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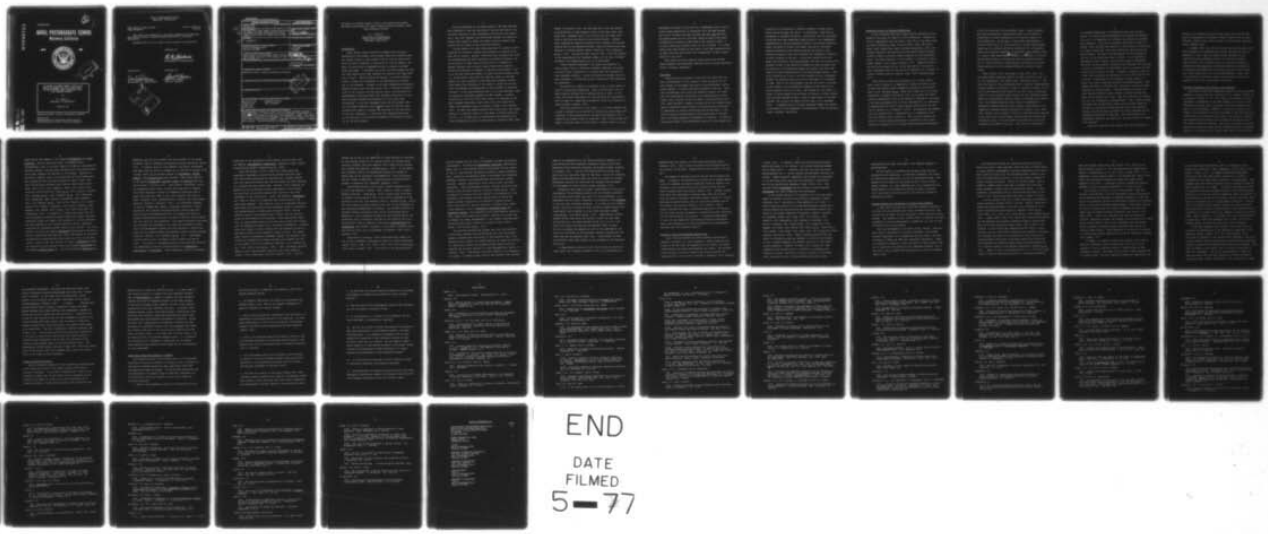

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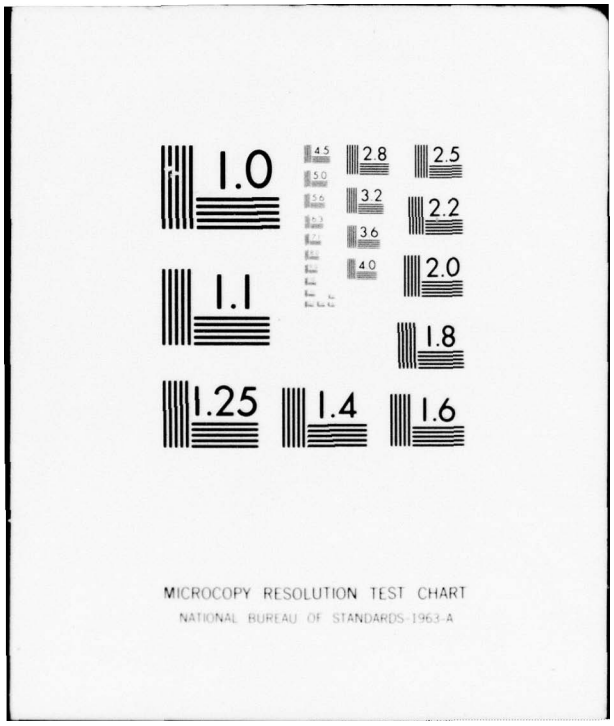
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THE NATURE OF PRIMARY ORGANIC FILMS IN THE MARINE ENVIRONMENT AND THEIR SIGNIFICANCE FOR OCEAN THERMAL ENERGY CONVERSION (OTEC) HEAT EXCHANGE SURFACES

by

E.C. Haderlie
Department of Oceanography

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Rear Admiral Isham Linder
Superintendent

Jack R. Borsting
Provost

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Prepared by:

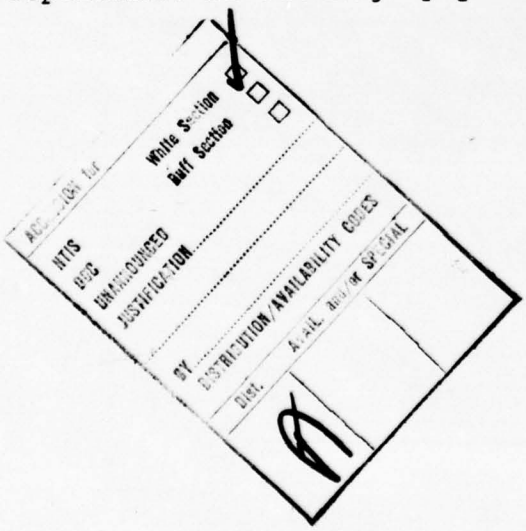
E. C. Haderlie
E. C. Haderlie
Department of Oceanography

Reviewed by:

D. F. Leipper
D. F. Leipper, Chairman
Department of Oceanography

Released by:

Robert R. Fossum
Robert R. Fossum
Dean of Research



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The development of bacterial slime films on the heat exchanger surfaces of OTEC power plants is likely to be of critical importance in determining if OTEC closed cycle systems are technically and economically viable. This report surveys our present state of knowledge as to the nature and behavior of primary films in the marine environment. Areas where further research is needed are indicated. Includes extensive bibliography.

