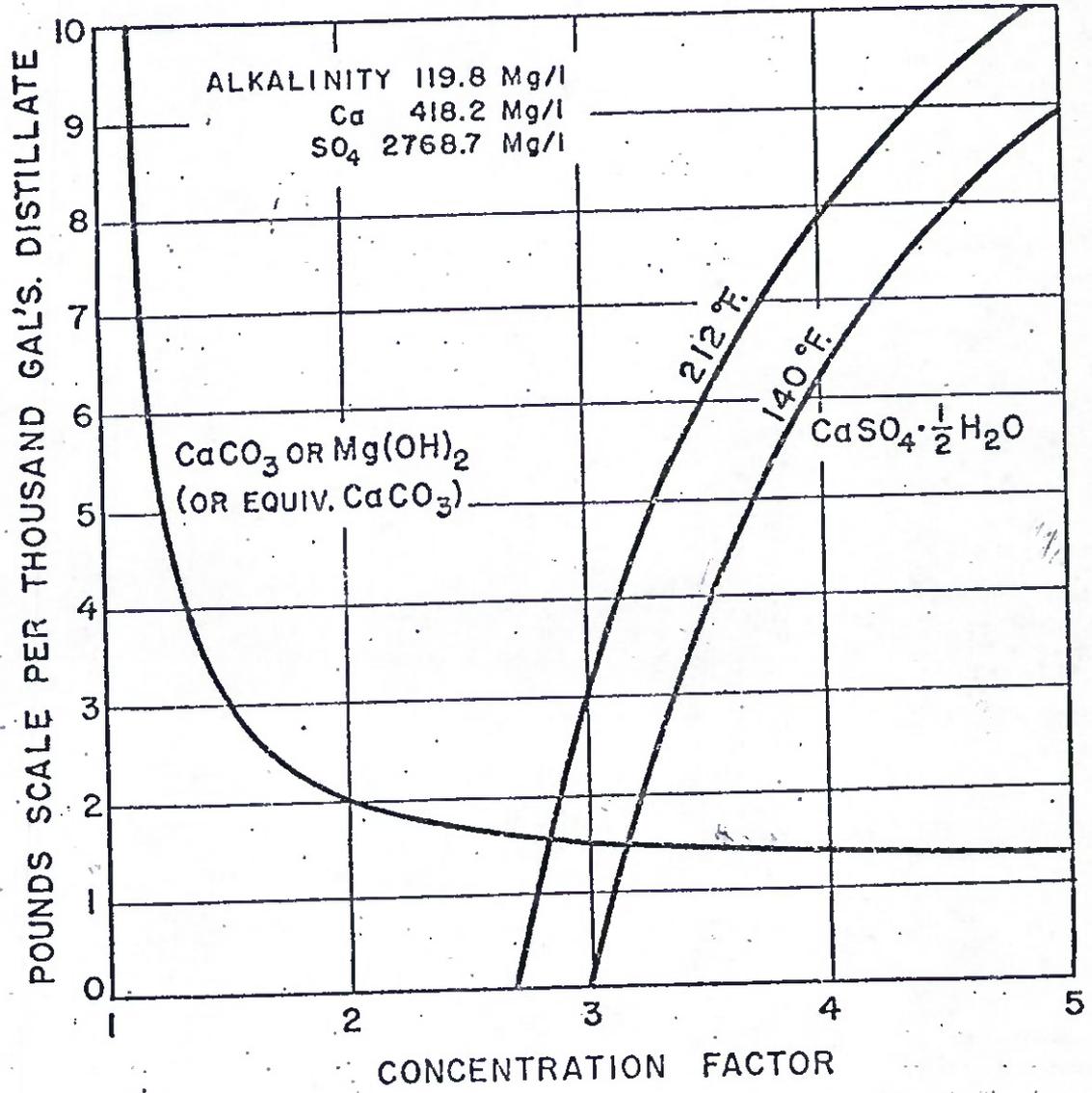


Figure 1

VI. MEANS OF REDUCING POTENTIAL SCALE

The amount of potential scale can be reduced by treatment of the feed to eliminate part or all of the scaling component or by operation in such a manner that the blowdown can carry away more of the scaling component in solution. The means of reducing potential scale by the latter method are rather limited, especially when applied to sea water. Increasing the blowdown rate would at first glance, seem to be an obvious possibility (75, 80). This will work for calcium sulfate, but not for calcium carbonate and magnesium hydroxide as shown in Figure I, since more blowdown requires more feed per gallon of distillate. The only other procedure that has been tried or suggested is chelation (53, 69, 118). This involves the addition of an organic material, such as ethylene diamine tetra acetic acid (EDTA), to the evaporator. The EDTA ties up magnesium and calcium ions in soluble complex that effectively removes them from solution so that they cannot form a scale precipitate. This chelation process will work for sea water evaporation. However, the total magnesium and calcium content of sea water is much larger than the amount that can form scale. For the EDTA to be effective it must remove all of this calcium and magnesium. Even at a fraction of its present cost, the consumption of EDTA is so high that treatment costs for sea water would be exorbitant. Much more practical, although still far too expensive at EDTA prices, would be a chelating agent for bicarbonate ions, if such were possible.

Means for treating the feed instead of the blowdown for reducing potential scale are much more numerous and practical. Most of the processes involving treatment of the feed act by precipitation of the scaling component before it can come into contact with the heating surface. The precipitate may or may not be removed before the feed enters the evaporator. In the latter case, solids fed to the evaporator cannot form true scale since this involves precipitation from solution directly on the heating surfaces. Means that have been used in one industry or another or have been suggested for sea water evaporation include the following:

1. Chemical treatment to precipitate as a more insoluble compound one of the ions forming the scaling compound.
2. Preheating by direct steam injection to reduce the solubility of the scaling component.
3. Backmixing of blowdown with raw feed to form an evaporator feed in which the solubility of the scaling component is so low that some will precipitate.
4. Heating and aeration of the feed to drive off carbon dioxide, thus increasing the pH and precipitating the scaling component.

5. Injection of acid to replace part or all of the carbon dioxide so that carbon dioxide loss during evaporation will not increase the pH to the point where scale can form.

Chemical Treatment

Chemical treatment is widely used in industry to remove ions that might otherwise cause scale formation. The most common case is water softening. Here, calcium and magnesium compounds are removed either by ion exchange resins or by treatment with soda ash and lime or caustic soda or sodium phosphate (42, 98). Sulfate may also be removed by treatment with barium chloride (8). However, as mentioned previously, there is much more magnesium and sulfate present than can possibly form scale. The consumption of chemicals for sea water softening by chemical treatment is therefore so high that cost of treatment would be prohibitive (76).

Silica is the only scaling component of sea water that might be removed at a sufficiently low cost by chemical treatment. The usual chemical used for silica removal is sodium aluminate (78, 121). However, silica content of sea water is objectionably high only near points of dilution by large rivers, where sea water distillation should not be needed.

In some cases, treatment chemicals are injected directly into steam boilers to prevent scale formation. The usual chemical is sodium phosphate, but others are also sometimes used (21, 47, 52, 79). The action is the same as external treatment, the calcium or magnesium being precipitated as a sludge of calcium or magnesium phosphate which is less soluble than the corresponding carbonate or hydroxide. The cost of this type of internal treatment is greater than the cost of the usual external treatment and is thus used only for residual hardness or in small boilers because of the greater convenience.

Steam Injection

The scaling ingredient can sometimes be precipitated by preheating the solution to a temperature appreciably higher than that reached in the evaporator. Direct steam injection must be used, however, to avoid scale formation in the preheater. This treatment is used in the Ramén process for the evaporation of sulfite waste liquor (102). The scaling ingredient in this liquor is calcium sulfate. Saturation is not reached until part of the water has been evaporated. Therefore, the liquor is evaporated part way, then passed through a preheater where high pressure steam is injected and then evaporated further. There may be more than one preheater at intermediate points in the liquor flow through the evaporator. The process works very well with sulfite waste liquor (107) and might be applicable to sea water evaporation. The only disadvantage is the increased consumption of steam, due not only to the added consumption by the preheater, but also to the limitation the process places on flowsheet design to achieve the best steam economy.

