New approaches to Marine Biofouling Control

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Abstract

Biofouling control measures are dependant on the type of industry, type of equipment, environment and the substratum. Cooling circuits of power plants invariably get fouled. Several biocides like chlorine, chlorine dioxide, ozone & organic biocides are being tried for fouling control. However chlorine has been the most sought after biocide due to its low cost, easy handling and quick degradation. The ban on tributyltin (TBT)-based paint products has been the cause of a major change in the antifouling paint industry. In the past decade, several competing technologies have reached the commercial market and claimed their effectiveness with respect to prevention of biofouling on ships and marine structures in an environmentally friendly manner. The interest in providing innovative antifouling technologies has led to a large number of studies for improved understanding of the process and the principles underlying, biofouling of surfaces. The efficiency of the antifouling coating increased with the ability for controlled release of the biocide from the matrix which was demonstrated by the TBT SPC technology. In the search for alternate antifoulants, studies have been oriented in two ways i.e. imitation of the natural antifouling process (natural product antifoulants) and the surface modification approach (low surface energy of the substrate or coating). Biofouling in power plants leads to flock blockage, increased condenser backpressure. In the search for marine natural product as antifoulants several antifouling compounds have been successfully identified, however compatibility of these compounds into commercial coatings with the desired leaching rates has been a stumbling block for their success. Some practical criteria to be considered in the development of such coatings is compatibility of compounds with polymer matrixes, environmental effects, legislation and registration of the compounds. Among the low surface energy materials tested the best was found to be a silicone elastomer poly(dimethylsiloxane) PDMS. The work initiated by NIOT to understand and study marine fouling is discussed in this paper. Further other alternative technologies towards environmentally favourable antifouling systems are outlined.

Key words: Antifouling, Natural Products, Foul-release coatings, Biomemtic.

I. INTRODUCTION

Oceans support a great variety of life by providing a dwelling place for numerous organisms from micro to the macro level. Being a major cover for our planet, they play a vital role in the proper functioning of the planet, preserving its life forms, maintenance of resources and determining the weather and climate.

Although human life is concentrated on the dry land, we rely on the ocean for transport, energy, food and mineral resources, waste treatment etc. Oceans harbour thousands of marine organisms, which are considered to be most valuable assets. Human intervention, affects life in the oceans directly or indirectly. Any problems faced during these interactions of humans with nature have to be dealt with in an amenable or agreeable way so as to live in harmony with nature.

II. MARINE BIOFOULING

Marine Biofouling is the undesirable accumulation of microorganisms, plants and animals on artificial surfaces. The adverse effects of biofouling of ship hulls are, high frictional resistance, due to roughness which leads to an increase in load, speed reduction and loss of maneuverability. It results in higher fuel consumption,

increase in frequency of dry docking, deterioration of the top coat i.e. antifouling coat and exposing the underlying anticorrosive coat to the marine environment and species invasion. Challenges also exist in making stable antifouling coatings, since many antifouling compounds are not compatible with the coating ingredients and binder systems.

III. SEQUENCE OF BIOFOULING

The first event in biofouling of a surface is the accumulation of an organic conditioning film comprising of chemical compounds (mostly protein and polysaccharides) making the surface wettable. This process occurs in the first few minutes. It is followed by colonization of bacteria involving two distinct phases - a reversible phase (adsorption) where van-der-vals forces hold it loosely and a non-reversible phase (adhesion) where exopolymers are secreted which holds the bacteria to the surface.

The growing bacterial lawn is composed of dead and living cells and their secreted slime together with the macromolecular film, constitutes the so-called primary film (biofilm). Diatoms, blue green algae, spores of macro algae and protozoans appear after the development of

primary film. Bacteria and diatoms represent the primary colonizers and spores of macroalgae and protozoans constitute the secondary colonizers in the process of microfouling. Aclear separation between microfouling and macrofouling is not possible. Larvae of macrofoulers (sessile marine organisms such as tunicates, coelentrates, bryozoans, barnacles, mussels, Polychaetes, etc.) which are called tertiary colonizers then attach to the Primary film.