The Nature of Primary Organic Films in the Marine Environment and Their Significance for Ocean Thermal Energy Conversion (OTEC) Heat Exchange Surfaces

E. C. Haderlie
Department of Oceanography
Naval Postgraduate School
Monterey, California

Introduction

Ocean thermal energy conversion schemes being seriously considered at the present time include closed-cycle systems where the thermal energy in warm surface water of certain ocean sites would be used to evaporate a working fluid (such as ammonia) the vapor of which would be expanded through a turbine to produce electrical power. A condenser utilizing cold water pumped up from the ocean depths would then condense the working fluid vapor back into a liquid. These closed-cycle systems, of various configurations, include heat exchangers in the evaporators or boilers and in the condenser. Because of the small temperature difference between surface water and deep water, even in the most favorable sites in the tropical and sub-tropical ocean, the resulting low thermodynamic efficiency means that enormous quantities of water must be passed through heat exchangers of very great size. Furthermore, in the heat exchangers there must be minimal tube wall thickness separating the sea water from the working fluid. Anything that tends to increase the thickness of the tube walls of the heat exchangers, or decreases heat exchange efficiency in any other way, will seriously jeopardize the technical viability of the OTEC concept.

From the beginning of the OTEC program it has been realized that biofouling in the sea could pose a serious challenge to the efficient operation of heat exchangers, particularly the evaporators, and could threaten the entire OTEC program, yet design engineers have tended to ignore the threat and have assumed that someone had the answer to any biofouling problem.

To most people, the term biofouling means the growth of such organisms as barnacles, mussels and seaweeds on a surface where they are not wanted. However, biofouling also includes thin films of microorganisms and their excretory or secretory products, and the formation of these films are the first in a sequence of dynamic chemical and biological events which occur whenever a clean solid substrate is exposed to the marine environment. And it is the very rapid development of these so-called primary films (or microfouling) which pose the greatest threat to the OTEC system, for their presence on the large heat exchange surfaces could reduce the efficiency of the system to below the critical level long before a macroscopically visible growth of organisms occurred. It has been calculated that on the heat exchanger tubes of titanium or aluminum proposed for OTEC systems, a primary fouling film 0.001 inch thick would cause a 10% decrease in the heat transfer coefficient, and a film 0.010 inch thick would cause a 50% decrease (Laity in Perrigo & Jensen, 1976; Stupian, 1976). We know from several studies that films within this range develop in a period of days or a few weeks in coastal waters of the U.S., but we know next to nothing about the possibility of films developing and rates of development at potential OTEC sites.

Dexter (in Stupian, 1976), who has made one of the few studies of microfouling in warm tropical waters of the open ocean (Sargosso Sea), estimates that a film 0.002-0.005 inch thick could form in less than one month in warm surface waters. Studies being supported by ERDA off Ke-ahole Point in Hawaii are now generating data on how important primary films are and how fast they develop in tropical Pacific waters (Fetkovich, 1976; Fetkovich et al., 1975). Preliminary data indicate that a film does develop on the experimental heat exchanger tubes, but the rate, ultimate thickness, and composition are yet to be determined.

A more complete knowledge of the nature and behavior of these primary films is therefore extremely important if we hope to prevent their occurrence or to remove them once attached to heat exchanger surfaces. Unless the problem of primary films on heat exchangers is solved the entire closed-cycle OTEC system may be unworkable.

The control or removal of microbial films in other areas is also of considerable importance. This is particularly true in waste disposal systems and in cooling towers on land. In one study the initial efficiency of a cooling tower was decreased by 80% in a span of 7 weeks due to bacterial slime film formation on tower surfaces (Purkiss, 1972).

The prime objective of this report is to bring together the diverse literature on the subject of microfouling and primary film formation on solid substrates in the marine environment, and to summarize our present state of knowledge. Most of the studies and papers cited here report on work done in coastal waters or in the

laboratory, and much of this work will undoubtedly prove to be of little direct application in connection with the OTEC program. But we have to begin with what is known and what has been done, and common sense tells us that even though we know little about microfouling at potential OTEC sites in the tropical ocean, it is quite likely that primary films will be a problem. It is also likely that these films will have many of the same characteristics as those that have been found to be cosmopolitan in many coastal regions of the world.

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Historical

Zobell and his colleagues in the 1930s and 1940s were the first investigators in this country to look critically at the early stages of settlement and growth of microorganisms, particularly bacteria, on solid substrates immersed in the sea. There then followed many years with only sporadic studies, for there were few investigators interested in the bacteriology of ocean waters. Then, starting in the mid-1960s, but particularly since 1970, there has been a number of scientists who have become interested in dissolved organic matter in sea water which can attach to substrates, in marine bacteriology and microbiology, in the initial stages of microfouling on solid substrates in the sea, and in the broad problems of bioadhesion in general. A review of publication dates in the Bibliography section of this report will

illustrate the blossoming of research interest in these allied fields during the past ten years. In particular, Corpe and his colleagues at Columbia University, and Mitchell and his co-workers at Harvard have made remarkable contributions to our fundamental understanding of marine periphytic bacteria and primary bacterial films, and Baier of Cornell and Neihof and Loeb at the Naval Research Laboratory have helped elucidate the nature of the "molecular fouling" layer that preceeds the attachment of bacteria to solid surfaces in the sea. In the work leading up to this report the scientific literature between 1935 and 1977 dealing with microbial films in the marine environment has been surveyed, and the majority of the pertinent papers and reports have been read. These are listed alphabetically in the Bibliography section. Complete citations are given in the bibliography so that interested workers can determine from the title if the paper is of interest to them. Most of the bibliographic entries are cited in the body of this report, but no exhaustive attempt has been made to abstract material from all of them. The purpose of this report is simply to bring together the pertinent literature, briefly discuss what has been learned and how it might be applicable to the OTEC program, and to point out where critical gaps in our knowledge exist.. A complete file of the most important papers and reports is maintained in the Department of Oceanography, Naval Postgraduate School, Monterey, California.