Backmixing

If a raw sea water feed were mixed with hot concentrated blowdown, the solubility of the scaling components in the mixture might be low enough so that some of the potential scale would precipitate (13). Such a process could not precipitate all of the scaling ingredient since the mixture would have a lower concentration of soluble components and a larger volume than the eventual blowdown and could thus hold more of the scaling component in solution. Appreciable improvement could be expected only if the concentration of the mixture were close to the concentration of the blowdown. This would require the recycle of much more blowdown than was eventually discharged. The process would thus be applicable only to single-effect or thermocompression evaporators, since the recycle of large quantities of strong blowdown solutions would ruin the steam economy of a multiple-effect plant.

Decarbonation

It is possible to remove all of the carbonate and bicarbonate ions from sea water as carbon dioxide gas by heating and aeration (13, 77). Removal of all the carbon dioxide results in precipitation of magnesium hydroxide to such an extent that there can be practically no subsequent formation of calcium carbonate or magnesium hydroxide scale (76). The only difficulty with the process is that the time required for complete carbon dioxide removal is too long to be practical (9, 17). If this were not the case, the process would be very economical since no chemicals are needed and the only extra costs are for power to aerate the solution and heat to replace that lost to the air.

Acid Injection

Carbon dioxide in solution acts as an acid and its removal makes the solution alkaline. It is the alkalinity that causes the formation of calcium carbonate and magnesium hydroxide scale (60, 77, 118). The effect of carbon dioxide loss can be counteracted by the addition of an acid or acid salt and potential scale eliminated (60, 118, 140). This method of treatment has long been used for hard water (104, 113) and has been proved completely successful in a number of practical sea water tests (60, 68, 75, 114, 140). The only difficulties are the cost of acid and the effect of overdoses of acid on corrosion of the evaporator. Weak acids have been used in the past for sea water, primarily to simplify handling and reduce corrosion resulting from accidental overdoses (75, 140). Acids or acid salts tried included citric acid, sodium acid sulfate, ferric sulfate, ferric chloride, hydrochloric acid, sulfuric acid, sulfamic acid, and aluminum chloride.

Citric acid has been used by the U. S. Armed Forces but is too expensive for most purposes. Ferric chloride, the salt of a strong acid and weak base which has acidic properties, is used in some shipboard and shore-based installations (60, 68). Ferric chloride has added advantage in that it can be formed in the evaporator by electrolytic corrosion of

sacrificial iron anodes, and its decomposition forms a precipitate of ferric hydroxide that can act as nuclei for crystal growth in solution.

The cheapest acid available commercially is sulfuric acid. There should be no difficulty in handling such a strong acid in a large commercial installation. It has been used for such purposes previously, as in the acidification of strong saline solutions to permit removal of hydrogen sulfide before evaporation (4). The cost of sulfuric acid for complete replacement of carbon dioxide in sea water is on the order of only \$0.03 per thousand gallons (85). The equipment cost for acid injection is negligible, so such treatment should be entirely practical and quite economical. The amount of acid that would have to be used is so small that the sulfate ion introduced would be negligible compared to the sulfate ion already present in sea water, and thus the solubility of calcium sulfate would not be affected.



VII. MEANS OF PREVENTING POTENTIAL SCALE FROM ACTUALLY FORMING SCALE

In many cases, it is impossible or impractical to eliminate all potential scale from the system. Means of preventing potential scale from actually depositing on the heating surface may be classified in two groups: those that carry away all of the scaling component in solution in the blowdown, and those that cause the potential scale to deposit on something other than the heating surface.

Supersaturated Blowdown

In the first case, the blowdown would not be permitted to reach equilibrium and would be more or less supersaturated. (If it were not supersaturated, there would be no "potential scale.") Operation must be controlled in such a manner as to prevent the supersaturation from becoming so high that deposition occurs in the limited time that the solution is in the evaporator.

One way to do this is to reduce the residence time in the evaporator. Experimental work on sea water (76, 77) shows that it takes an appreciable time for calcium carbonate to start to deposit, sometimes as long as 60 minutes for calcium carbonate to start to deposit, sometimes as long as 60 minutes at 212°F. This has also been noted with respect to hard water (124). Also, the evolution of carbon dioxide takes place at a relatively slow rate (9, 60, 77), as indicated by the data of Table III (1). Thus, the increase in pH due to CO₂ evolution is reduced by shortened residence times and this reduces the supersaturation of the blowdown with respect to calcium carbonate and magnesium hydroxide. A similar case is met in water treatment (56), where the effluent of the plant may contain 100 ppm of CaCO₃ while it could contain less than 20 ppm at saturation. The excess calcium carbonate will not deposit unless the water is brought into contact with a large surface area of calcium carbonate, as in filter, or is held for a long time, as in the water distribution mains. The same effect of time has been observed with calcium sulfate. Experimental work with sulfite waste liquor saturated with calcium sulfate (111) has shown that as much as three times the normal amount of calcium sulfate can be kept in solution for periods up to an hour, depending on conditions.

The rate of carbon dioxide loss is also reduced by operation at lower temperatures. Thus, low-temperature evaporation should reduce the tendency to form scale in sea water evaporators. This has been confirmed by most tests (17, 67, 80) but contradicted by others (13, 60). The latter results may have been obtained in evaporators with longer residence times at lower temperatures due to the decrease in heat transfer coefficients with a decrease in operating temperature.

TABLE III

Rate of Carbon Dioxide Removal from Sea Water

Initial volume - 350 ml.
 Aeration - 500 ml./minute
 Temperature - 212°F

<u>Time-minutes</u>	<u>% CO₂ removed</u>
10	25
18	38
28	46
48	58
68	66
88	74
108	80
128	86
148	92
168	96
188	98
208	100

<u>Temperature °F</u>	<u>Time to Remove 1/2 of CO₂</u>	<u>Time to Remove 2/3 of CO₂</u>
164	160 min.	5 hours
185	75 min.	155 min.
199	45 min.	93 min.
212	32 min.	66 min.

The flash process of sea water evaporation makes it possible completely to prevent loss of carbon dioxide from the solution while it is in contact with the heating surfaces. Thus, supersaturation with respect to calcium carbonate and magnesium hydroxide is kept to a minimum. In this process (92), sea water is heated, under pressure, up to a fairly high temperature. The pressure is then released in stages and the flash vapor formed is condensed in the heaters to form the product water. All heat transfer is to unconcentrated sea water and, although some scale does form, the scaling rate is much lower than it would have been if carbon dioxide had been lost during heating.

The supersaturation that can be achieved can in some cases be influenced by certain additives. The principal additives in current use are phosphates. Success with the use of phosphates in municipal water treatment has encouraged a number of attempts at their use in sea water distillation. Apparently, these attempts have been made with little or no consideration being given to the mechanism of action of phosphates in preventing scale. Phosphates were first proposed for water treatment in 1934 (50). Concentrations of only 2 ppm were able to prevent precipitation of as much as 600 ppm of calcium carbonate in excess of the normal solubility. This is much less than would be needed for any sort of chelation action or chemical reaction with the calcium carbonate, so the process was called a "threshold treatment." Numerous theories have been proposed for the mechanism by which phosphate prevents precipitation. One theory is that it simply inhibits precipitation (44, 135); another is that it prevents carbon dioxide loss (18); another is that it deranges the crystal so as to make deposition more difficult. However, the theory now generally accepted (22, 56, 101, 105, 116) is that the phosphate is absorbed on all metal surfaces and on any chance nuclei formed. The absorbed phosphate layer greatly hinders further deposition on these surfaces and, in effect, removes them from action as seeds. Thus, the solution becomes similar to a perfectly clear laboratory solution in which very high supersaturations can be obtained before spontaneous nucleation has produced enough nuclei to use up all of the phosphate.