IV. EVENTS LEADING TO BIOFOULING OF A SURFACE

The processes of microfouling and macrofouling sometimes exhibit an overlapping time sequence. Irreversible adhesion of bacteria occurs in time scales of less than 5 to 30 minutes upon immersion. Diatoms colonize from less than 30 minutes onwards and spores of macroalgae and protozoa settle immediately after this process. This is followed by settlement of larvae of macrofoulers. Ecological succession of the organisms following this time sequence is still debatable and the diversity and density is dependent on specific geographical location. Hence, for each location microfouling experiments have to be designed in time scale ranges of 0 to 15 days with daily sampling. Macrofouling experiments have to be investigated at time scales of 0 to 12 months at fortnightly intervals.

V. SETTLEMENT OF ORGANISMS

Settlement and recruitment are important processes affecting population structure and can vary across spatial and temporal scales. Factors influencing settlement are larval supply; abundance and environmental parameters, which are, site specific. Settlement choices may influence recruitment patterns but post-settlement processes may influence population dynamics more than larval processes.

VI. ECONOMIC LOSSES DUE TO BIOFOULING

Ships with fouled hulls, for instance, require 40 percent more fuel to travel at the same speed compared to unfouled vessels. It significantly increases the emissions of CO₂ and other greenhouse gases. Biofouling can also clog water intake lines in power plants and lead to shut down. The global costs of this excess burning of fossil fuel amounts to US \$7.5 billion per annum but in addition there are indirect environmental penalties caused by the release of 20 million tones of CO₂ and other greenhouse gases. If the world fleet was totally fouled, an extra 70.6 MT of fossil fuel would be burned per annum, liberating >210 MT CO₂ and >5.6 MT So₂.

European Union companies are world-leaders in anti-biofouling coating technology with 70% of the global market share. Next to the EU are the companies of Japan and the United States. Many of the technologies in use, however, are being subject to restrictions due to novel and more stringent environmental protection criteria, namely to eliminate the currently-applied biocides. For example, the most commonly used and most effective antifouling materials available for submerged marine structures are paints based on copper and organo-tin (TBT), but the use of the latter will be prohibited by 2008.

A number of co-biocides are currently under environmental and legislative scrutiny and restrictions will continue to grow, especially, first in Europe and to other countries like Japan, United States of America, Australia etc where the legislative framework includes the 6th Environmental Action Plan (Decision N. 1600/2002/EC), the EU Water Framework Directive (2000/60/EC) and the Biocidal Products Directive (98/8/EC).

The current state-of-the-art in fouling control technology use controversial biocides such as copper and pesticidal formulations that prevent fouling by killing the organisms. Fouling has been controlled traditionally by antifouling paints that contain biocides (i.e., compounds that are toxic to the organisms). But, regulations, at present require that antifouling paints must not cause adverse effects in the environment and the search is on for more environmentally friendly ways of deterring marine life from hitching a ride on the hull of a vessel.

VII. THE COST OF FOULING

- Fouled ship hulls burn 40% more fuel at an additional, annual global cost of \$7.5 million.
- Control of fouling of water intakes, piping systems and heat exchangers in desalinization and power plants, costs over \$15 billion per year.
- Control of fouling on membranes used in wastewater and desalination systems costs over €1 billion per year.
- Fouling of aquaculture systems in fish farms costs an average producer €100,000 per year.

In the search for marine natural product as antifoulants several antifouling compounds have been successfully identified, however compatibility of these compounds into commercial coatings with the desired leaching rates has been a stumbling block for their success. Many of these compounds are now being used as replacements in combination as booster biocides to copper or organic biocides like Irgalol, Sea Nine etc. Several other compounds have also been tested such as pharmaceuticals. Some of the other significant

approaches to control biofouling involve the negative ion approach, biomemtic molecules, low pulsed electric field and nanotechnology. In this paper effort taken by NIOT to understand and control marine fouling is described in detail.

Performance of Naval Materials under Immersed Condition in Sea Environment.

Control of corrosion and biofouling related damage is a primary concern for structural integrity of marine structures. Naval applications include operation of several underwater equipments like sonar's, ROV, sensors, ships and submarines. Metals and alloys used underwater either in the shipping industry or in offshore structures and equipments are prone to these problems, which impede their operation. Further, these surfaces have to perform in an aggressive environment subjected to biofouling, electrochemical and microbial corrosion. Repair time. costs, and sudden failure in submerged structures, are a few of the issues related to corrosion and biofouling of marine structures. It is reported that many marine structures had performed differently under actual conditions compared to laboratory test conditions. The main objective of this program is to study the corrosion, marine fouling & performance of antifouling coatings. The materials selected for the study include mild steel, titanium, stainless steel SS 316L, copper and cupronickel, galvanised iron. In-situ test data on materials will contain information on: the extent of deterioration of the surface like corrosion rate and potential, pitting resistance, pit propagation, microbial density and diversity, density and diversity of fouling organisms, living and non living biomass on surfaces, coating strength and effect of hydrographic parameters on the observed results on materials. Results will be directly applicable to the marine industry and will improve the knowledge on performance of material in harsh environment and will provide data on under-water corrosion, oceanographic parameters and performance of coatings. Among the metallic materials tested copper, cupronickel and galvanised iron showed better performance in preventing settlement macrofouling organisms.