Molecular Fouling or Surface Conditioning

It has long been known that organic matter dissolved or suspended in sea water can adsorb to solid substrates. Perhaps the first to demonstrate this was Zobell (1943) but it has more recently been confirmed by Bader, Hood and Smith (1960) and others. Adams (1969) showed that glass, although biologically inert, has surface reactivity and the surface silica bonds attract various hydroxyl, methyl, and amino groups dissolved in the surrounding water. Sea water contains, on the average, 1-3 mg/liter organic carbon (Menzel, 1974; Riley & Chester, 1971). Apparently much of the non-living organic matter in the sea occurs in the form of small aggregates which is the result of adsorption to a variety of nuclei including tiny air bubbles (Riley, 1963; Tosteson et al., 1973).

Thus when any clean solid substrate, be it glass, metal, wood, stone or plastic, is immersed in natural sea water a layer of nonliving organic matter immediately adsorbs to the surface. Baier (1970) and Baier et al. (1968) have looked into the various mechanisms of adhesion, and Baier (1973) has studied the events occurring immediately after a new surface is immersed in sea water. It has been determined that the first acquired film is a monolayer of glycoprotein and that it might require several hours for the film to develop to a thickness of 200 Å. As molecules are adsorbed they are changed from a 3 dimensional to a 2 dimensional form and this modifies their reactivity. The "critical surface tension" of the now coated surface may be modified so that strong bonding is possible with the exuded mucopolysaccharide components

of the first arriving living bacterial cells. Baier considers that such glycoprotein "conditioning films" are an essential prerequisite to later adsorption of any cellular material to solid substrates. He was able to make direct measurements on the thin films using (a) surface-specific infrared spectroscopy (based upon an internal reflection technique),(b) ellipsometry (based upon external reflection of polarized, monochromatic rays), (c) contact angle measurements (leading to inference of relative surface-free energy of the material and any acquired coating), and (d) contact potential determination (reflecting the initial resting potential and the change effected by acquired organic films).

Loeb & Neihof (1975) and Neihof & Loeb (1972, 1974, 1977) have made several detailed studies of marine condition films, or, as they appropiately call these films, "molecular fouling". They note that material with electropositive or strongly electronegative surface charges are unlikely to exist in natural sea water, for as soon as such materials are placed in the sea a rapid interaction occurs with the dissoved organic matter and this adsorbed material imparts a characteristic negative charge to surfaces after adsorption. The adsorbed layer may also alter the hydrophobic or hydrophilic characteristics of the surface, charge density, and chemically functional groups available for reaction (Bull, 1964). Loeb & Neihof (1975) studied a variety of solid materials immersed in sea water from various coastal regions and from tropical and subtropical water in the Carribbean off Panama and in the Gulf of Mexico 350 km WNW of Key West. They used the techniques of

(a) microelectrophoresis for determining electrical surface charge, (b) contact angle measurements for determining wettability, and (c) ellipsometry for studying the kinetics of adsorbed film formation. This latter technique (described in detail by Rothen, 1968) involves the analysis of the elliptical polarization of a beam of polarized light after reflection from the surface being studied. The data gives information on the thickness of the film if the refractive index in known. In one experiment performed by Loeb & Neihof, platinum was placed in Chesapeake Bay water; within minutes a molecular film developed and continued to grow in thickness at an appreciable rate for a period of hours, levelling off at about 20 hours. Assuming a refractive index of 1.338, they calculated the molecular film to be 800 Å thick after 20 hours. To determine if the adsorbed film was organic in nature they used a technique described by Armstrong et al. (1966) whereby sea water is radiated with ultraviolet light which photo-oxidizes all organic matter. Surfaces exposed to natural sea water develop molecular films; suraces in photo-oxidized sea water do not develop such films. Thus the films must be organic, and this was confirmed by electrophoresis. Loeb & Neihof further confirmed that the molecular fouling film was electronegative, and that it consisted of humic materials which were probably derived from the excretory products of living organisms and the decompostion products of dead ones. The films proved to be exceedingly tenacious and remained on surfaces removed to organic-free sea water.

Once this relatively thin organic film has developed on a

surface it is possible that the surface would then have the capacity to cencentrate low molecular weight organics such as carbohydrates, organic acids (such as humic or fulvic acids) and amino acids (Duursma, 1965).

In summary then, the very first event which occurs when a new solid substrate is introduced into natural sea water is the adsorption of a thin layer of organic matter derived from the dissolved organic substances found in all natural sea water. Loeb & Neihof (1975) correctly point out that most studies of immersed surfaces have not distinguished between the adsorption of dissolved substances from the natural sea water and the somewhat later colonization by living microorganisms. Corpe (1977) in his excellent up-to-date review (which should be read by all workers in the field) also stresses this point.