A great deal of practical and theoretical work has been done on the performance of phosphates in treating hard or partially softened waters (54, 104, 108). In general, it has been found that the amount of calcium carbonate that can be held in solution decreases with increasing temperature and that the phosphates are less effective with magnesium carbonate, still less with magnesium hydroxide precipitation (56). While most phosphates will work to some extent, the ones known as hexameta phosphates, molecularly dehydrated phosphates, glassy phosphates, or "Calgon" are the most effective. It has been found that these materials will even remove old scale deposits in some cases (56, 86). The explanation of this action is

rather difficult; it may be either the effects of gradual erosion or the very strong absorption of phosphate on the individual crystals, thus loosening the bond between crystals (56). It is well established that large excesses of glassy phosphates will remove scale deposits. This is probably due to a chelation action (43, 69, 115).

Some other materials may have an effect similar to the phosphates in preventing precipitation. Among those known are the aluminates and zinc (124, 132).

The application of this type of threshold treatment, alone, to sea water evaporation seems to have little chance of success (60). The principal reason for failure is that the supersaturations developed during evaporation are usually much higher than have been successfully handled before with phosphates. However, it does seem possible that phosphate threshold treatment might prove extremely valuable as a supplement to acid treatment. The use of acid alone to eliminate all potential scale requires rather low pH's, which result in increased corrosion. A threshold treatment with phosphate might make it possible to operate with a blowdown that was appreciably supersaturated. This would permit a reduction in the quantity of acid used, with a consequent increase in pH's and reduction in corrosion.

VIII. PRECIPITATION AWAY FROM HEATING SURFACE

If potential scale must be allowed to deposit, it can be prevented from depositing on the heating surface by providing another more extensive and more favorable surface on which deposition can occur. As mentioned previously, seed crystals of the scale-forming ingredient provide the most favorable surface on which deposition can occur, but a number of other materials have been used. This method of scale prevention has been used successfully in a number of industries, including water treatment, steam generation, salt production, and waste sulfite-paper-pulp liquor evaporation.

The use of seeds has the effect of reducing the supersaturation of the solution below that needed to initiate crystallization on the heating surface. Unfortunately, almost all the experimental work has been done under isothermal conditions. This work has shown the effect of the quantity of seeds and of the seeding material on the rate at which supersaturation is discharged. For instance, Scholander (111) has shown the relative effects of temperature, agitation, and quantity of seeds on the rate of precipitation of calcium sulfate in sulfite waste liquors. He has also shown that gypsum, sulfite mud, Fe_3O_4 (magnetite), and anhydrite were effective as seeds and that strontium sulfate, barium sulfate, calcium oxalate, and calcium carbonate had little or no effect as seeds for calcium sulfate deposition. In softening water, it has been found that the smaller particle sizes of calcium carbonate and a 3-5% seed concentration were effective (55, 83, 88, 109, 123, 124, 143). Work along similar lines has been done in connection with calcium bicarbonate decomposition (65, 124), brine purification (62, 128), brine evaporation (12), and waste sulfuric acid disposal (97).

While the application of such seeding methods to the prevention of scale in evaporators has been successful, there is practically no quantitative data on the conditions required. The first successful application was in evaporators for the production of common salt (16). Here, it has been found that a calcium sulfate scale can be prevented by maintaining about 20 gpl calcium sulfate in suspension (7, 58). The same process will prevent magnesium hydroxide scale in salt evaporators. Reference (4) describes the results achieved and the similarity of salt production to the evaporation of sea water. Similar results have been achieved in use of seeding to prevent scale in sulfite waste liquor evaporators (63, 142), sulfate liquor evaporators (73), sodium sulfate evaporators (6), tannin extracting plants (130), sugar evaporators (31), and steam boilers (48).

The application of seeding methods to prevention of scale in sea water evaporators has been tried both in the laboratory and on a pilot plant scale. Laboratory tests (77, 118) showed that, under conditions of the test, there was practically no scaling if 300 ppm magnesium oxide (which would hydrate to magnesium hydroxide) were added to the evaporating sea water. However, when tried in a military-type thermo-compression still, the seeds could not be kept in suspension and were

J. Hd. Dr. Leiter report am 23.09.97

M.F.G. Ho

ineffective (118). This was probably a fault of the still design, which was not built with this possibility in mind.

Another less direct application of the seeding method of scale prevention is the so-called "contact stabilization" method developed by Langelier and co-workers (75, 76, 77, 78) for use in sea water evaporators. An external bed of sand or similar solids is added to the evaporator system. Brine is pumped out of the evaporator through the sand-filled "stabilizer" and back to the evaporator at a rate as high as 10 times the feed rate. The scaling constituents are deposited on the sand particles, which soon become coated with scale and act as seeds of the scaling ingredient. The process would not be expected to be as effective as the usual seeding process, since brine is boiling away from contact with the seeds and must increase appreciably in supersaturation before it can be transferred to the stabilizer (85). Nevertheless, this external stabilization method has made possible a reduction of as much as 90% in scaling rate of sea water evaporators (85, 118). The only other evidences of such a process in use are ones in which a bed of crushed stone was placed between the heater and separator of a forced-circulation evaporator to precipitate the scaling ingredient (125, 130).

Seeds of a foreign substance are sometimes almost as effective as seeds of the scaling ingredient. Once precipitation starts on these seeds, they actually become seeds of the scaling ingredient. An added advantage of foreign seeds is that they can frequently be introduced as a very large number of very small particles. Then, the limited quantity of scaling ingredient, when deposited on these particles, cannot grow them to a size large enough to permit them to settle rapidly and become ineffective. The principal applications of foreign seeds have been in steam boilers and sugar evaporators. Here, it has been found that powdered or colloidal graphite, iron, nickel, soot, talc, clay, aluminum, copper are effective as seeds (8, 41, 137). Probably the chemicals added for internal boiler water treatment form precipitates that are also effective as seeds. Thus, trisodium phosphate will form calcium or magnesium-phosphate precipitates in suspension. An example outside use in steam boilers is the trisodium phosphate that is sometimes added to salt evaporators (89). The amount added is far less than needed to combine with all the calcium and magnesium, but is enough to form seeds that can eliminate scaling. An example of the use of foreign seeds with sea water is the use of alluvial mud in suspension to prevent scale when heating sea water to high temperatures for use in the mining of sulfur (2). Another is the use of impalpable silica in British sea water evaporators (68). An example of the use of seeds prepared by internal chemical treatment of sea water is the standard Navy boiler compound, in which the phosphate and soda ash would both combine with calcium and magnesium in sea water to form seeding precipitates.

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Circulation in some parts of steam boilers may be rather poor and it becomes difficult to keep the seeding solids or products of internal treatment in suspension. If these are allowed to settle out, they may bake out on the surfaces or plug the piping. A number of products have been used to limit the growth of precipitates and help keep them in suspension. The most common additive used for this purpose is tannin (19, 35, 41, 47, 52, 64, 98, 121), although a great number of organic agents have also been used, such as starch, various protein products, and plant extracts (64, 70, 117, 121). Most of these materials have a second function of reducing the adherence of scale deposits.

IX. MEANS OF REDUCING SCALE ADHERENCE

If scale must be allowed to form, various treatments or methods of operation may be used to assist in its removal during operation. Some require only the addition of a chemical to modify the scale deposit, while others require special designs of equipment or treatments to remove the scale at frequent intervals.

