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MINERALIZED SCALE FORMATION DURING OTEC OPERATIONS -A PRELIMINARY CAUTION-

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October 1977

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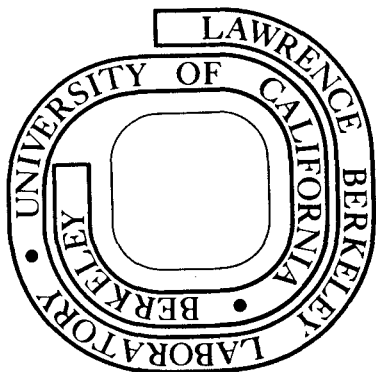
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MINERALIZED SCALE FORMATION  
DURING OTEC OPERATIONS  
-A PRELIMINARY CAUTION-

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## ABSTRACT

Besides the obvious corrosive scales and bio-fouling films formed on surfaces exposed to sea water, mineralogic scales such as carbonates, phosphates, silicates, and oxides may form on critical metallic and non-metallic components in the water circulatory system of an Ocean Thermal Energy Conversion (OTEC) plant. Such minerals may precipitate or replace previous compounds due to (1) physical-chemical changes in the circulating sea water caused by plant operations and (2) nucleation and crystallization sites on exposed surfaces of the plant not found in open ocean sea water. Mineralogic scale is formed similar to boiler scale and pipe scale found in fresh water municipal water systems and to mineralized stones and deposits in organisms such as kidney stones and calculus on teeth. As sea water contains about 3.5% dissolved material, the problem of mineralogic scale formation potentially is more serious in oceanic operations than for fresh water systems. Specifically most mineralogic scales being non-metallic have low thermal conduction properties and their formation would degrade the efficiency of heat transfer on heat exchange surfaces. Also these scales are harder than bio-fouling films and would be more difficult to clean using conventional methods. Several techniques for the prevention or cleaning such scales are available although their efficacy on systems the size of OTEC is unknown at present.

## INTRODUCTION

The following discussion is intended to be only a brief overview of the potential problems caused by the formation of mineralogic scales built up during the operations of an OTEC plant. The author is in no sense an expert on scale or scale formation. However, because of his geologic and oceanographic experience and his long professional association with hydraulic and sanitary engineers, he may possess a comprehensive view of the problem, which is useful to identify broad concerns at this preliminary stage of OTEC's development. Once more specific engineering design criteria and operating technologies are accepted then more precise questions can be posed and analysed by experts in the various disciplines which treat scale formation. Accordingly this paper will provide only prudent guesses as to the potential problems and possible solutions to mineralogic scale formation.

### DEFINITION OF MINERALOGIC SCALE

Scale may be defined as any foreign material deposited on functioning surfaces that impedes the efficiency or reduces the working life of some useful part or operation. Technically, adherent solids are called scales, whereas, loose material formed are called sludge (Hamer and others, 1961, p. 172). Scale deposits may be formed as the result of either organic or inorganic processes or combination of the two. A completely organic scale would be a bacterial or algal film, with a purely organic composition, coating a surface. An example of a pure inorganic scale would be a calcium sulphate deposit precipitated on the walls of boiler tubes due to local saturation caused by the temperature gradient between the boiler fluid and the outside walls. However, organic processes can change local physical chemical condition, such as pH, producing local precipitation of inorganic material. Also, organisms can produce inorganic material as stiffeners or structures (bones, shells, etc.) whose physical properties and chemical composition are essentially identical with inorganically produced minerals. To avoid the dilemma of deciding the functional origin of the particular scale, in this paper, the focus will be on the product and its potential effect on the operations of an OTEC plant. Thus mineralogic scale is used here as all scales with a non-organic composition isostructural and isochemical with recognized minerals. Furthermore, scales due to electrochemical processes such as corrosion will not be discussed as that subject is treated elsewhere. The advantage of identifying scale by its mineralogy is that the physical properties of individual minerals, such as hardness, crystal habit, etc., can be found conveniently in standard mineralogy texts and tables.

### MECHANISM OF FORMATION

Scale formation may be passive or active.

Passive scale is formed by chemical reactions taking place in the environmental media (sea water) on the plant surface. In essence passive scale will form whether the plant is operating or not, so is a function of the material utilized. Active scale is formed as a result of changes in the local environment produced by plant operations such as pumping (potentially changing pressure, temperature, flow velocities, etc.) or heat exchange (changing temperature).