Bacterial Attachment and Bacterial Film Formation

The organic films which immediately adsorb to solid substrates immersed in natural sea water and build up in a period of hours to a thickness of 800 Å (=3.12 x 10^{-6} inches) are probably of little importance in themselves to the OTEC concept, for a film of this thickness would have little influence on the heat transfer efficiency of heat exchangers. However, as soon as an organic film is present living bacterial cells are attracted to the film and ultimately settle on and colonize the surface, and in doing so secrete muco-polysaccharide materials which anchor the bacterial cells to the organic film-coated surface. This layer of bacteria, plus the secreted extracellular materials and accumulated debris ultimately results in a relatively much thicker layer which in the past has

been referred to as the "primary film", "bacterial fouling film", or "slime layer" (Horbund & Freiberger, 1970). The latter name has been applied because the film ultimately becomes thick enough to feel slippery or slimy. It is this bacteria-associated film which is of concern to the OTEC program, for the film may build up to a thickness incompatible with efficient heat exchanger operation at the small delta t of OTEC sites. At the present state of our knowledge, however, we do not know if film-forming bacteria are abundant, common or rare in warm tropical surface water at potential OTEC sites (but we have no reason to believe they are not present), nor do we know how fast bacterial films, if any, will develop. The only published data presently available from tropical water are from the Sargasso Sea (Dexter, 1974, 1975) where "microfouling" occurred on surfaces exposed in the upper 500 m of water. The known cosmopolitan occurrence of periphytic bacteria (i.e., those living in contact with a surface) in coastal waters in both temperate and sub-tropical regions, and the ability of many of these to form relatively thick film on surfaces, leads one to conclude that film-forming bacteria probably occur in all ocean waters. The fact that the U.S. Navy currently has a serious problem in keeping periscope head windows and radomes on nuclear submarines free of film-forming organisms indicates the bacteria are there. These submarines often patrol open ocean water, far from coastal areas, and often at considerable depth. Optical oceanographic instruments attached to buoys in the tropics and near the bottom at great depths often become inoperable due to the formation of a translucent film over the optical sensors. We must

assume, therefore, that film-forming bacteria occur in the ocean at potential OTEC sites, and that their behavior is similar to that exibited bv the ubiquitous film-forming bacteria in coastal waters which have been investigated in some detail. By reviewing what has been learned regarding these bacteria from coastal waters we will be in a much better position to plan and execute research projects at OTEC sites which will generate data that are crucial in making decisions on the technical viability of the OTEC program.

The fact that bacteria and other microorganisms and their products are responsible for the rapid formation of microbial films on solid surfaces immersed in the sea has long been known. Zobell and Allen (1935) found that glass slides exposed for as little as 1 hour in natural sea water attracted bacteria which attached to the surface firmly enough that they were not dislodged by normal washing. They also demonstrated that although bacteria potentially capable of settlement were present in the ambient water in numbers of only hundreds per ml, once settled the bacteria divided and grew rapidly to numbers of over 700,000 per cm^2 of surface area within 24 hours and to several millions after a few days. This was the first indication that a solid substrate enhanced the growth potential of certain marine bacteria. Other workers have reported that bacteria from aquatic habitats live primarily attaced to solid substrates or to one another rather than as free cells (Bott & Brock, 1970). Zobell and Allen reported that between 40 and 50 species of marine bacteria could be isolated from the surface of glass slides immersed in sea water at La Jolla, California, for a few days, and from these they

named several new species in the genera Achromobacter and Flavobacterium. Most of these were short, rod-shaped bacilli (pseudomonads) from 1-2 μm long, nearly all showed a gram-negative staining reaction, and most were enclosed within well-defined capsules which cemented the bacteria to the surface. Bacteria in the form of spheres (cocci) and curved spirilla were seldom seen. This pioneering work was later extended by Zobell (1939, 1943, 1946) and has been confirmed many times by other workers (Bott & Brock, 1970; Cviic, 1953; Campbell & Cobet, 1970; Corpe 1970a, 1972a,1973,1974a,1974b,1977; Corpe et al. 1976; DiSalvo & Daniels, 1975; Friedman et al., 1969; Gerchakov et al., 1977; Hendricks, 1974; Himmelfarb, 1964; Horbund & Freiberger, 1964; Marshall, 1971, 1973; Marshall et al., 1971a 1971b; O'Neill, 1971; O'Neill & Wilcox, 1971; Sechler & Gunderson, 1973; Starr & Skerman, 1965; Waksman, 1941; Whedon, 1940; Wilcox, 1970; Wood, 1950,1967; and Zvyagintsev, 1959). In general all workers have found that the first organisms to settle are motile forms that exibit a positive chemotaxis toward the organic film adsorbed to a solid substrate, and once attached to the surface reproduce rapidly, apparently stimulated by increased nutrient levels on the surface. The first bacteria to arrive are mainly Pseudomonas species which are motile, polarly flagellated, gram-negative, short rods capable of secreting extracellular polysaccharides which anchor the cells to the substrate. Within a few days (usually 3-5 days), Pseudomonas species are replaced by other bactera such as the stalked Caulobacter sp., the budding Hyphomicrobium sp., and the filamentous Saprospira sp.