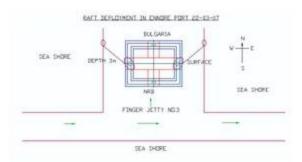


Fig 1. Test Rig designed for deploying test materials for marine applications

B. Deep sea corrosion

Efficient exploitation and conservation of the oceans poses great technological challenges for scientists and engineers who must develop materials, structures and equipment for use in harsh environment of the oceans. In deep waters, the deterioration of materials is due to the cumulative effect of various environmental conditions like hydrostatic pressure, temperature, pH, dissolved oxygen, salinity, sea current etc. In-situ corrosion measurements on the effect of deep sea environment on some metals. alloys and composite materials were carried out in the deep ocean at depths of 500, 1200, 3500, and 5100 m for 168, 174 and 174 days in the Indian Ocean. Zinc, magnesium and aluminium were attached to mild steel in order to study the galvanic coupling of steel with these metals.. Metallic tensile specimens were cut from a sheet and prepared as per ASTM standard and minimum of four replicates were attached to the deep- sea mooring at each depth level. Tensile, compressive, flexure and interlamellar shear stress tests were performed on carbon fibre reinforced composite specimen. In order to correlate the performance of materials in deep-sea environment, seawater current and temperature data were also collected at same period

Corrosion data on aluminium revealed that corrosion rate increases as the depth increases. This is due to the effect of hydrostatic pressure, which reduces the ionic radii of chlorine ions and facilitates easy penetration of these ions into surface layer. Titanium, titanium alloy (Ti-6Al-4V) and stainless steels did not show any deterioration at all depths studied. Test results indicate that carbon fibre reinforced composite did not show any change in properties like tensile, compression flexural and interlamellar shear compared to control (unexposed) specimens. The deposition of calcium carbonate on galvanically coupled mild steel with zinc, aluminium and magnesium corresponds to availability of calcium in the deep ocean. EDS analyses on exposed coupons did not reveal calcium element below the calcium carbonate

compensation depth (CCD) at 3800 m in Indian Ocean. Potentio-dynamic polarization studies were conducted on some metals and alloys in seawater collected from Indian Ocean at the surface and 500 and 1200m depths. These studies indicate that the behaviour of materials in deepsea environment is a cumulative effect of oceanographic parameters. Tensile test results on stainless steels SS-304 & SS-316L), titanium and titanium alloy (exposed) specimens did not show any significant change in their tensile properties. Microbiological investigations on the exposed materials indicate that except carbon fibre reinforced composite all other metals and alloys harboured bacterial colonies.

C. Study of Corrosion of stainless steel in the presence marine Bacterial Biofilms using AFM

This work outlines the principles of application of scanning probe microscopy (SPM) as a tool for studying physico-chemical and biological phenomena and discusses the potential use of atomic force microscopy (AFM), a form of SPM, for investigation of bacterial biofilms formed on metal surfaces and for studying corrosion of these surfaces in the presence of such biofilms. The role of biofilms in the deterioration of metals and their allovs in both fresh water and marine environments has been of considerable interest to industry worldwide. Problems associated with corrosion due to the formation of biofilms are widespread and have serious economic and safety implications. However, to date, it still remains to be elucidated how much a role the microbially-influenced corrosion (MIC) plays and what are the key mechanisms involved. Methods frequently used for microscopic investigations of biofilms and MIC include techniques of scanning electron microscopy (SEM), environmental SEM (ESEM) and different forms of light microscopy. Although useful, these techniques have their drawbacks. SEM has the disadvantage of a lengthy sample preparation and sample distortion due to the requirement for dehydration. Light microscopy overcomes the problem of specimen shrinkage, but it does not have the resolving power nor the magnification that SEM offers. ESEM techniques need some improvement in order to achieve the image resolution required for detailed observation of biofilms in their fully hydrated form. Conventional microscopy techniques do not allow realtime visualisation of the surface of a bacterial cell or of the events involved in MIC such as initiation of pitting or synthesis of extra cellular polymeric substances (EPS). Methods which permit in vivo observation of bacterial biofilms on metallic and non-metallic surfaces such as differential interference contrast and confocal microscopies, lack resolution to simultaneously image individual cells and the substratum.