Modification of Scale Deposits

Material adsorbed on the surface of a crystal will usually inhibit growth of that crystal and reduce adherence of that crystal to similar crystals. This is especially true of organic materials and is the basis of a number of proprietary boiler compounds. These organic materials become included in the scale and weaken it enough so that it will flake off in operation (59). Starch is the material most commonly used in sea water distillation and is a component of the standard Navy boiler compound (10, 13, 20, 60, 71). A great profusion of other organic materials has been used to reduce scale buildup in one industry or another. Among the more common are tannin, proteins, dextrin, and various oilseed extracts (see page 25). Dispersing agents and sequestering agents such as used in Britain (10, 13, 60, 68, 80, 81) also fall in this class.

Somewhat similar results can be obtained by precoating the heating surfaces with a material to which the scale does not adhere tightly. Various tube coatings or tube materials have been tried, such as Teflon (26), rubber (26), glass (72, 82), varnish (59), wax (59) and oil (57, 96, 118). Unfortunately, while such treatments do reduce scale adherence, the coatings themselves usually have such a low thermal conductivity that they are almost as detrimental as the scale they are intended to prevent (59).

Another proposed process (94) would co-precipitate a more readily soluble scale constituent with scales such as calcium sulfate, which cannot be removed easily with acid. Such a process would increase the scaling rate but would simplify chemical scale removal. This usually happens naturally in a sea water evaporator, where calcium carbonate and magnesium hydroxide are the acid soluble scale components.

Continuous Removal of Scale Deposits

The maintenance of a clean heating surface by continuous removal of scale deposits usually involves impractical methods of construction or severe operating conditions. Among the methods that have been tried are porous heating surfaces (27), pulsating rubber tubes as heating surfaces (26), evaporators built with scrapers (15), and the circulation of abrasive particles past the heating surface (31, 100). There are no known methods that appear to have any practical application to sea water evaporation.

Intermittent Scale Removal

Some methods have been developed that can be used for scale removal at such frequent intervals that the thickness never becomes great enough to affect heat transfer seriously. Three methods have found practical use. One is the intermittent acid injection treatment for sea water stills developed by Langelier (20, 78). This treatment has an advantage relative to continuous acid injection in that the acid consumption is greatly reduced. The savings in cost are appreciable if citric acid is used, but negligible if a cheap acid such as sulfuric acid is used.

Another method uses cold shock to distort the heating surface and crack off the scale. Heating surfaces susceptible to such distortion are flat plates, oval tubes, bent tubes, and coiled tubes. Surfaces consisting of bent tubes (40), coiled tubes (45, 60), oval tubes (14) and essentially flat plates (141) have been used in sea water evaporators with only partial success. Cold shocking will remove some, but not all of the scale (71).

An intermittent method of scale removal that was developed for use in evaporation of sulfite waste liquor makes use of a reversible heating surface (46, 93, 107). The heater is made of flat plates and is connected by suitable valving so that each side is condensing steam half the time and heating the scaling liquor the other half. Scale forms on a surface during the time it is exposed to the liquor and is then dissolved off by the condensing steam after reversal. The process requires an expensive type of construction and imposes rather serious limits on the flowsheets that can be used. It is not anticipated that this "Rosenblad Process" will be practical for sea water distillation.

X. SCALE PREVENTION GADGETS

A great many proprietary compounds and treatment devices have been offered as means of completely preventing scale and any other troubles that might be met in the use of water. Most of these make use of magnets, very weak electrical currents, radiation, etc., to achieve their purported results. Excellent reviews of the usefulness of these devices have been published (23, 28, 131, 138). Some have even been tried in sea water evaporators (32, 33, 34, 38, 39). These gadgets should not, however, be confused with some boiler compounds (60) or electrical devices using currents large enough to affect pH or give corrosion products that can act as seeds (20, 68, 119). These latter devices have been successful in some applications and have been tried with sea water solely on the basis of such previous success (20, 36, 37, 60, 118, 139).

XI. SUGGESTIONS FOR FUTURE RESEARCH

Practically all of the investigations done in the past have been hit-or-miss trials at finding successful methods of scale prevention, studies of the effect of various additives on rates of scale formation, or isothermal studies of rates of reaction or rates of precipitation. No fundamental work has been done to outline the effect of various variables on the conditions that can be reached before scale starts to form in a heater or evaporator. Practically nothing is known about the relative effects of surface, temperature difference, temperature level, velocity, residence time, and type and quantity of seeds on the degree of supersaturation that can be achieved before scaling starts. An investigation of the effect of such factors on solutions of several scaling substances should make possible the selection of scale prevention techniques on something better than a trial and error basis.

An investigation of this type should start with simple solutions and only a few of the more important variables until more is learned regarding the relative effect of these variables. Eventually, the investigation might be widened to include an evaluation of the limits of effectiveness of the various treatment compounds that have been effective to a highly variable degree with no apparent reason for the variation.

A P P E N D I X

Properties of Sea Water and Its Concentrates

Means of Expressing Concentration

Since the relative abundance of the various ions in sea water is remarkably constant, the most accurate common measure of concentration is obtained by chemical analysis for one of the more abundant ions. Chloride ion can be determined most easily and accurately by titration with silver nitrate using potassium chromate as an indicator. This titration precipitates the bromide and iodide along with the chloride.

Chlorinity is defined (within .045%)(126) as the total amount of chlorine, bromine, and iodine in grams contained in one kilogram of sea water (i.e. parts per thousand), assuming that the bromine and iodine have been replaced by chlorine.

The normal titration for chloride is usually done with a fixed volume rather than a fixed weight of sea water.

Chlorosity is defined as the total amount of chlorine, bromine, and iodine in grams contained in one liter (measured at 20°C) of sea water, assuming that the bromine and iodine have been replaced by chlorine.

All analytical data reported by this office will be in terms of chlorosity. Chlorinity can be obtained by dividing the chlorosity by the specific gravity of the sample at 20°C. The relation between chlorosity and density is shown in Figure III (calculated from "The Oceans" (126) and data by Armour (1)).

Another common measure of concentration is salinity.

Salinity is defined as the total amount of solid material in grams per kilogram of sea water when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine, and all organic matter completely oxidized.

The empirical relation between salinity and chlorinity, as established by the International Commission (126), is

$$\text{Salinity} = 0.03 + 1.805 \times \text{Chlorinity.}$$

The computed curve showing the relation between salinity and chlorosity is given in Figure III.

Another expression of concentration is the thirty-second scale, for which no written definition has been located. However, it is apparent that this is merely the salinity expressed in fractions, i.e., the number of thirty-seconds = Salinity x 32/1,000.

The actual total dissolved solids content of sea water is exceedingly difficult to measure in practice and is not usually used as an expression of concentration, but can be obtained from the following empirical equation:

$$\text{Total solids (grams per kilogram)} = 0.073 + 1.8110 \times \text{Chlorinity}$$

Concentration Factor, which is the ratio of salinities (or chlorinities) of an evaporator blowdown to raw sea water, has been used rather loosely in many reports. For instance, at Fort Story, concentration factors have been related to a raw sea water feed that is much more dilute than normal sea water. In this office, concentration factors will be based on a hypothetical sea water feed having a chlorinity of 19.381, a salinity of 35.01, and a chlorosity of 19.862. These concentration factors will thus be more closely related to the actual concentrations of scaling components and other physical characteristics of the solutions involved.

The relation between the various expressions of concentration is shown in Figure V.

Total Alkalinity is a measure of the concentration of carbonate and bicarbonate in sea water and is usually expressed as milligrams of equivalent CaCO_3 per liter of sea water. The alkalinity is usually obtained by titration with an excess of acid and backtitration with alkali to the methyl orange endpoint, but a standard method of analysis is not available. The ratio of alkalinity to chlorosity in undiluted normal sea water at the surface is about 6.030. Evaporation will usually be accompanied by some loss of CO_2 , so this ratio will not hold for sea water concentrates. Almost all of the alkalinity is bicarbonate.