Depending upon the site studied, any one of these, or all three, ultimately come to dominate the bacterial fouling population (Corpe, 1973). In coastal water at Port Hueneme, California, pseudomads have been found to settle in numbers up to 1260/cm^2 of surface after 2 hours; after one day several species of Pseudomonas, Achromobacter, and Flavobacterium were isolated. Later other bacteria in the genera Micrococcus, Sarcina, Vibrio and Bacillus were also found (O'Neill & Wilcox, 1971). Using special techniques, including removable plastic films, workers have been able to compare the initial bacterial fouling on transparent materials such as glass and plexiglass (used in most early studies) with that on steel, aluminum, monel, phosphorbronze, plastics, and other opaque materials (Sechler & Gunderson, 1973). All substrates immersed in water at Kaneohe Bay, Hawaii, ultimately attracted a similar microflora, but although rod-shaped bacteria settled and grew before other microorganisms settled, the numbers and kinds of bacteria found during the first 2-3 days of exposure varied greatly with the nature of the substratum. The scanning electron microscope has also been used successfully to study the succession of periphytic microorganisms on metal and glass surfaces in natural sea water and the results confirm the sequence noted by earlier workers (DiSalvo & Daniels, 1975; Gerchakov et al., 1977). Rod-shaped bacteria settle first, followed by other bacteria and marine fungi. Nine genera of filamentous marine fungi have been isolated from experimental surfaces including species of Aspergillus, Penicillium and Nigrospora. Some filamentous fungi may ultimately

contribute to the thickness of the microbial fouling layer, and one species, Leptosphaeria albopunctata, produces a highly viscous polysaccharide exudate (Szaniszlo et al., 1968).

Young and Mitchell (1973a, 1973b) have investigated the chemotactic responses of motile marine bacteria and have found that these forms concentrate on surfaces with a primary organic film, the implication being that they can detect the film nutrients at a distance and move toward them. Marshall (1973) observed the behavior of motile bacteria as they approached a solid surface and found that two distinct phases were involved in the final attachment of the living cells. First, the bacteria (Pseudomonas spp.) move in close to the substrate and rotate slowly at the water-glass interact. This Marshall calls the reversible sorption phase where the electrostatic and hydrophobic forces of attraction are balanced against a double-layer repulsion force. The net negative charge of the bacterial cell surface and the negative charge of the surface of the substrate would cause mutual repulsion, so these bacteria must be actively moving toward the surface, that has adsorbed an organic film, following a concentration gradient. During this phase no direct contact with the substrate surface is made and the cells can be removed by simple rinsing. The second phase involves irreversible attachment whereby the bacterial cells produce an extracellular bridging polymer which cements the cell to the organic film on the substrate (Marshall, 1971; Marshall et al., 1971a, 1971b; Jones et al., 1969). Small rod-shaped bacteria appear to have some selective advantage over other bacterial groups in this irreversible sorption (DiSalvo, 1973). This ad-

vantage may be due to the capability of these bacteria to reproduce at low nutrient levels or to a special ability to produce extracellular polymeric fibrillar material that closes the gap between cell surface and substrate (Friedman et al., 1969). If the metabolic synthetic ability of pseudomonad bacteria is blocked by agents such as the antibiotic chloramphenicol, then the bacteria will not attach irreversibly, indicating that the extracellular polymer is essential for attachment (Marshall, 1973).

Film-forming bacteria often exibit surface organelles such as pili (see Hodgkiss & Shewan, 1966), fibrils, blebs or droplet-shaped structures. Corpe et al. (1975) studied these structures to dermine if they played a role in the initial attachment of the bacterial cells, but with negative results. Marshall et al. (1971a) felt that these structures played little role in the attachment of the pioneering pseudomonads to surfaces. But bacteria settling on surfaces already colonized by the initial film-formers may be adhering to a very different surface from that encountered by the pioneering group of bacteria, and many of the bacteria that ultimately settle (such as species of the genera Hyphomicrobium and Caulobacter) have stalks, holdfasts or long hyphal filaments which may play an active role in attachment (Poindexter, 1964; Starr & Skerman, 1965).

Corpe and his collegues have investigated many aspects of the initial attachment of periphytic bacteria to solid substrates (Corpe, 1970a, 1970b, 1971, 1972a, 1972b, 1975, 1977; Corpe et al., 1976; Corpe & Winters, 1972). The nature of the secreted extra-

cellular polymer and its role in attachment has been particularly investigated. The bacterium Pseudomonas atlanticum (described by Humm, 1946) is a film-former found in ocean water on both coasts of the U.S. and has been extensively studied in these investigations. During the irreversible phase of attachment this bacterium secretes a viscous acid polysaccharide which contains glucose, galactose, mannose, galacturonic acid, pyruvic acid, and other components. Other pseudomonads produce a polymer containing some nucleic acids and small amounts of protein (Brown et al., 1969). In addition to bridging the cell surface of the bacterium to the substrate, this polymer collects various kinds of debris and rapidly creates a physically and chemically complex surface. Corpe also found that bacteria settling in numbers later (after 3 days exposure), such as Caulobacter halobacterioides and Saprospira grandis, also produced an acid polysaccharide secretion. Other workers have found that bacterial capsules and "slime" may be composed of simple homopolymers or very complex heteropolymers containing many sugars linked in a variety of ways (Stacy & Barker, 1960; Stanier et al., 1970).

The secreted extracellular polymer may cover the substrate surface some distance from the producing cell, and the polymer appears to adhere more tenaciously to the substrate then to the bacterial cell surface, for violent washing can remove the bacterial cells while leaving the attached polymer behind, and this material may be quite resistant to later decomposition (Martin & Richards, 1963). The polymer futhermore appears to be composed of two layers. A compact acidic layer on the bacterial cell surface

seems to be responsible for the initial bacterial adhesion, but once settled the cell produces a secondary fibrous acidic polysaccharide which eventually replaces the primary polymer (Fletcher & Floodgate, 1973). And the film-forming bacteria retain enzymatic activity long after death of the cells, so that the remaining debris and polysaccharide layer may serve as a center of intense biochemical activity for some time and influence the settlement and development of later foulers (Coupe & Winters, 1972).

