



Marine Biodeterioration

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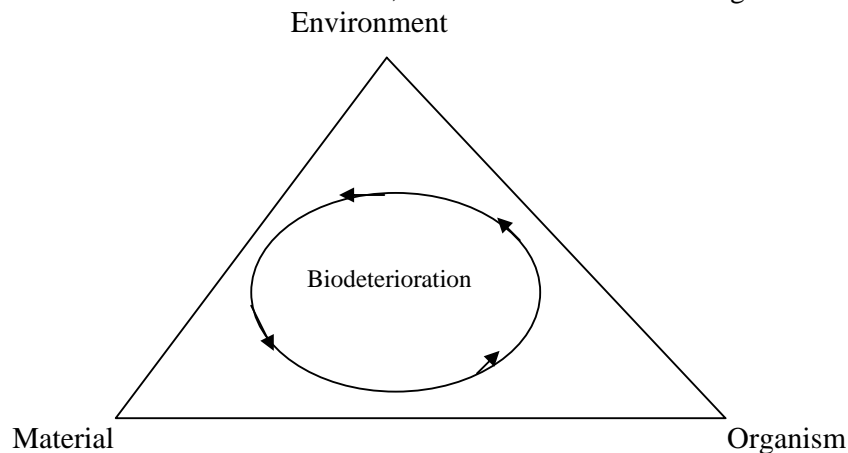
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Biodeterioration or biodegradation of materials can be defined as any undesirable change in the properties of a material caused by the vital activities of biological agencies organisms. Though these are considered synonyms, Starkey (1976) defined biodeterioration as 'biological that are destructive or yield undesirable products or both'; and biodegradation as 'breakdown of undesirable materials to harmless or tolerable products'.

There are 3 factors to be taken into consideration for prevention of any form of biodeterioration. These are the 'material, the environment and the organisms'.



The removal or alteration of any one of these can prevent the growth of organisms which cause decay. The control of the environment instead of application of biocides is the oldest and still the most widely used method for preventing biological deterioration.

There are different forms of biodeterioration, viz., (i) Biofouling which is in the form of deterioration occurring when the mere presence of an organism or its excrement renders the product unacceptable. (ii) Chemical assimilatory biodeterioration occurring when a material is degraded for its nutritive value. In the field of marine biodeterioration, the important areas are bacterial deterioration, fungal attack, boring problem, biofouling and biocorrosion.

In India around 1,80,000 crafts comprising of catamarans, dug out canoes, built up boats and modern mechanised boats are employed for fishing. Of these majority are of wood and a loss of millions of rupees is incurred annually due to biodeterioration of these boats. Wooden objects contain more than 70 % of cellulose which is a good material suited for biological agencies. The bacterial and fungal attack and boring problem are more concerned

with small boats. With the advent of extended voyages, larger vessels made of steel are in use whereby fouling closely associated with biocorrosion became a major problem.

Bacterial deterioration

Bacterial deterioration of wooden material is a slow process. Many wood destroying bacteria are able to attack cellulose, but some are capable of attacking lignified cell wall also, particularly when wood is exposed for long time to wet condition. *Bacillus* Spp., *Pseudomonas* spp. *Vibrio* spp., *Aerobacter* spp. and *Aerogenes* Spp. were reported from wooden materials. They either inhabit wood or utilize cellulose as food. Bacteria initially colonise the parenchyma cells of wood rays and resin ducts, but later walls of cells are attacked and degraded by cellulase or pectinase activity or a combination of both. The process in deterioration of wooden objects in ground contact is slower, but opening up the pit membranes make gaseous exchange easy. This causes the conditions inside the wood more aerobic suitable for fungal growth and open pathways make fungal hyphae to pass from cell to cell.

When immersed in sea water bacteria initiate the problem of fouling. The initial step in fouling is the bacterial colonization of surfaces followed by attachment of protozoa, fungi and microalgae resulting in 'biofilm' formation which is followed by macrofouling.

Fungal deterioration

Biological deterioration of wood is caused by wood inhabiting fungi both on land and in water. They differ from ordinary green plants in form and method of nutrition. They are unable to produce their own food and are parasitic/saprophytic in nature deriving food from the cell cavities of the host wood. Fungi possess certain enzymes capable of digesting the cellulose. Due to enzymatic action the timber becomes soft and light, spongy, inflammable and emit a mucky and unpleasant odour. Eventually fungal attacked wood gets fully soaked in water and becomes heavy and loses the nail holding properties and strength properties. In dry condition, the wood cracks and these gradually become longer and deeper resulting in the failure of such structures. Fishing crafts have to be periodically repaired or replaced and the cost of this runs to several lakhs of rupees. Hence the problem is of considerable economic importance and proper maintenance is essential.

Based on the development and the type of deterioration they cause on the wood, two types are distinguished

- a. wood staining fungi
- b. wood destroying fungi

Wood staining fungi

Fungi of this group do not destroy the wood but produce certain stains on the surface, which are troublesome because of their objectionable appearance. The wooden objects may take different shades of blue, black, brown and green. Most staining fungi could cause soft rot under prolonged favourable conditions. Protection against such decay can be accomplished by kiln drying or temporarily by surface treatment with a water solution of anti-stain fungicide.