Composition of Sea Water

A comprehensive summary of the elements present in sea water is given in Reference (126). This data, reduced to a chlorinity of 19.00 (salinity of 34.325 chlorosity of 19.462, specific gravity at 20°C of 1.0243), is as follows (in parts per thousand):

Sodium (Na)	10.5561
Magnesium (Mg)	1.2720
Calcium (Ca)	0.4001
Potassium (K)	0.3800
Strontium (Sr)	0.0133
Chloride (Cl)	18.9799
Sulfate (SO ₄)	2.6486
Bicarbonate (HCO ₃)	0.1397
Bromide (Br)	0.0646
Fluoride (F)	0.0013
Boric acid (H ₃ BO ₃)	0.0260 (undissociated)
Iodide (I)	0.00005
Silicon (Si)	0.00002 to 0.004
Others - approximately	0.0013
Total dissolved solids	34.4830
Water - balance	965.517

When sea water is evaporated, the elements deposit as chemical compounds. If these elements are combined in the form in which they usually deposit, the above analysis would indicate that sea water having a chlorinity of 19.00 would contain the following quantities of the major compounds (in parts per thousand):

NaCl	26.780
MgCl ₂	3.214
MgSO ₄	2.233
CaSO ₄ ·2H ₂ O	1.548
KCl	0.725
CaCO ₃	0.109
NaBr	0.083
Water, etc.	965.308

This analysis is based on the assumptions that strontium is deposited with (and analyzed volumetrically with) the calcium and that bicarbonate decomposes to carbonate before precipitation occurs. The above analysis will be used in all calculations dealing with the recovery of salt and other byproducts by solar evaporation of sea water, since it corresponds to slightly diluted sea water. The actual sequence in the deposition of salts on solar evaporation is shown in Figure II, which has been compiled from the data of Usiglio (133), Oka (95), and various published and unpublished analyses of solar pond bitterns.

Normally, sea water has a salinity ranging from 34.5 to about 35.75, and a salinity of 35.0 is nearer the average than the 34.325 of the above table. The Hydrographic Laboratories of Copenhagen, Denmark, have prepared a so-called "Normal Water" that has been distributed to all oceanographic institutes as a primary standard for analytical determinations. This Normal Water has a chlorinity of 19.381, corresponding to a salinity of 35.01, a density at 20°C of 1.0248, and a chlorosity of 19.862. Sea water of this analysis will be used in all calculations involving the distillation of sea water. The resultant analysis of this "Normal" sea water would be as follows in parts per thousand by weight and grams per liter measured at 20°C:

	<u>Parts per Thousand</u>	<u>gpl</u>
Na	10.7678	11.0348
Mg	1.2975	1.3297
Ca	0.4081	0.4182
K	0.3876	0.3972
Sr	0.0136	0.0139
Cl	19.3605	19.8406
SO ₄	2.7017	2.7687
HCO ₃	0.1425	0.1460
Br	0.0659	0.0675
F	0.0013	0.0014
H ₃ BO ₃	0.0265	0.0272
I	0.00005	0.00005
Si	0.00002 to 0.004	0.00002 to 0.004
Others	0.0013	0.0014
Total solids	<u>35.1745</u>	<u>36.0468</u>
Water	<u>964.8255</u>	<u>988.7532</u>
Total	1000.0000	1024.800

Total alkalinity - mg/l. 119.8

Properties of Sea Water Concentrates

Density

The densities versus chlorosity and temperature are shown in Figures III and IV. The first of these is most useful for estimating chlorosity from density measurements made at or near room temperature. The second is useful in calculating mass flow rates from volumetric measurements. These curves are based primarily on the data of the Armour Research Foundation (1).

Specific Heat

No accurate data are available on specific heat of sea water concentrates. Figure VI is based on pure NaCl solutions having NaCl contents equal to the salinities (i. e. 35 salinity = 3.5% pure NaCl solution). Actually, specific heat data for pure NaCl solutions is not too reliable. The data shown is an extrapolation of low-temperature data from International Critical Tables.

Boiling Point Rise

The boiling point rise data of Figure VII are based on the work of Badger and Baker (5) on pure NaCl solutions and were calculated on the assumption that the NaCl content was equal to the salinity. The only available data on sea water is that of Armour Research Foundation (1) on atmospheric boiling points. These check quite well with the curves of Figure VII.

Viscosity and Thermal Conductivity

Data for pure NaCl solutions, converted to corresponding chlorosities, are shown in Figure VIII.