Considering the number of recent investigations on the nature and behavior of film-forming bacteria and the secreted extracellular polymers which anchor the cells to a solid substrate, it is remarkable that so little information is available on the thickness of the film that ultimately develops. In a study off San Clemente Island, California, scientists from the Naval Undersea Center have investigated film thickness on glass sides and epoxy radomes (Hoyte et al., 1973; Kenis et al., 1974). Experimental surfaces exposed 100-200 feet below the surface in water 600 feet deep for periods up to 182 days developed films 0.010 to 0.013 inch thick, and visible microfouling was apparent after 182 days. The film thickness was measured as soon as the experimental surfaces were recovered, so the thickness recorded includes both the slime film and the adherent water film. Unfortunately no data are available from these studies on the thickness of the bacterial film alone.

In experimental studies on slime films formed by bacteria in fresh water, the ultimate thickness of the fully developed film

depended upon the velocity of flow across the surface (Bott & Pinhiero, 1976). After 8 days the slime film was 250 μm thick at low velocity (94 gal/sec); 100 μm thick at high velocity (230 gal/sec).

The numbers of bacteria found in the sea varies greatly with depth. In general, the surface film of water has a complex association of interface organisms collectively known as neuston, and included in this association are many bacteria which are not found at depths below the surface (Tsyban, 1971). Several studies have shown that experimental surfaces which come into contact with the sea-air interface, even while passing through it, collect many more attached bacteria per unit area than surfaces that do not contact the interface (DiSalvo, 1973; Sieburth, 1965). DiSalvo reported the rapid irreversible sorption of 10^3 bacteria per cm^2 within minutes of exposure to surface sea water containing 10^3-10^5 free bacterial cells per ml. In designing experiments at sea to study subsurface film-forming bacteria investigators should take precautions to avoid contaminating the experimental surfaces with this bacterial neuston.

Bacterial Films and Subsequent Macrofouling

Once a film of bacteria and their secreted extracellular polymers is present on a solid substrate, organic materials dissolved in the sea water may aggregate on the surface, and additional bacteria and other microorganisms may attach. The polymers of the original colonizing bacteria may greatly enhance the agglutination of living cells (Tosteson & Almodovar, 1972; Tosteson

& Corpe, 1973). In addition, debris and non-living particulate matter may adhere to the surface. The surface therefore becomes one of rather intense biochemical activity, and very soon other microorganisms such as benthic diatoms and protozoans colonize the surface. These organisms, especially the diatoms, may contribute to the so-called slime layer and are eventually a distinctive part of the microfouling community (Corpe, 1972a, 1973). The colonial diatom Lichmophora and the colonial ciliate protozoan Zoothamnium are often conspicuous as microfoulers.

Is the primary bacterial film essential for the later development of diatoms, protozoa, and eventually barnacles, mussels, bryozoans, etc.? The answer to this question is not clear. A large literature exists on the so-called ecological seccession of fouling communities starting with the film-forming bacteria and ending in the climax community of barnacles, mussels, tunicates and seaweeds (Aleem, 1957; Crisp, 1965, 1974; Daniel, 1955; Haderlie, 1974; Himmelforb, 1964; Horbund & Freiberger, 1970; Kaylov & Gorbenko, 1967; Knight-Jones, 1951; Liberatore, 1972; Meadows & Williams, 1963; Miller 1946; Miller et al., 1948;O'Neill, 1975; Scheer, 1945; Wilson, 1955; Wood, 1950, 1967; Woods Hole Oceanographic Institution, 1952). Nearly everyone believes that one group of organisms in some way changes or conditions the surface so that a second community can develop, and so on to the climax fouling community. However, as Corpe (1977) points out, "The suggestion that microfouling of a surface is a necessary prerequisite of heavy, destructive fouling is lacking in data that would constitute a proof, since barnacles and other fouling

organisms have not been cultivated in the complete absence of microorganisms".

As this report is concerned with primary films and their influence on the efficiency of OTEC heat exchangers, the nature of macrofouling communities will not be considered further. The question of the effect of the primary films on later fouling growth, however, is a very important one, for if macrofoulers do indeed depend for settlement and growth on primary bacterial film, then control of the bacterial film could be a method of macrofouling control.

Possible Methods for Prevention of Primary Film Formation

In past years fouling control has been primarily directed at the large fouling organisms that cause increased frictional drag on the hulls of ships, or which physically block sea water piping systems. The presence of thin, primary films on surfaces have been considered of little significance in themselves, but only as they influenced later fouling growth.

With the development of the OTEC concept, however, these primary films on surfaces in the marine environment have assumed enormous importance, for in themselves they may reach a critical thickness to render the OTEC heat exchangers ineffective. There is at present, therefore, a great interest in these primary films, how to keep them from forming on heat exchanger surfaces, and if this fails, how to remove them periodically so that the surfaces remain clean.

The traditional method for controlling gross fouling has been by the use of toxic coatings, where the salts of heavy metals (or more recently organometals) have been employed as toxic agents which leach out slowly into the surrounding water forming a halo over the surface which repells or kills the larvae or spores of fouling animals and plants. The use of certain metals, such as copper or copper alloys, have made it possible for salt water piping systems to remain free of macrofouling growth. In other instances, disinfectants such as chlorine has been added to sea water to kill larval forms before they have a chance to settle.