The formation of specific mineralogic scale is governed by physical-electro-chemical processes of which the following are probably the most significant: saturation, replacement, nucleation, scavaging, plating, and templating. The factors that govern the state of saturation are ionic concentration, temperature, pressure, and for many substances pH and Eh. If the fluid bathing the working surface is saturated with respect to various compounds in solution, ideally precipitation should occur spontaneously in the fluid. However actual precipitation can not be predicted from the knowledge of the bulk properties of the fluid and individual equilibrium constants. Actual precipitation is governed by kinetics (Nielsen, 1964) which may or may not be known, particularly in such a complex liquid such as sea water. All that classic state of saturation studies can indicate is the tendency of either precipitation or dissolution to occur. Unfortunately surfaces are attractive sites for precipitation as they are (1) convenient attachment foundations for crystal growth, and (2) generally at different temperatures from the fluid (particularly in heat exchangers) causing local temperature gradients which enhances saturation in various compounds.



Once certain scales form on surfaces, their adherence and hardness (thus the ability to remove them) may be modified by replacement reactions. In replacement the crystallography and chemistry of a pre-existing mineral is changed by the exchange of ions between the crystal and the fluid. A reaction of concern for OTEC is the replacement of phosphate ions for carbonate ions in pre-existing calcium carbonate scale, producing calcium phosphatic scale. Such reaction is likely if phosphate rich sea water is brought from depth. This replacement reaction occurs naturally in the formation of phosphatic nodules by replacement of calcium carbonate in areas of natural upwelling (Ames, 1959; Emery and Atlas, Dietz, 1950). The resultant change in hardness of the scale is shown by comparing chalk ( $\text{CaCO}_3$ ) with teeth (calcium phosphate).

Production of condensation nuclei during operations also may enhance scale formation. Sludge rather than adherent scale is a more likely product. The nuclei spalling off surfaces (corrosion products, erosion products, biogenic shells or tests from films, etc.) become attachment areas for precipitation, and particularly in supersaturated solutions often trigger flash precipitation.

Scavenging, especially of metallic ions, may occur chiefly on surfaces exposed to oxidizing conditions. Goldberg (1954) has proposed this mechanism to explain the inclusion of metallic ions in oceanic ferro-manganese crusts and nodules. In essence, the water flowing over hydrated oxides of iron and manganese converts the surface into an electrode, which attracts metal ions from sea water. The ions then move into a favorable position in the crystallographic lattice of the oxide. The original ferro-manganese crust results from precipitation of iron and manganese as oxides on surfaces in oxidized sea water sim-

ilar to the formation of desert varnish on land. Rates of growth on pre-existing metal surfaces are high. For example, a shell casing dredged up off Southern California had a growth rate on the order of millimeters per year (Goldberg and Arrhenius, 1958,p.199).

Plating is a process akin to scavenging except that the charge may develop directly on the working surface. In plating, major ions are attracted to the surface which form precipitation sites for compounds such as calcium carbonate. A charged surface may be implanted to produce scale as a corrosion preventive (Castle, 1951) or naturally a charge may develop on a working surface due to fluid flow past the surface.

Minerals also can be formed by organic templating. Unlike electro-chemical plating where opposite charges attract, in templating an organic or mineral organic structure provides both the proper charge and geometric configuration for selection of specifically charged and sized ions. Such a process permits apatite to be selected as tooth material and secondarily as calculus between existing teeth. This mechanism may play a role in the formation of other calculi such as urinary bladder stones analysed by Prien and Frondel (1947). Scale formation by templating is likely to occur as a secondary effect of organic film formation in a sea water system.

### PREVIOUSLY IDENTIFIED SCALES

Previous knowledge of mineralogic scale formation is based on experience gained from municipal water systems (Hamer and others, 1961) and marine boilers and evaporators (Latham, 1958). In addition, possible analogs of scale formation in an OTEC system may be found in natural systems, particularly those involving sea water or in organisms whose bodily fluids approximate the composition of sea water (Vinogradov, 1953). Such analogs would include deposits from (1) mineralized springs, (2) evaporite basins, and (3) as organic internal stones, such as urinary and dental calculi. In neither case, the industrial or the natural, is the experience absolutely applicable to OTEC. For example, municipal water systems use fresh water, whereas the pumped fluid in an OTEC system is sea water. Although marine boilers use sea water they function at elevated temperatures whereas OTEC heat exchangers operates at essentially ambient sea water temperatures. Finally the materials used in an OTEC plant are unlikely to be "natural" materials and definitely are not alive. However, use of such previous examples gives some idea of the physical-chemical limits of scale formation and may focus on potential problems which may be avoided by effective design strategies.