Wood destroying fungi

Wood destroying fungi are those capable of disintegrating the cell walls and thereby changing the physical and chemical characteristics of wood. Wood undergoes marked change in colour, texture and strength properties and eventually the wood becomes soft and spongy. Well-known wood destroying fungi consist of 2-sub groups, brown rot and the white rot types of *Basidiomycetes*. Both use cellulose and other carbohydrates as nourishment, but only white rot type is capable of breaking down lignin.

Soft rot fungi belonging to the cellulose-decomposing group are usually the first fungal colonisers of wood. They consume sugars or simple carbohydrates. *Zygomycetes*, *Ascomycetes* and *Fungi imperfectii* belong to this group. Usually the attack is superficial and generally occurs in the wooden pieces exposed to high moisture content and on ground contact. In degree of wood deterioration this is intermediate between stain and decay

Factors affecting fungal deterioration

Wood structure: The wood structure viz. the presence of extractives, resins etc. influences the resistance to decay or the natural durability of the timber. Sapwood will be susceptible to decay with a readily available supplementary source of nutrients in the ray parenchyma and the absence of toxic extractives in the cell walls. The heartwood can be highly resistant to decay with the presence of toxic extractives and with the absence of nutrients.

Moisture: Microbiological deterioration can occur only if the wood material has a moisture content exceeding 20 %. Decay fungi and stain fungi can cause severe damage only when the moisture content is above the fibre saturation point (30 %) level but at the same time the development of decay is retarded by excess moisture.

Air: A supply of air is necessary for the growth of wood destroying fungi. An amount of air equivalent to more than 20 % of the volume of the wood must be available before decay can take place. Wood saturated with water is devoid of sufficient air for fungal growth and consequently does not decay.

Temperature: Fungi can grow in wood at a fairly wide range of temperature, about 15 to 30 °C. The activity decreases at temperature above and below this range and effective growth ceases at about 5 to 10 °C at the lower limit and 35 to 40 °C at the higher limit.

Nutrition: Energy for most of the cell building materials for the organisms are supplied by carbohydrate fraction consisting of cellulose, starches and sugars and for some organisms by lignin fraction. The cellulose, hemi cellulose and lignin constitute 95 % of the substance of most woods, sufficiently abundant to meet the requirement of organisms.

pH: All decay fungi produce optimum development at about pH 6, though soft rot fungi grow at pH 8 or 9.

Light: Light is needed for typical sexual reproduction among decay fungi.

Effects of fungal decay in woods

- i. Alter physical and chemical characteristics of wood
- ii. The normal colour is modified and distinctive odours are imparted to wood.
- iii. Reduces density
- iv. Modifies heat and electrical conductivity of wood.
- v. Reduces mechanical strength properties

Boat parts subjected to fungal decay: Salt-water members above waterline are more liable to fungal decay than water exposed surfaces. Stem, transom planks, frame heads, beam-ends and bulwork, stanchion ends and bulkheads are the parts most affected. Poor material (use of sapwoods and unseasoned wood), warm climate, fresh water leaks and dead air spaces are factors responsible for the decay.

Prevention

Taking certain precautions while construction of the boat and during service can prevent the problem. Using decay resistant heartwood seasoned to below 20% moisture level and avoiding infected wood would resist the problem. All water should be kept out and all the seams should be well caulked. Metal fastenings should be kept tight. Exterior paint will keep out moisture but painting inside the hull planks may be avoided allowing the hull planks to breathe. The moisture that has entered into wood can be got rid of by drying or airing.

Suitable commercial wood preservatives should be used at the time of construction and be repeated periodically while in use. Pentachlorophenol, Copper Chrome Arsenate (CCA) and Creosote are some recommended wood preservatives, which can be applied either by brush application or by pressure treatment. The 'dual treatment' incorporating a waterborne preservative such as CCA followed by an oil borne preservative such as creosote gives superior protection to wood against fungal decay.

Marine wood borers

Destruction of wood by marine wood borers is of great economic concern. Wooden structures exposed to marine environment are subjected to attack by a range of wood boring marine organisms designated as 'marine borers'. They attack ships, log rafts, harbour piles and many other waterfront structures causing structural damage by boring deep into the wood making them unserviceable within a short span of time. These animals are distributed throughout the salt waters of most of the world but are more prevalent and destructive in the tropics than in the temperate regions.

The marine borers that cause the greatest amount of damage are categorized into two: bivalve molluscs and crustaceans each characteristic in its general appearance and method of attacking wood. The molluscan borers may be separated into two families - the Teredinidae or the wood-boring shipworms, and the pholadidae or rock borers. The important genera of wood boring molluscs are *Teredo*, *Bankia*, *Nausitoria* and *Martesia* of which the first three are superficially worm like in appearance and are known as 'shipworms'. The damage caused by shipworms is internal and can become quite extensive without being apparent. The larvae make very small entrance holes on the surface of the wood, but once within the wood they increase rapidly in size and develop the characteristic worm like bodies. As the animal advances into wood, it secretes a protective calcareous lining for the burrow. As a result of

the continued boring, the structural strength may be greatly reduced. *Teredo elongata*, *T. manni*, *T. furcifera*, *T. milleri*, *Bankiella carinata*, *B. liliobankia* and *Nausitoria hedlei* are the species important to India.