It is not certain that any of these techniques are effective against bacterial primary films in the sea. Several sudies have shown that marine bacterial films are little affected by toxic paints incorporating heavy metals or organotin (Cobet et al., 1972; Corpe, 1977; Jones, 1967; Miller et al., 1948, Waksman et al., 1943). Indeed Corpe (1974b, 1975) found that film-forming bacteria and the secreted acid polymeric cementing material actually were able to bind and precipitate copper salts, with no harm to the bacteria It has further been demonstrated that cobalt, nickle, lead and zinc are also bound by extracellular polymers of bacteria. The evidence also points to the possibility that primary film-forming bacteria may settle on surfaces coated with antifoulant and accelerate the leaching process making the paints effective for a shorter period of time against macrofouling (Dyckman et al., 1973). Copper or lead in concentrations up to 4×10^{-4}M have been found to actually stimulate the growth of film-forming bacteria

when the nutrient levels were high (Corpe, 1975), and 4% of all marine bacteria studied in one investigation were stimulated by copper in concentration of 0.2 mg/l (Starr & Jones, 1957). In an experiment in warm surface waters in the Sargasso Sea, Dexter (1974) found that microfouling occurred on copper and copper alloys exposed to the water. A continuous layer of diatoms and bacteria embedded in slime ultimately developed on 70 Cu/30 Ni alloy.

Heavy metals are toxic in most living systems. They may interact with proteins in the cell membranes, causing denaturation of the proteins and impairment of membrane permeability, they may react with sulfhydryl groups and thus prevent formation of disulfide bonds, or they may inactivate enzyme systems. Heavy metal toxicity can often be neutralized by sulfhydryl compounds and chelating agents such as ethylene diamine tetraacetic acid (Gorini, 1961; Jones, 1964). Corpe (1974) expressed the view that bacterial proteins, especially enzymes, are probably just as sensitive to heavy metals as are those in other living organisms, but that marine bacteria possess or produce natural chelators which modify the action of heavy metals. Other organisms in the sea are also known to produce metal binding substances and natural chelators (Goldberg, 1957; Siegel, 1971).

In summary, it appears unlikely that primary slime films on OTEC heat exchangers could be controlled by the use of toxic coatings or even by employing copper or copper alloys as heat exchanger surfaces. What then could be done to keep surfaces free of primary films? The only technique successfully employed so far

in controlling marine bacterial films is irradiation of the surface with ultraviolet light (Cobet et al., 1972; DiSalvo, 1971; DiSalvo & Cobet, 1974). On submarine periscope headwindows, ultraviolet light was administered internally at a level of 10-30$\mu W/cm^2$ at the water-glass interface of the headwindow. This treatment kept the surface completely free of bacterial films and other microfoulers for 6 weeks. It would be interesting to know if ultraviolet radiation prevents bacterial films from forming by repelling or killing the bacteria themselves before they settle, or by preventing the formation of molecular fouling (see above) that occurs on surfaces prior to the settlement of bacteria. DiSalvo (1971) also reported that several laboratories using piped sea water were able to control microorganisms in the aquarium water by irradiating the incoming water with immersed, enclosed ultraviolet lamps. Again, however, it is unlikely that this technique would be practical in OTEC heat exchangers due to their size and the enormous amount of water that would have to be irradiated.

It has been suggested that microbial slime films might be controlled by manipulation of the wettability properties of the substrate surface (Dexter, 1975, 1977; Dexter et al. 1975). This might be possible if the surfaces were designed so that their critical surface tension for wetting by organic material precisely matched the specific environment where they would be exposed. More work is needed on this idea to see if it might be practical in OTEC heat exchangers. The use of fluorpolymers to create low energy surfaces has also been proposed as a method of abating biofouling films (Jones & Ostrozynski, 1975; Ostrozynski & Jones,

1975, 1976).

Chlorine has been used extensively to disinfect drinking water, effluents, and sea water used in cooling systems. There is no question that chlorine, at a level of a few parts per million, is effective in controlling most bacterial growth. In waste water disposal systems chlorine controls slime forming organisms (Fair & Geyer, 1958). On the other hand, one set of experiments conducted in sea water indicated that microfoulers (bacteria and diatoms) had a very high resistance to chlorine released into the water by localized generation by electrolysis (Lovegrove & Robinson, 1968). Critical experiments are needed at potential OTEC sites to determine if the addition of chlorine to intake water could prevent the formation of slime films on the heat exchanger surfaces.

Young and Mitchell (1973a, 1973b, 1973c) reported on the phenomenon of negative chemotaxis in primary film-forming bacteria, and this has recently been investigated further (Chet et al., 1975; Chet & Mitchell, 1976a, 1976b). It has been determined that the positive chemotactic response of motile marine bacteria can be reversed if sublethal concentrations of toxic agents are added to a medium that would normally attract the bacteria. Such bacteria are repelled from and actively avoid unfavorable areas containing non-lethal amounts of such compounds as acrylamide, benzoic acid, and tannic acid. Surfaces coated with these repellants in the form of non-toxic paints attracted a bacterial film of only 10^6 bacteria/cm^2 after 12 days compared to 5×10^{12} bacteria/cm^2 on uncoated surfaces. Some years ago Sieberth and Conover

(1965) reported that the floating seaweed Sargassum produced tannins which prevented epiphytic bacteria from settling and growing on the branch tips of the plant. Thus it might be possible to control some bacterial films by the use of non-toxic coatings. As Corpe (1977) noted: "It is clear that this is a most significant observation, but has not yet been thoroughly explored". Young and Mitchell (1973c) also reported that sublethal concentrations of copper and lead repelled marine bacteria in much the same manner as the hydrocarbon compounds. This is a particularly interesting observation, for, as noted above, antifouling paints containing copper in lethal concentrations for most marine organisms are tolerated well by film-forming marine bacteria.