Table 1 lists previously identified scale forming minerals based chiefly on fresh water experience. Unfortunately the variety of minerals found on the list precludes any simple avoidance system. Many of the minerals listed, on one hand, form due to high temperature gradients found in steam boilers. Such temperature are unlikely to be encountered in OTEC-type heat exchangers. On the other hand, as shown in Table 2 the composition of fresh water is so dilute, except for silicon and iron, compared with

Table 1

## KNOWN SCALE-FORMING MINERALS

<u>Major Cation</u>	<u>Mineral Name</u>	<u>Formula</u>
	BOILER SCALE <sup>a</sup>	
Calcium	Portlandite	$\text{Ca(OH)}_2$
	Calcite	$\text{CaCO}_3$
	Anhydrite	$\text{CaSO}_4$
	Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$
	Crestmorite	$\text{Ca}_5\text{H}_2(\text{Si}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O} + \text{Ca}_5(\text{PO}_4, \text{SiO}_4, \text{SO}_4)_3(\text{F}, \text{O})$
	Hillebrandite	$\text{Ca}_2(\text{SiO}_4) \cdot \text{H}_2\text{O}$
	Wollastonite	$\text{CaSiO}_3$
Xonotlite	$\text{Ca}_6(\text{OH})_2\text{Si}_6\text{O}_{17}$	
Magnesium	Brucite	$\text{Mg(OH)}_2$
	Periclase	$\text{MgO}$
	Hydromagnesite	$\text{Mg}_5[\text{OH}(\text{CO}_3)_2] \cdot 4\text{H}_2\text{O}$
	Hydrotalcite	$\text{Mg}_6\text{Al}_2[\text{OH}_{16}\text{CO}_3] \cdot 4\text{H}_2\text{O}$
	Chrysotile	$\text{Mg}_6(\text{OH})_8(\text{Si}_4\text{O}_{10})$
	Sepiolite	$\text{Mg}_{2,5}[(\text{H}_2\text{O})_2(\text{OH})(\text{Si}_4)_{10}] \cdot 2\text{H}_2\text{O}$
	Mg Hydroxyphosphate	$\text{Mg}_3(\text{PO}_4)_2 \cdot \text{Mg(OH)}_2$

Table 1 (continued)

<u>Major Cation</u>	<u>Mineral Name</u>	<u>Formula</u>
<u>BOILER SCALE<sup>a</sup></u>		
Silicon	Acmite	$\text{Na, Fe}(\text{Si}_2\text{O}_6)$
	Analcime	$\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$
	Cancrinite	$(\text{Na}_2\text{Ca})_4[\text{CO}_3(\text{H}_2\text{O})(\text{AlSiO}_4)_6]$
	Sodalite	$\text{Na}_8[\text{Cl}_2(\text{AlSiO}_4)_6]$
	Pectolite	$\text{CaNaH}(\text{SiO}_3)_3$
Iron	Hematite	$\text{Fe}_2\text{O}_3$
	Goethite	$\text{FeO}(\text{OH})$
Copper	Atacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$
	Chalcopyrite	$\text{CuFeS}_2$
<u>DENTAL CALCULI<sup>b</sup></u>		
Calcium	Carbonate Apatite	$\text{Ca}_5(\text{PO}_4, \text{CO}_3\text{OH})_3(\text{OH})$
<u>URINARY CALCULI<sup>c</sup></u>		
Calcium	Whewellite	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
	Weddellite	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
	Carbonate Apatite	$\text{Ca}_5(\text{PO}_4, \text{CO}_3\text{OH})_3(\text{OH})$
	Hydroxyl Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$

Table 1 (continued)