Fig 2. Fouling sequence in stainless coupons exposed for eight months in marine environment

Marine species of bacteria isolated and purified were grown marine broth. Coupons made of stainless steel AISI 304 (15 x 15 mm) and were incubated in the culture medium. Biofilms developed on surfaces of steel were viewed under AFM. This demonstrates the capability of using AFM to collect information which enables not only qualitative, but also quantitative analysis of the image such as measurements of the biofilm thickness and roughness of the substratum. There is little doubt that the continuous development and improvement of SPM techniques opens up great possibilities for investigation of microbe-material interactions. These types of studies will allow better understanding of the fundamental aspects of deterioration of metals due to the biofilm formation - thus helping in designing novel, more effective and environmentallyacceptable biocorrosion control and prevention measures

D. Marine Natural Products as Antifoulants

Ban on use of heavy metal-based formulations and certain pesticide-based formulations have necessitated research into non-toxic antifoulants. Research to explore and identify novel benthic marine organisms for secondary metabolites possessing antifouling activity has been initiated. Performance (Qualification) of these compounds under field trials, use of bioassay methods for direct purification, identification and development of antifouling compounds, development of procedures for incorporating into antifouling formulations and field-testing of qualifying compounds with a realization for incorporation into paints formed the objectives of the study. Fifty species of sponges were assayed for antibacterial activity against marine bacteria. A protocol has been developed for assessing efficacy of natural products for inhibition of bacterial adhesion on surfaces. From the above assay, 8 sponge extracts were identified active N-methylpyrrolidone a secondary metabolite possessing potent antibacterial activity against marine biofilm bacteria has been isolated and characterized from a marine sponge Clathria frondifera..

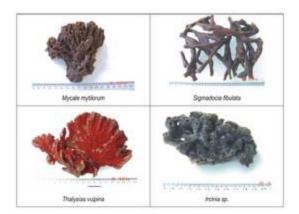


Fig 3.

E. Surface Modification Approach to control Biofouling

International Maritime Organization's ban on the use of TBT and heavy metal based formulations due to their destructive effects on marine biota has resulted in environmental regulations controlling the use of these compounds. There is an increasing pressure to find novel non-toxic antifouling technologies to control marine biofouling. In this context recent research is now focused on two approaches to this problem: the development of a) foul-release coatings that work on the principle of either low surface free energy or coating ablation and b) coatings that incorporate a compound(s) that is nontoxic or at least environmentally benign. The principle of developing the foul release coatings lie on their Wettability hydrophobic & hydrophilic, Surface energy & Tension, Surface roughness, Surface micro / nanotopography, and Shear Low elastic Modulus. In the study, stress polydimethylsiloxanes and metal substrates and antifouling coatings were ranked. Silicone Coupons have demonstrated better ability to be fouling free in the field. PDMS surfaces were free of hard-shelled fouling (Barnacles and Polychaetes) for a period of six months of field exposure. Only a single sponge colony was observed on coupon after six months, which also detached subsequently. Further, research on development of the coatings involves changes in the Oil concentration and type on fouling of PDMS coatings, cross linker composition on the fouling of PDMS coatings, filler concentration and type on the fouling of PDMS coatings, biocide and booster biocides on performance of PDMS coatings and surface microetching on performance of PDMS coatings are under progress.

F. Surface Microtopography of Molluscan shells as Antifouling Agents

Among the 14 species tested four Molluscan shells viz: Phalium sp, Babylonia spirata, Conus sp., Strombus sp. remained fouling free on their outer surfaces. Ranking of species based on wettability coefficients were in the order of the least Phalium sp < Babylonia spirata< Conus sp. < Strombus sp. < Rapama bulbosa < Tudicla spirillus < Bursa spinosa < Turritella attenuata < Donex sp. < Turiculla sp. < Tonna dolium < Hemifuses pugilinus < Turbo sp. < Trochus sp. to the most wettable. Incidentally the ones with the lowest surface wettability were found to possess surface roughness values of less than 200 nm and were the least fouled surfaces.