Removal of Primary Films Once Formed

At the present time the possibility of successfully preventing microbial films from forming and building up to critical levels on OTEC heat exchangers appears to be quite remote. If the OTEC program is to succeed, therefore, some method must be found to periodically remove the primary film and keep the heat exchanger surfaces clean. This will probably involve chemical or mechanical techniques or a combination of both. Several methods of cleaning heat exchanger tubes of scale and other deposits are currently used in many industries, but it is uncertain if these methods can be efficiently adapted for use on OTEC heat exchangers.

Some data are available on chemical agents that will remove film forming bacteria from glass surfaces. Corpe (1974a) reported that 5 minute exposure to sodium hydroxide, solutions of anionic

and nonanionic detergents, chelating and oxidizing agents, and protein denaturants removed pseudomonads after they were "irreversibly" attached. On the other hand distilled water, dilute buffers, salt solutions, and cationic detergents did not remove attached bacteria. Meadows (1965), in contrast, reported that marine bacteria which settled on surfaces in normal sea water became detached when these surfaces were subsequently exposed to dilute sea water or washed with distilled water. Considering the volume of water flowing across the heat exchangers surfaces of any of the proposed OTEC power plants, and the amount of chemicals needed to effectively clean the surface, this option would appear to be impractical. The use of mechanical scrubbers (Amertap, MAN brushes, etc.), and abrasive slurries have been used successfully in the past in controlling gross fouling and scale build-up in industrial heat exchangers, but few data are available on how effective these methods might be on marine primary films. The experimental CAVIJET system (see Conn & Rudy, 1977) which can remove gross fouling growth from flat surfaces would seem to be impractical in the tubes of heat exchangers.

Primary Films and Corrosion

Another potential problem for heat exchangers circulating sea water across one surface is the affect primary films have on corrosion processes. In the case of macrofouling, there is considerable evidence that in some cases fouling organisms such as barnacles can adhere so firmly to the metal substrates as to prevent sea water or other corrosive agents from contacting the

surface and as a result no corrosion occurs. In other cases, a rich fouling growth on a surface may allow anaerobic bacteria such as Desulfovibrio to appear in numbers and their metabolic products can lead to enhanced corrosion of the metal surface. In the case of primary films, however, we have little specific information on how they influence corrosion. Kalinenko (1959) exposed aluminum, brass, and bronze plates in natural sea water and found that bacterial films soon developed and these films accelerated the electrochemical processes of corrosion. Neihof and Loeb (1977) speculated on the possible influence on metal corrosion of a molecular fouling film, and suggested that these thin organic films may not act as corrosion inhibitors but may affect corrosion rates. It is known that corrosion rates of any one metal may vary at different exposure sites. It is possible that differences in thickness or compactness of the organic films adsorbed from different water masses may be an explanation for this phenomenon.

Areas Where Additional Research is Needed

The foregoing review of the current state of our knowledge regarding the nature and behavior of primary films on surfaces in the marine enviroment points out many areas where additional information and data are needed. If the problems associated with the development of microbial films on OTEC heat exchangers are to be solved we need more research to more fully answer the following questions:

1. What is the fundamental nature of the molecular fouling

film and how does it "condition" the surface so that film-forming bacteria settle?

2. At potential OTEC sites, how severe is the primary film problem likely to be? Most of our present information is based on laboratory or coastal studies.

3. What is the distribution, horizontally and vertically, of pseudomonad film-forming bacteria in the open sea? Is ocean water below depths of 500 m free of potential film-forming bacteria and other fouling organisms as has been reported (Dexter, 1974)?

4. What is the detailed chemical and physical nature of the acid polymers secreted by film-forming marine bacteria, and exactly what role do the polymers play in anchoring bacterial cells to surfaces?

5. Are there agents which could be added to the sea water or applied to the heat exchanger surface which would block synthesis of the extracellular polymers and thus prevent irreversible settlement of bacterial cells?

6. How does the velocity of sea water flowing over a heat exchanger surface influence the formation of bacterial films? Most studies to date have been done under static conditions with experimental surfaces exposed to non-flowing sea water.

7. Do the first arriving and settling bacteria in the primary film prepare or condition the surface for later arriving bacteria?

8. What are some of the environmental factors that influence the rate of growth of bacterial films?

9. Is the formation of a microbial film essential for the later settlement of macrofouling organisms?

10. How can the surface of metals and plastics be altered to make them unattractive to film-forming bacteria and other microorganisms? Is it possible to manipulate the initial wettability properties of heat exchanger surfaces so that bacterial films will not develop? Can the negative chemotactic behavior of film-forming bacteria to non-lethal concentrations of hydrocarbons be taken advantage of to repell bacteria from settlement on heat exchanger surfaces?

11. Is chlorination of sea water a really effective method of controlling potential film-forming organisms?

12. What mechanical and chemical methods could be efficiently employed to periodically remove the bacterial films from OTEC heat exchanger surfaces and keep the surfaces clean?

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