<u>Major Cation</u>	<u>Mineral Name</u>	<u>Formula</u>
	Brushite	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
	Whitlockite	$\text{Ca}_3(\text{PO}_4)_2$
Magnesium	Struvite	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$
FERRO-MANGANESE CRUSTS <sup>d</sup>		
Iron	Goethite	$\text{FeO}(\text{OH})$
Manganese	S-Birnessite	$\text{Mn}_7\text{O}_{13} \cdot 5\text{H}_2\text{O}$
	Sodium Birnesite	$\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}$
	Manganous Manganite	$4\text{MnO}_2, \text{Mn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
	Todorokite	$\text{MgMn}_6\text{O}_{12} \cdot 3\text{H}_2\text{O}$
	Psilomelane	$(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$
	Woodruffite	$2(\text{Zn}, \text{Mn}) \cdot 5\text{MnO}_2 \cdot 4\text{H}_2\text{O}$
	Kryptomelane	$\text{KMn}_8\text{O}_{16}$

<sup>a</sup>From Clark (1948, p.362-363)

<sup>b</sup>From Shafer and Hinde (1974)

<sup>c</sup>From Prien and Frondel (1947m p.957)

<sup>d</sup>From von Heimendahl and others (1976, p.70)

All mineral formulae standardized ala Struntz (1957)

Table 2

COMPARISON OF THE COMPOSITION OF  
"AVERAGE RIVER WATER WITH 35 ‰ SEA WATER

Element Ion or Compound	Average River <sup>a</sup> (Parts per Million)	35 ‰ Sea Water <sup>b</sup> (Parts per Million)
Cl	7.8	19,000
Na	6.3	10,500
Mg	4.1	1,300
SO <sub>4</sub>	11.2	2,650
K	2.3	380
Ca	15	400
HCO <sub>3</sub>	58.4	140
Si	13.1	6
Fe	.67	.02 - .002

<sup>a</sup>From Livingston (1963, p.641)

<sup>b</sup>From Sverdrup and others (1942, p.176)

sea water that the increased concentrations may more than compensate for the lower temperatures, especially as most minerals are less soluble with decreasing temperature. Also, because of the greater variety of ions found in sea water compared with fresh water more exotic minerals may form on OTEC surfaces. Without precise design specifications for flow rates, pipe composition and configuration, intake and discharge depths, etc., for OTEC systems it is impossible to accurately predict the composition, amount, and location of mineralogic scale formation.

As Table 1 shows a vast majority of the minerals found as scale are non-metallic and as such would reduce the efficiency of any heat exchanger surface. A comparison of thermal conductivities among some of the common metals and potential scale forming minerals in Table 3 shows how great the reduction is. Thermal conductivity data are not available for the majority of minerals listed in Table 1. However, non-metallic minerals certainly would have thermal conductivity values on the order of those listed in Table 3 or at a minimum of 10 times less than metals.



Table 3

THERMAL CONDUCTIVITIES OF SOME METALS  
AND  
SCALE FORMING MINERALS<sup>a</sup>

<u>Metals</u>	<u>Temperature of Measurement (°C)</u>	<u>Thermal Conductivities (10<sup>-3</sup> cal/cm sec °C)</u>
Aluminum	25°	538
Copper	0°	96
Iron	0°	180
Nickel	0°	174
Zinc	0°	280
 <u>Minerals</u>		
Anhydrite: CaSO <sub>4</sub>	20°	13.4
Calcite: CaCO <sub>3</sub>	0°	10.8 to 12.9
Gypsum: CaSO <sub>4</sub> H <sub>2</sub> O	20°	3.1
Hematite: Fe <sub>2</sub> O <sub>3</sub>	20°	25
Quartz: SiO <sub>2</sub>	0°	17.3 to 32.5

<sup>a</sup>Clark, S.P. (1966, p.460-482).