MATERIALS REMAINING IN SOLUTION IN SEA WATER BITTERNS

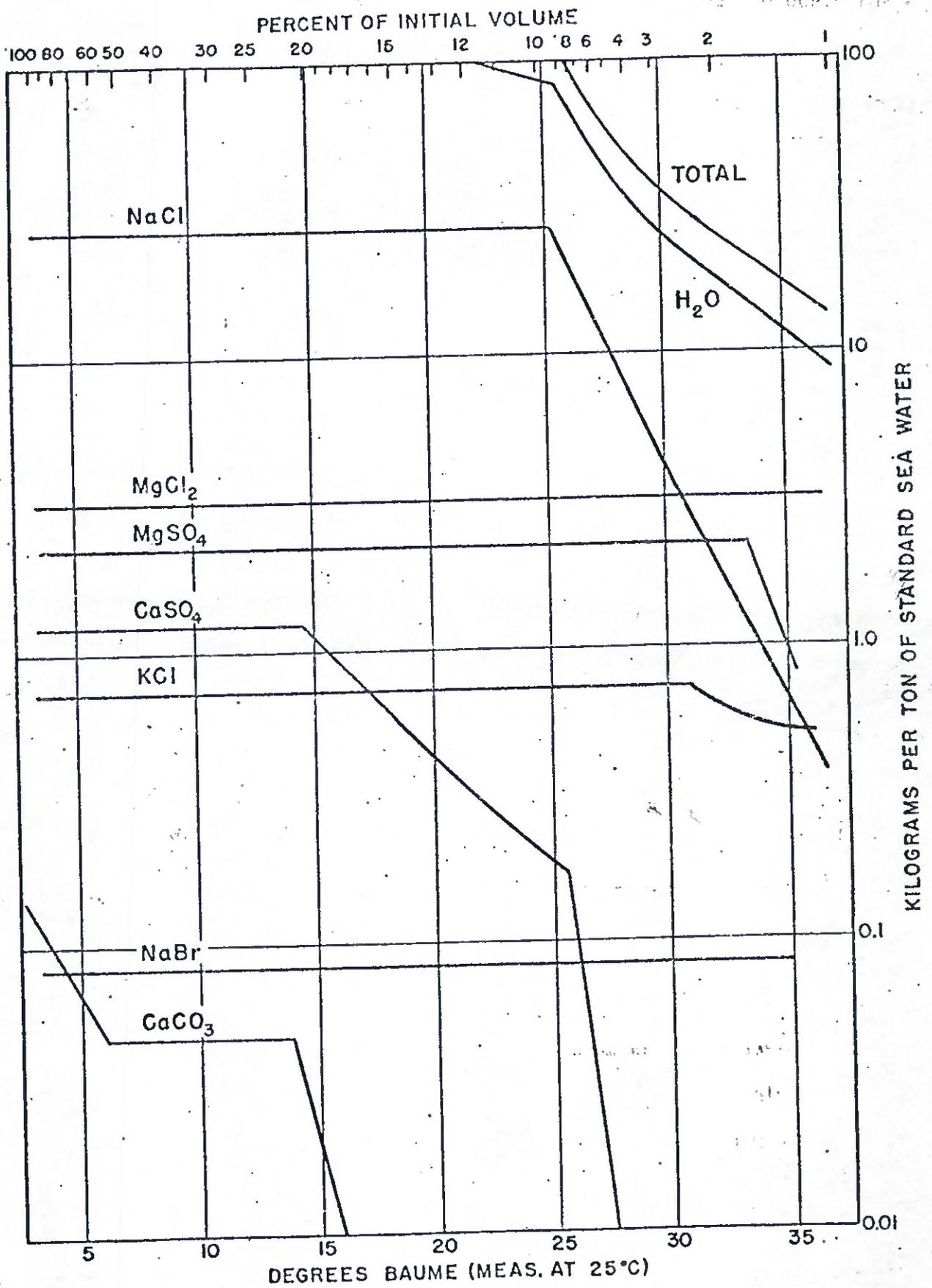
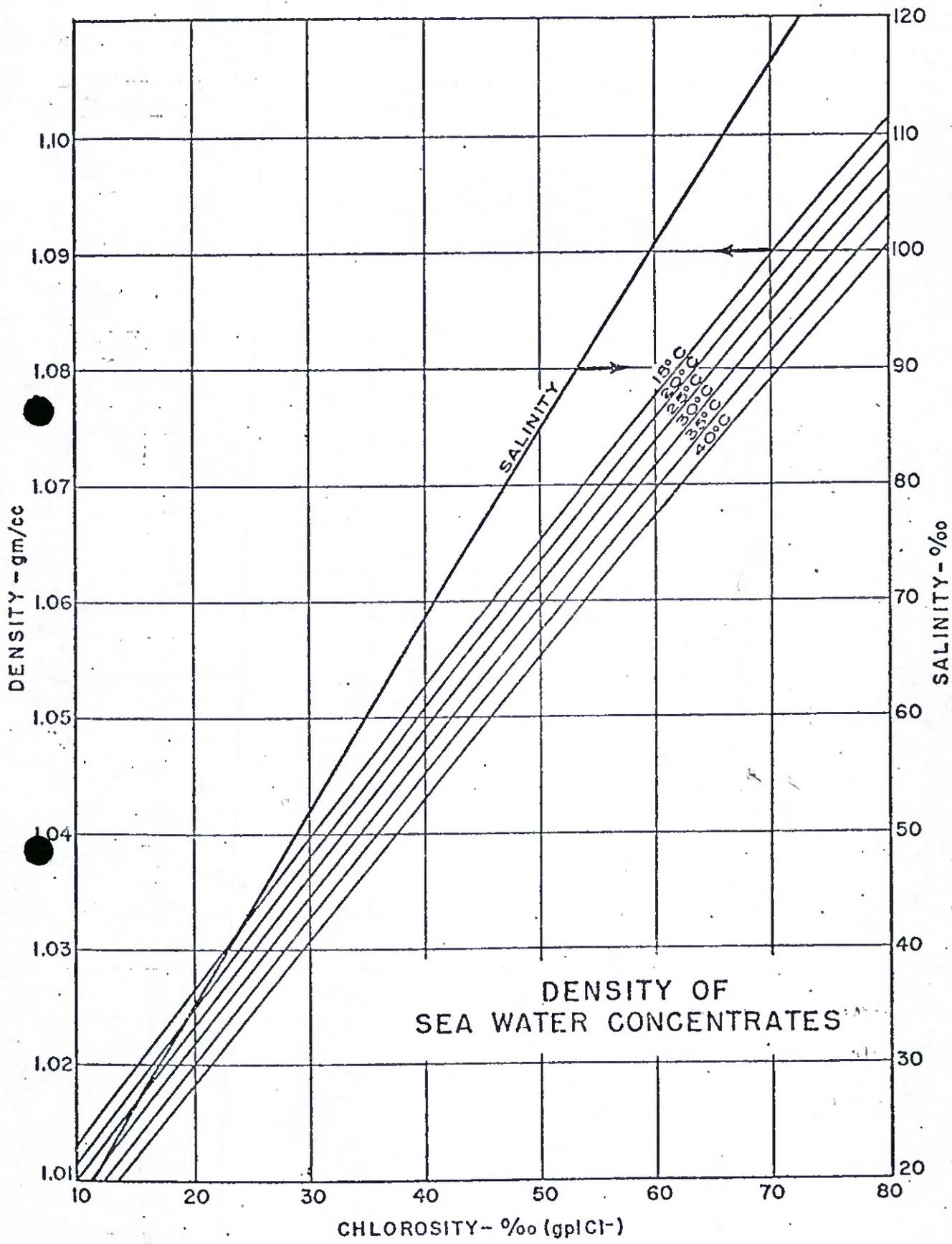