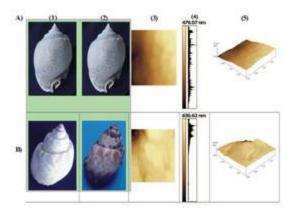


Fig 4. Atomic Force Microscopic studies on surface profiles of molluscan shells

G. Marine Organisms mediated Biodegradation of Polymers

Accumulation of polymers and plastics in marine debris is a severe environmental hazard. Some of the polymers like low-density polyethylene, high-density polyethylene and nylon are being used extensively in seabed pipelines and fishing gear respectively. These polymers pose a serious problem to the marine flora and fauna as well as coastal human habitats. These polymers are probable materials that can be used for underwater instrument packages for long-term applications. Their life and performance can be evaluated. The main objectives of this program are to test the biodegradability of LDPE and HDPE and nylon by various marine based microorganisms in the lab, screening of marine based microorganisms for the biodegradation of LDPE, HDPE and nylon, identifying the best organisms and carry out similar studies under marine conditions. The other objectives include, optimization of degradation conditions, identification of extra nutrients needed for bioremediation, Identification of the possibility of bioaugmentation and characterization of microbial metabolites involved in degradation. Marine bacterium (Bacillus cereus, Bacillus sphericus, Vibrio furnisii, and Brevundimonas vesicularies) were found to degrade nylon 6 and 66 in mineral salt medium at 35°c at PH 7.5,

under submerged enrichment conditions with the polymer as the sole carbon source. The nylon samples were exposed as the sole carbon source to the marine bacteria under submerged enrichment culture conditions. The degradation showed the formation of new functional groups namely NHCHO, CH₃, CONH₂, CHO and COOH. Viscosity average Molecular weight was reduced by 42% in the case of Nylon 66 and 31% in the case of Nylon 6, in three months. Physical degradation was observed by measuring the weight loss and through epi-fluorescent microscope. Degradation of the polymer was observed through the decrease in the viscosity average molecular weight, weight loss, formation of new functional groups as well as in physical damage to the fibres visible under an epi-fluroscent microscope.

VIII. SEAWATER INTAKE SYSTEMS IN POWER PLANTS

Both nuclear and thermal power stations located in coastal region use enormous quantities of seawater as a coolant in the condensers. Fouling of cooling water conduits of power stations lead to a decreases in the diameter of the cooling water pipes resulting in reduction of water flow and a fouling induced pressure drop, clogging of condenser tubes, condenser tube leakages, reduction in heat transfer, blockage of intake gates and tubes and pump vibration. Microfouling of heat exchanger tubes is a serious problem resulting in the loss of heat transfer rate across the surface. A 250-µm thick slime layer can cause a 50% reduction in the heat transfer efficiency of heat exchangers.

With the setting up of multi-mega watt power plants, often on the seacoast for easy availability of plentiful seawater for condenser cooling, fouling of seawater intake systems, heat exchangers and condenser circuits also has become a problem of considerable concern. Biofilm could also lead to temperature gradients promoting corrosion in certain industrial applications. In certain other cases, it can lead to the growth of anaerobic bacteria under the film. The power plants use huge amount of water to complete the steam cycle and keep the electronic turbines turning. Such volumes make it uneconomical to use treated water, so the sources are streams, lakes and the sea. But these waters contain bacteria and algae that can cause slime built-up on condenser tubes and may as well contain the planktonic young of barnacles, mussels etc., that attach and form mats on conduits and other plant structures. Uninhibited colonization by both these micro and macro fouling organisms will cause reduced efficiency and finally result in shut down of plant. In the current global economy there is increasing pressure for higher efficiency and lower cost of electricity. Fouling organisms are more