POSTULATED SCALE FORMATION  
FOR OTEC SYSTEMS USING  
BULK PROPERTIES OF SEA WATER

Given the range of conditions under which an OTEC plant will operate, that is temperature: 30<sup>0</sup> to 50<sup>0</sup>C; pressure 100 to 1 atmospheres; salinity 34 to 38 ‰; pH: 7.6 to 8.3; and Eh: generally oxidizing; and the ionic composition of sea water (see Sverdrup and others, 1942) only the carbonates, calcite and aragonite, are near or above saturation. Carbonate chemistry is discussed in a companion paper by Morse and others (1977). Deposition of carbonates are most likely in the evaporator system as surface tropical waters are supersaturated and somewhat less likely in the condenser system. Calcium phosphatic minerals (apatite to collophane) may replace eventually pre-existing carbonates deposited in the condenser system or even precipitate from solution (Atlas and Pytkowicz, 1977) due to artificial upwelling of phosphate rich water from depth. Such replacement or precipitation is less likely in the evaporators because surface sea water is depleted in phosphates due to concentration in organisms. Sulfates, a troublesome problem in steam boilers, are unlikely to form in OTEC pipes because of the low working temperatures, unless the evaporator fluid is heated to above 40<sup>0</sup>C (see Hamer and others, 1961, p.431-435). Hydrated calcium sulfate-gypsum is the most likely sulfate scale formed. Sulfides could form in anaerobic (anoxic) sections, through the agency of sulfate reducing bacteria, particularly in the condenser if the cooling water is drawn from the oxygen minimum zone, with additional oxygen reduction in the pipe due to decay of entrained organisms. Sulfide deposition locally is possible also in the evaporator if the entrained dead organic matter is permitted to adhere to heat exchanger surfaces.

Fortunately the biomass entrained in the cold water pipe should be much less than in the evaporator intake system where ambient oxygen values should be larger. Oxides particularly ferro-manganese complex mixtures will be deposited on exterior and possibly interior surfaces exposed to flow of oxygenated waters. Lower oxygen values in the pipes due to decaying entrained organisms would tend to inhibit oxide formation on interior pipe surfaces. Oxide deposition on exterior surfaces would occur on both concrete or metallic structures although the rate of deposition would be greater on metallic surfaces. Formation of silicates, because of the low levels of silica maintained in sea water due to utilization by organisms probably will not be a problem particularly in the evaporators. However, as silica increases in concentration with depth (Sverdrup and others, 1942, p.245) silicates are most likely to be deposited in the condenser.

### AVOIDANCE OF SCALE

Based on experience, chiefly in fresh water, great success in avoiding scale formation has been achieved by pretreating the fluid which comes in contact with the working surfaces (Hamer and others, 1961). Pre-treatment includes (1) pre-precipitation of critical ions by addition of chemicals which reduces the state of saturation of scale forming minerals, or coagulates potential scale into removable sludge; (2) filtration to remove unsettled pre-precipitation flocs which could be condensation nuclei in the process stream or be deposited on the working surfaces; (3) ion-exchange (water-softening) removal of selected ions and their replacement with more soluble ions; (4) evaporation to precipitation with periodic blow-down which converts the feed fluid to one of low concentrations; (5) reduction of pH by acid or ferric chloride which generally increases the solubility; and (6) addition of a surface active agent which modify the crystal habit or inhibits crystallization of scale forming minerals.

For OTEC systems because of the large volumes of water flowing by the heat exchangers only methods (5) pH reduction and (6) addition of surface active agent seem at first glance feasible pre-treatment strategies. Effective quantities of pH reducers required are given in Table 4. As brought out at the 1977 Seattle OTEC conference acid addition is likely to be prohibitively expensive. Also the usefulness of pH reduction must be tempered by the environmental effects of dumping low pH water into the ocean. Of the three compounds listed in Table 4 HCl and sodium bisulfate probably have the least residual long-term toxicity due to the high concentration of such ions in sea water and the buffer capacity of the ambient ocean.