Figure 11



DENSITY OF SEA WATER CONCENTRATES

Figure III

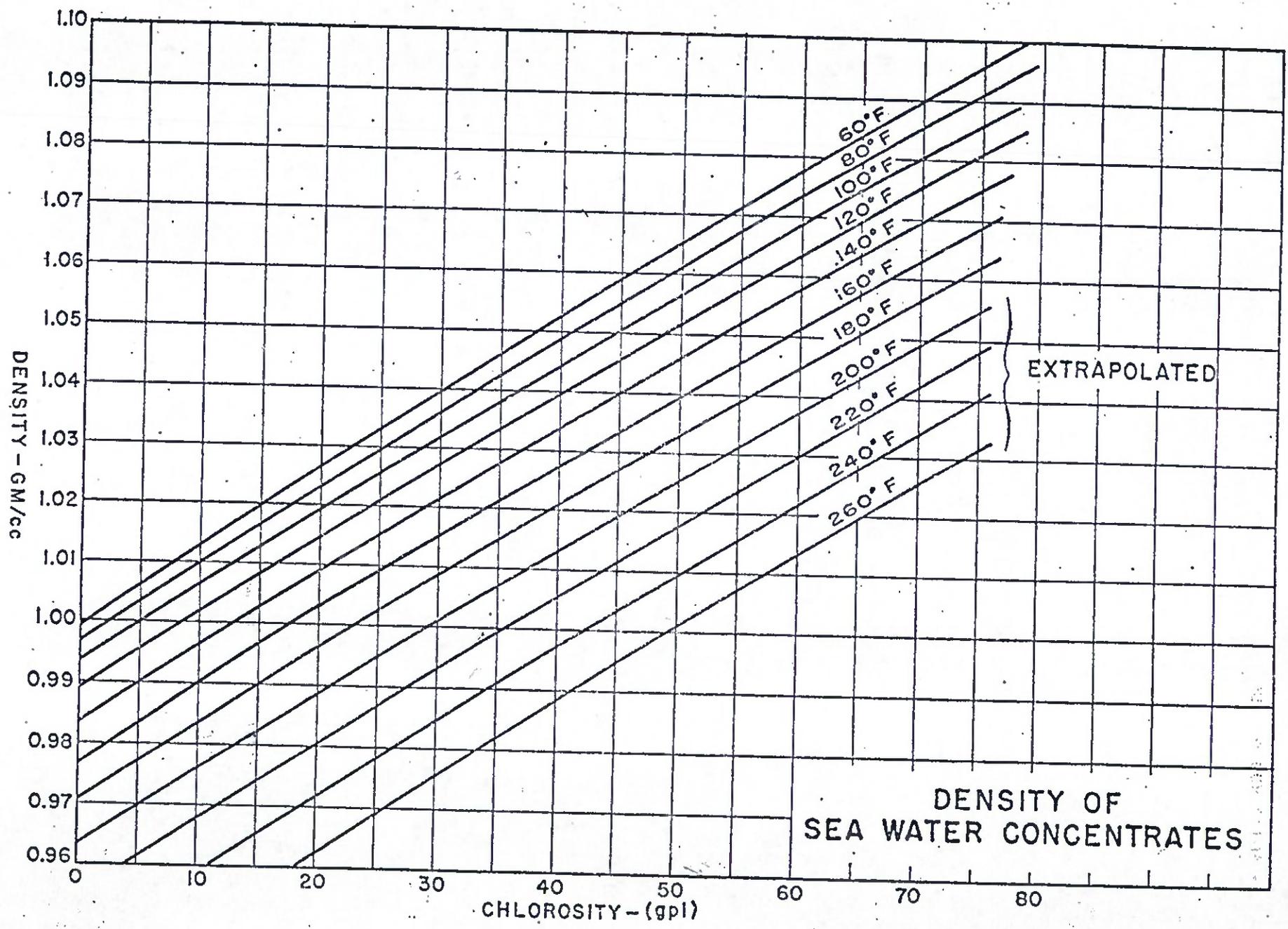


Figure IV

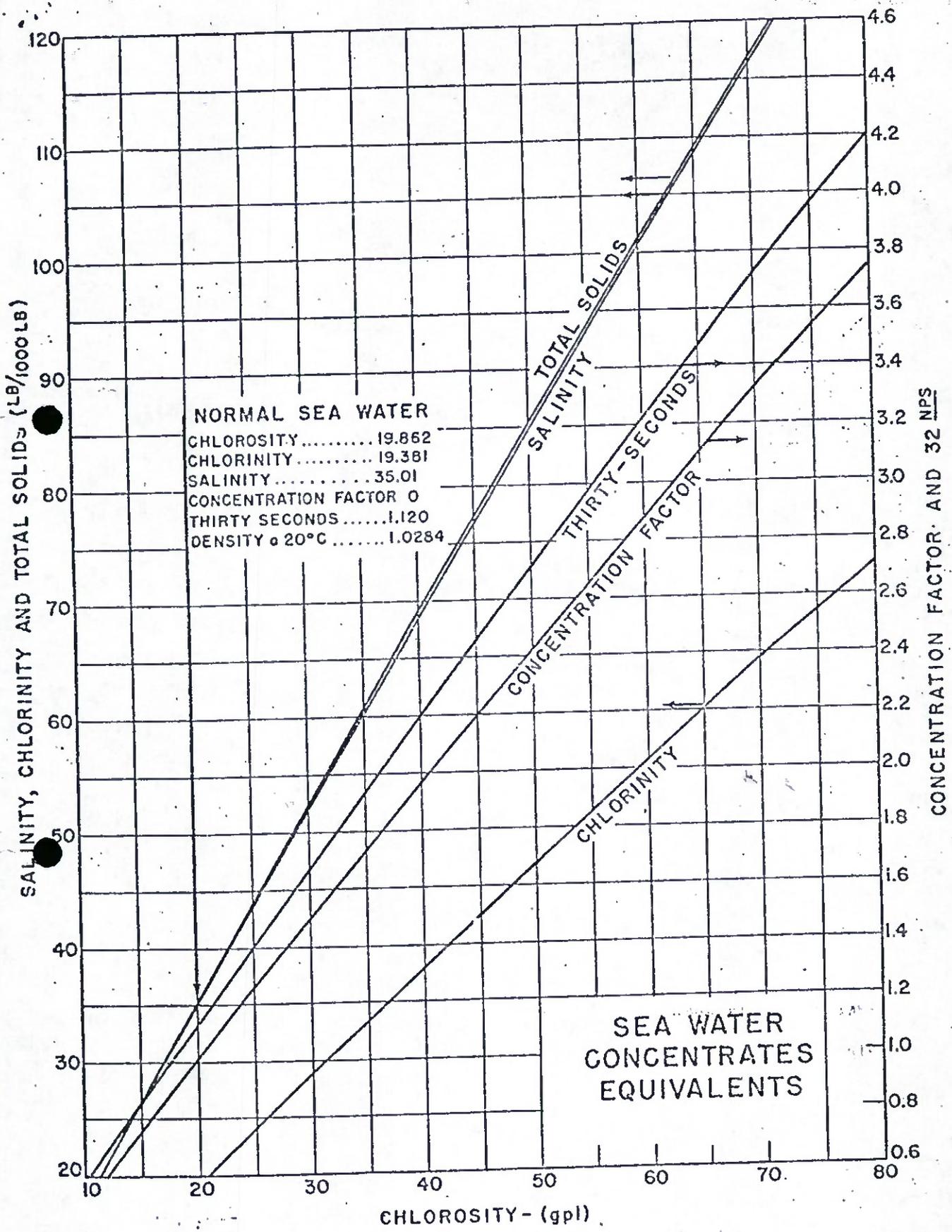


Figure V

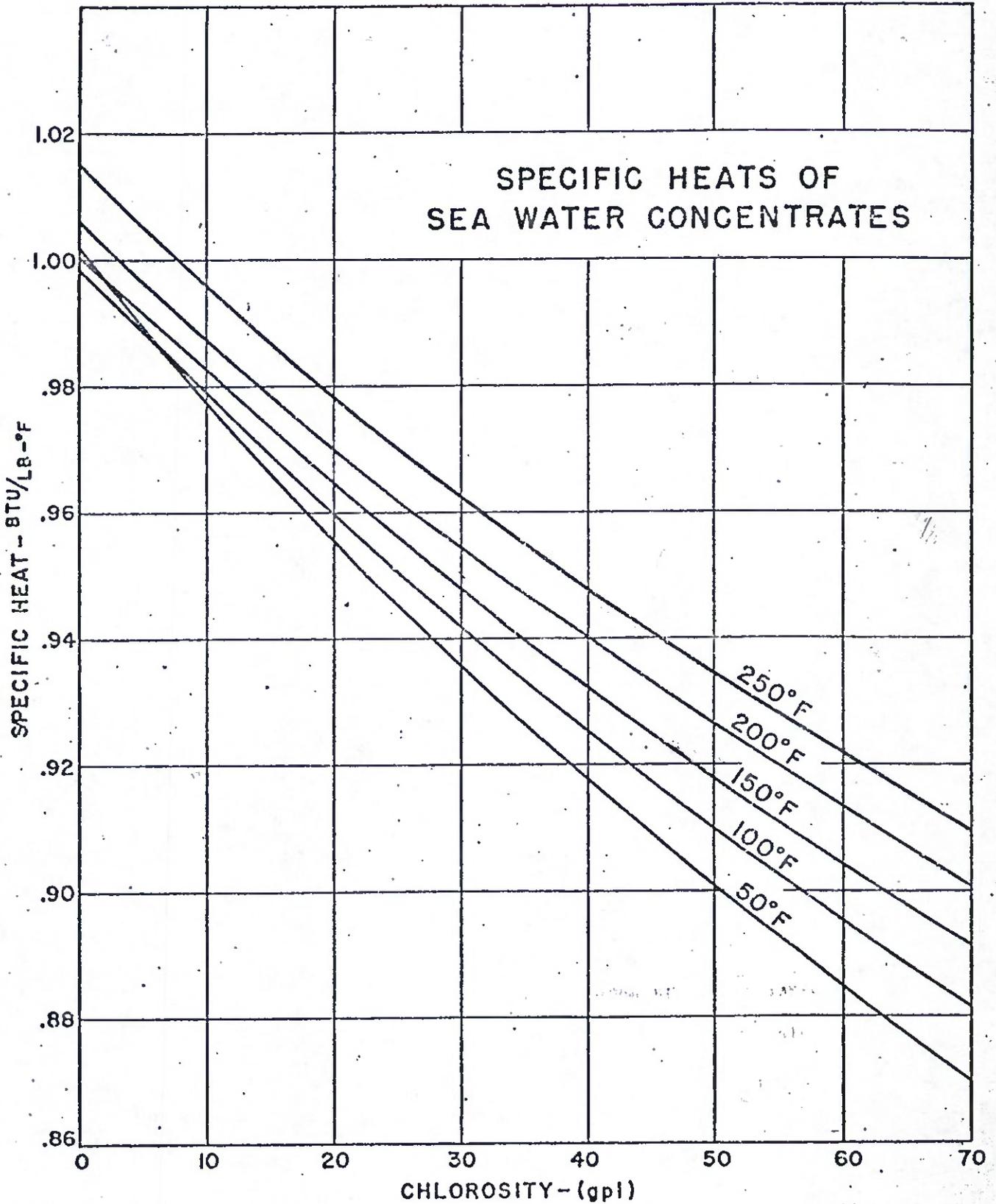