difficult to control the longer they remain undisturbed after gaining a foot hold. Besides accelerating corrosion, the biofilms may lower the rate of heat transfer as it happens in condenser tubes, resulting in the loss of valuable energy. In some applications, increase in fluid friction can result from the presence of a biofilm. This generally calls for higher pumping power as in pipes and tubing of petroleum industry, adding to fuel cost. Biological organisms are present in virtually all-natural aqueous environments. In seawater, tendency for organisms is to attach to and grow on all structural materials, resulting in the formation of biological film or biofilm. At shallow depths, the oxygen supply is normally at or close to saturation. Biological activity likewise is at a maximum and includes both plant and animal life. Any biofouling beyond depths of 20 to 35m is entirely animal, since plants cannot exist below the depths to which solar radiation penetrates into the sea. Usually there is less fouling as one proceeds away from shore, since major source of animal embryos is from breeding activities near the shore. Also there is usually considerably less fouling with increase in depth at any given distance from shore. The film itself can range from a microbiological slime film on fresh water heat transfer surfaces to a heavy encrustation of hard-shells fouling organisms on structures in coastal seawater. Seawater intake system experiences problems due to marine corrosion and fouling. A consultancy project was undertaken for Tanir bavi Power Plant Mangalore which is a floating power plant. A systematic observation was done on corrosion of ballast water tank, pumps seawater intake system and naphtha pipeline a detailed report was submitted and on the basis of this report, the Plant has taken preventive measures by appropriate coating to the seawater pipelines

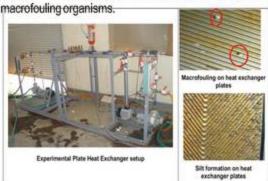
IX. BIOFOULING ON COOLING TOWER FILLS: NTPC LTD

NTPC Limited requested NIOT to carry out a site survey for assessing the nature of the problem in the cooling tower of 3000 MW Talcher Super Thermal Power station, Kaniha, Talcher, Orissa and suggest corrective measures to solve the problem. Severe clogging of fills was observed in the cooling towers 3, 4, 5 and 6 A & B. The nature of the substance was debatable to as to whether it was biological in nature or silt deposition. Further the source for such deposition was also baffling. Further, because of this fill clogging there was a loss in condenser vacuum of 40-milli bar. This type of problem was not observed in the splash type of cooling towers viz: 1 and 2A & B. The sequence of events, which gave rise to this problem, is summarized herewith. Cooling water carries with it a diversity of microbes both bacteria and algae (both micro and macroalgae). The natural phenomenon of these

organisms is to attach to surfaces and grow by multiplication. The problem assumed paramount importance once it came to such a level that operation of the tower became critical due to the clogging of fills. Analysis of the deposits revealed a high level nearly 30-45% composition of silica and silicates. Silica and silicates are known to precipitate / coagulate / adsorb when available at higher levels. At super saturation levels they are found to be less soluble. Further the thermal difference caused by passage through the condensers would result in precipitation. The already available bacterial polymer glue served as a convenient trap for the silicate ions. This is in totality the scenario witnessed currently.

X. BIOFOULING & ITS CONTROL ON PLATE HEAT EXCHANGERS

Heat transfer in Plate heat exchangers are vital as even a small loss in temperature would influence the temperature of various emergency cooling systems including moderator which is critical for power production. Plate heat exchangers are finding increasing applications in seawater cooled systems like nuclear power plants and desalination plants because of their compactness and heat transfer efficiency upto 1.0 ± 0.5°C. However absolute heat exchanger cleanliness is essential for these exchangers as the gap between successive plates is less than 3.7 mm which can afford very little tolerance to any fouling. These several directions of research developed in the last years and only some of them would be mentioned in the lecture. It might be as well that a variety of solutions, adequate to each application and service will provide a fouling protection without damage to the environment. Aflow through set up is designed by NIOT to assess the rate of buildup of macrofouling organisms on heat exchanger surfaces at seawater flow rates of 1, 2 and 3 m/s, and to assess the season-wise biofouling potential and to identify the major dominant groups of bacteria, algae and invertebrates on heat exchanger surfaces towards evolving an effective control method. Studies show that increase in velocity reduces the incidence of settlement of larval forms of



XI. CONCLUSION

The marine fouling metals and degradation of polymers in tropical waters like that of Indian seas is also influenced by the diversity of fouling organisms and environmental factors prevailing in that region. Hence, the results often obtained from laboratory tests may be totally different in the filed. The success of oil and natural gas exploitation and design of newer ships, forced us to think of newer technology to exploit marine living and nonliving resources in eco-friendly and cost effective manner. Any such new technological development involves development of newer materials and protection of structures against marine corrosion and fouling. Hence, the marine Industry needs the expertise of experts from different disciplines such as electrochemist, marine biologist, materials engineers, polymer chemist, oceanographers to work together to understand this field of science.

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