Table 4

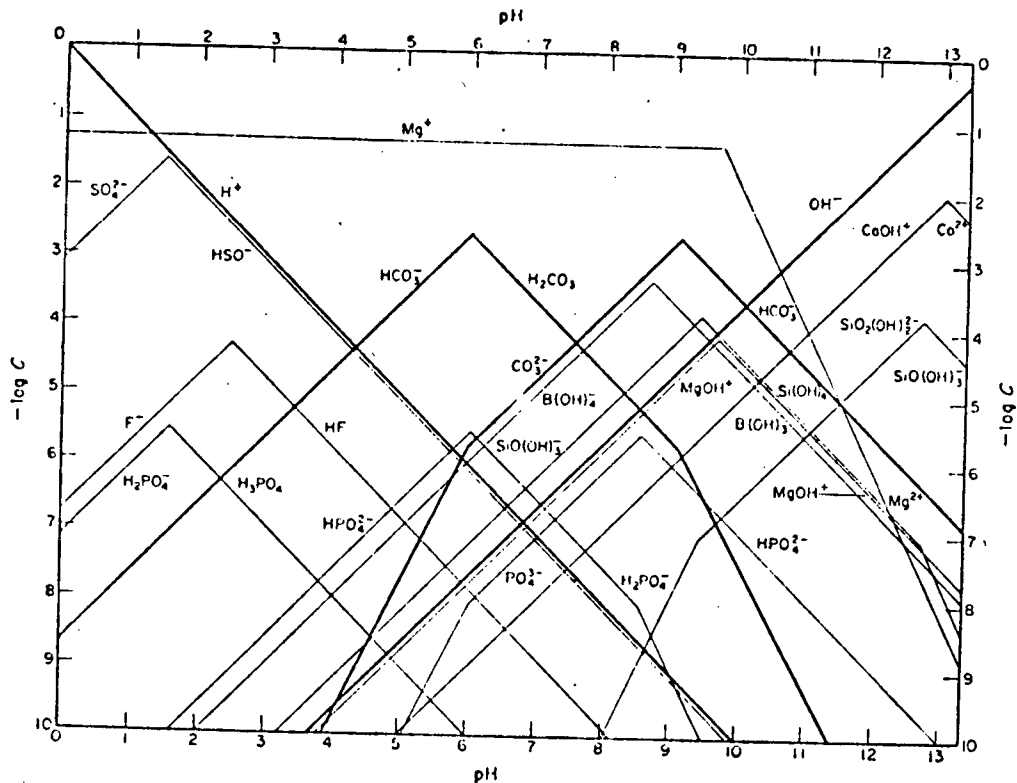
pH REDUCTION<sup>a</sup>

<u>Reagent</u>	<u>Effective Addition for Scale Prevention Pounds/Ton of Seawater Treated</u>
HCl plus a corrosive inhibitor	0.32
Sodium Bisulfate	0.53
Ferric Chloride	0.225 - 0.51

<sup>a</sup>From Hamer and others (1961, p.154).

Large amounts of iron from ferric chloride additions potentially may have more impact on the local water chemistry as iron is in low concentrations in sea water and is readily utilized by organisms. The addition of low pH water to the environment may be analogous to the introduction of acidic fluids to sea water from natural submarine volcanic sources (see examples in White and Waring, 1963, p. K-23). Reduction of the ambient pH would have positive bio-fouling properties the effect of pH modification on sea water chemistry is shown in Fig. 1 (Edmond, 1970) which diagrams the concentration of major inorganic species in sea water as a function of pH. Such a diagram used in conjunction with information on the equilibrium constants for potential scale forming minerals would be useful in estimation of states of saturation produced by pH modification. The most attractive scale prevention scheme is the use of surface active agents because of the small concentrations of material used. A list of those agents previously used are given in Table 5. Some of these compounds such as polyphosphates act like a reverse template by coating specific ions so they cannot combine to form a scale-forming precipitate. Others, such as the sodium salt of methane disulphonic acid in doses as low as 20-30 parts per million modify the crystal habit of  $Mg(OH)_2$  scale so that it does not adhere to the working surface long and flakes off after reaching a critical thickness (Hamer and others, 1961, p. 154). The environmental effects of surface active agents are not known for operations the size of OTEC. Surface active agents possibly could produce physiological effects on organic processes across membranes if used in large amounts even at low concentrations.

Figure 1



Bjerrum plot for sea water showing the inorganic protolytes occurring in total concentrations greater than  $10^{-6}$  M. Values for concentrations and thermodynamic constants are given in Table 1. The horizontal lines representing concentrations in regions where variation with pH is small are omitted in accordance with SILLÉN (1959) save in the case of magnesium where the precipitation of  $Mg(OH)_2$  is illustrated. The representation for species of acids other than carbonic, boric and phosphoric is only diagrammatic owing to uncertainties in the constants. These uncertainties do not significantly affect the arguments concerning the treatment of  $Ar$ .

From Edmond (1970, p. 741)

Table 5

pH REDUCTION<sup>a</sup>

<u>Reagent</u>	<u>Effective Addition for Scale Prevention Pounds/Ton of Seawater Treated</u>
HCl plus a corrosive inhibitor	0.32
Sodium Bisulfate	0.53
Ferric Chloride	0.225 - 0.51

<sup>a</sup>From Hamer and others (1961, p.154).



In summary, although chemical pre-treatment of the feed sea water could prevent various types of scale formation, the large volumes of sea water used require such large quantities of chemicals at probably considerable cost to preclude all but limited amounts of pre-treatment.