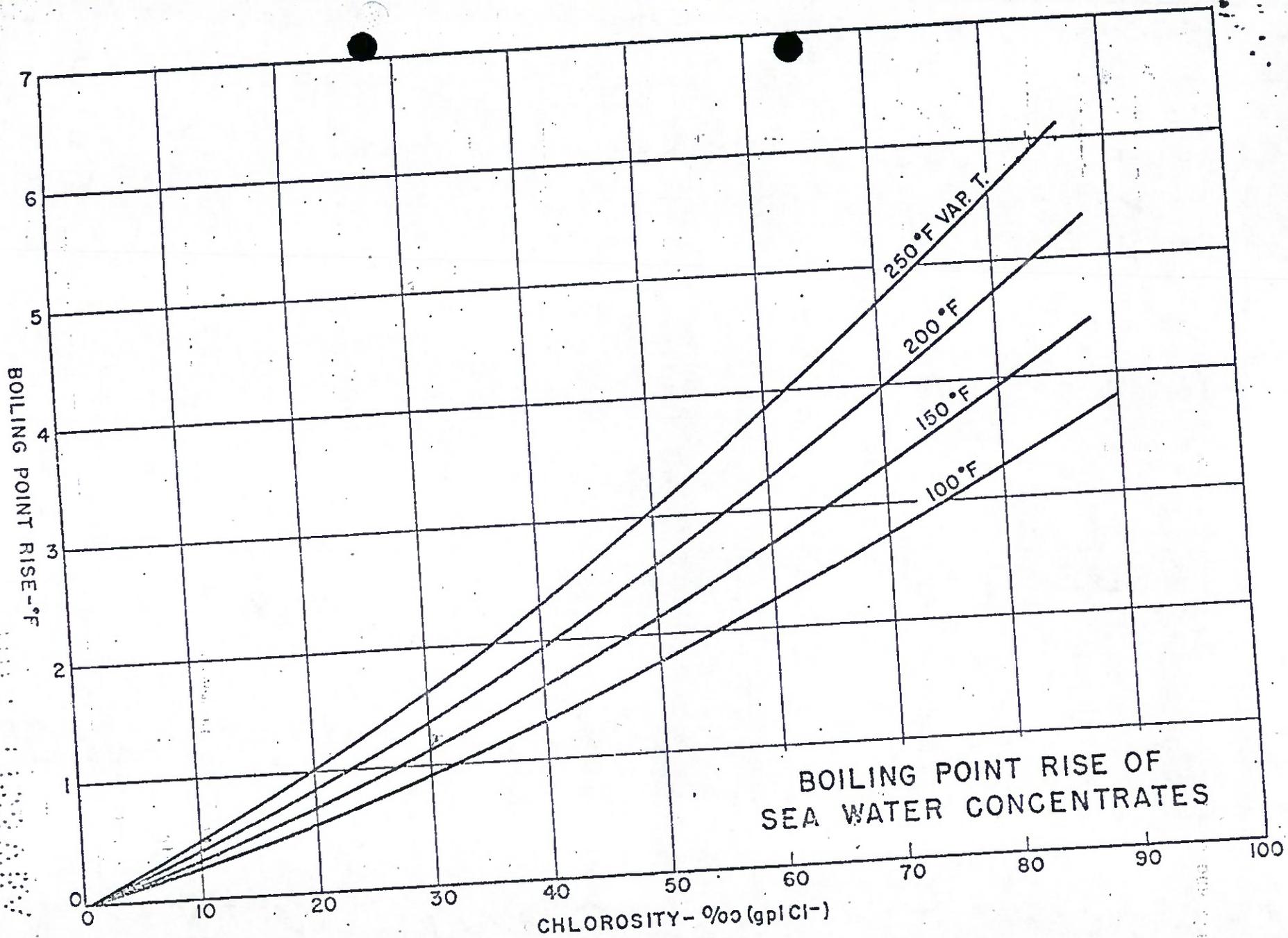


Figure VI



BOILING POINT RISE OF
SEA WATER CONCENTRATES

Figure VII

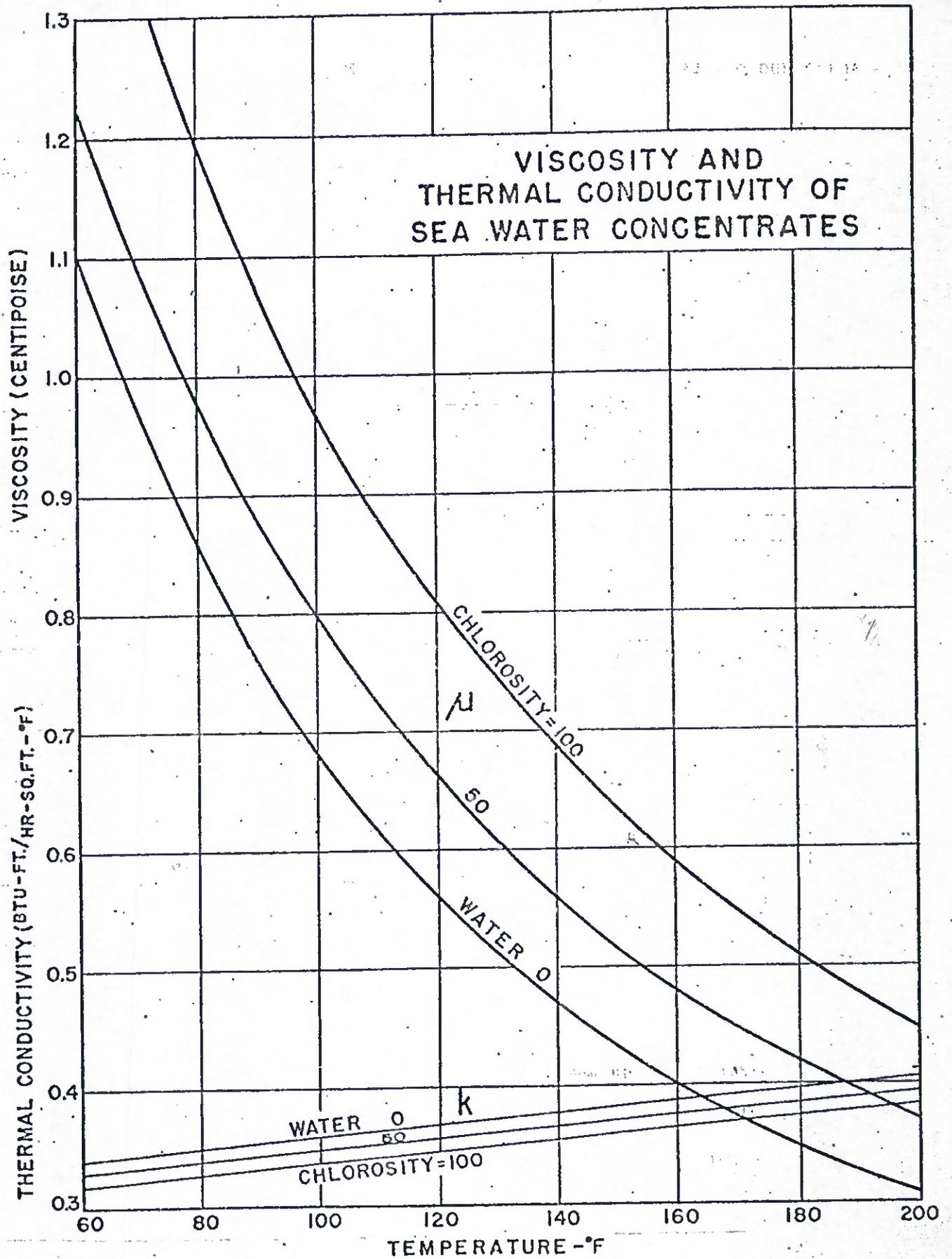


Figure VIII

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