A simpler and more fundamental way to avoid or reduce scale formation is by proper design strategies. In general solubilities are increased by mixing, preventing local concentration gradients. Thus the geometry of the flow system in a section, where scale may be a problem, should include graceful curves and avoid angular bends which could cause dead spot in the flow. Accordingly vane type heat exchangers, although they increase the exchangeable surface area, also are prime surfaces for scale formation, particularly at the base of the vane. The natural analog of this type of scale formation is shown in the location of calculi on teeth.

Bubbles due to depressuration in the condenser could act as precipitation nuclei and bubble formation on the walls of the heat exchangers may degrade the thermal conductivity of the system and enhance scale formation (Matthews, 1948, p.57). Bubble traps before the heat exchangers may mitigate the problem; although the best solution is to design the system so that the dissolved gases in sea water stay in solution for the indicated pressure drop by adjusting the distance between the cold water intake and condenser.

Both organic and inorganic particles in the ambient water plus corrosion and cleaning debris also could act as precipitation nuclei. This may be a more severe problem in the evaporator as near surface water above the top of the pycnocline are likely to be more turbid than

deep water. The larger flow volume probably prohibit the use of screens fine enough to remove most of the particles. However, it might be feasible to place coarse screens and an expansion chamber with an easily drainable or flusable sediment trap just ahead of the heat exchanger sections.

### REMOVAL OF SCALE

Once scale has formed removal is difficult without removal of the affected portion from the working stream. Chemical methods, such as acid treatment of the fluid are effective if used before the scale builds up. Unfortunately, due to kinetics (Nancollas and Reddy, 1974) precipitation of many materials is easier than to re-dissolve them, especially if the scale formation has proceeded to the replacement stage or additional minerals with different saturation states and kinetics has deposited on the pre-existing scale. Increasing the chemical dosage, such as using more acid, may solve the scale problem but disproportionately increase the environment problem in the effluent. Because of the hardness of mineralogic scale, mechanical techniques designed for the removal of organic films may not be effective against adherent scale. The use of more abrasive techniques have the disadvantage of potentially abrading the surface as well as removing the scale.

Electrical methods have been used on a small scale in scale removal (Castle, 1951). Initially the formation of scale, such as calcium carbonate, is promoted by plating at the appropriate current density. Then the polarity of the surface is reversed periodically such that the scale is repelled from the surface and flakes off. Whether the proper charge density can be maintained is questionable economically on large surface areas such as found on OTEC systems. Also, during the plating step the thermal efficiency of the heat exchanger will be degraded. Due to the complex ionic composition of sea water, continual maintenance of a surface charge which would prevent formation of calcium carbonate scale, probably would enhance formation of some other mineralogic scale.

SUMMARY OF FINDINGS

- I. Mineralogic scale is part of the overall problem of degradation of the working capacities of surfaces by natural processes acting in sea water. As such mineralogic scale should be considered in the context of a continuum ranging from purely organic films to inorganic solid scales forming on surfaces of OTEC plants.
- II. Mineralogic scale may be a very serious problem in open ocean tropical sites because of the physical-chemical changes encountered during OTEC operations. In fact, mineralogic scale may be more of a problem than bio-fouling particularly in open-ocean site with low biologic seed populations.
- III. Avoidance and early removal of mineralogic scale is preferable to removal after significant accumulation because of the hardness of scale and the unfavorable kinetics of re-solution. Avoidance can be enhanced by design strategies which minimize precipitation sites. Continuous or semi-continuous mechanical removal schemes seems environmental preferable to extensive use of dissolving chemicals.

RECOMMENDATIONS FOR FURTHER STUDIES/ACTION

- A. All pipe/heat exchanger designs should be examined for optimum flow geometries to avoid dead spots.
- B. Bio-fouling avoidance/removal schemes should be investigated for possible subtle enhancement of mineral scale formation.
- C. State of saturation information should be calculated for potential scale forming minerals as a function of flow strategies (that is depth of intake versus depth of discharge including any mixing).
- D. Monitoring schemes at test sites should include parameters useful for kinetic and state of saturation calculations.
- E. During pilot plant tests of the flow of sea water through heat exchangers, chemical/mineralogical analyses of film/scale material should be made as well as biological analyses; preferably as a function of cross-section to determine the time-thickness hierarchy of scale formation.

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