The pholadidae look very much like small clam in appearance and bore into wood, clay, soft rock, shells and even into plastic and poor grades of concrete. Pholadidae is represented by *Pholas* and *Martesia* of which *Martesia* is of importance to India because of its widespread distribution, density of attack and rapid succession of generation. The young attack wood by boring small entrance holes and once within the wood, they continue their boring and excavate the wood sufficiently to accommodate the growth of their imprisoned bodies. *M. striata* and *M. fragilis* are common to India.

Crustacean borers are distinct from the molluscan borers in their method of attack, general structure and appearance. They do not become imprisoned in the wood but are able to move about. The young and adult alike attack the wood making narrow galleries, which seldom reach very deep. The damage done by this group is less serious than by shipworms as this is more evident to inspection and the excavation proceeds less rapidly. The animals make extensive network of tunnels in the wood, which are eroded away by wave action, which exposes unattacked surface for fresh attack. The important crustacean borers are of two orders 'Amphipoda' and 'Isopoda' and are represented by three major genera viz. *Limnoria*, *Sphaeroma* and *Chelura* of which the latter is of minor importance to India. *Sphaeroma* commonly called as 'pill bugs' grow to a size of 13 mm long while *Limnoria* is much smaller growing to a size of 6 mm only. *S. terebrans*, *S. annandeli*, *S. walkeri*, *L. tripunctata*, *L. bombayensis*, *L. insulae* and *L. andamanaensis* are active in Indian waters.

Control of marine borers

The degree of resistance to borer attack depends on the species of timber and different localities probably due to the presence of different species of borers. The problem is more pronounced in tropical waters than in temperate waters. Traditionally indigenous preparations such as fish oil, crude oil, cashew nut shell liquid, coconut oil, sand, cement, black tar, fuel oil etc singly or in combination are used for protection. Since most of these preparations lack toxic property, CIFT has recommended treatment of wood with chemical preservatives or use of physical barriers applied to the surface of the timber. Use of Creosote, an oil borne preservative was found to be successful in preventing teredenid attack. Water borne preservatives such as copper-chrome- arsenic (CCA) compounds are very effective against borers especially to crustacean borers. Dual treatment - an initial treatment with a water borne preservative followed by an oil borne preservative (Creosote) treatment - is very effective against both types of borers and is recommended for areas of very severe borer attack.

Physical barriers such as metals (Copper, aluminium etc.), concrete and plastic have been used to achieve protection viz., the hull below the waterline area of boats is sheathed. Instead of copper, which is very costly, aluminium-magnesium alloy has been recommended by CIFT and the sheathing has been standardized. Fibreglass reinforced plastic (FRP) sheathing also is a proven method of protection.

Marine Fouling

Fouling does not destroy materials directly. It is the settlement of marine fouling organisms on all structures made of wood, steel, FRP, aluminium and ferrocement exposed to seawater. Immediately after a substrate is immersed in seawater, fouling settlement starts and

the sequence of processes are formation of a primary film or slime film (formed by bacteria, fungi, diatoms and protozoa enmeshed in detritus), fixation of larvae of macroscopic organisms (algae, tubeworms, bryozoans, hydroids, barnacles, mollusks) and finally the growth of the fouling community. In the case of ships because of fouling the roughness of hull and the fuel consumption are increased while speed is reduced. Corrosion process in the marine medium is closely related to the failure of antifouling coatings. Underwater or splash zone of marine structures are subjected to a very harsh environment where corrosion and biofouling combine to cause loss of millions of rupees annually.

Bacteria, fungi, diatoms and algae are the most frequent vegetable organisms attached while hydroids, bryozoa, tunicates, serpulids and barnacles are the animal species generally recorded. Of these the barnacles especially of the genus *Balanus* are the most aggressive, deteriorating the organic coating, affecting the continuity and favouring corrosion. Variation in temperature, salinity, pH, oxygen content and pollution influence this process.

Fouling Control

A periodical coating of antifouling coatings seem to be the only accepted method for fouling prevention throughout the world. In the AF paint film, biocides must be released during the lifetime of the coating and must cover a wide spectrum of fouling species. Different antifouling coatings were developed over the years according to the type of ship, area of operation of ships, trading speed, vessel activity in days per year, maximum length of stay in port and docking intervals. Fouling normally occurs when a vessel is stationary and does not take place at speeds less than 6 knots.

Cuprous oxide, an inorganic toxicant and tributyl tin oxide (TBTO) is an organic toxicant most commonly used in the antifouling coatings. Paints based on organometallic compounds such as TBTO and tributyl tin fluoride (TBTF) provide 4 to 5 years of fouling free life. However the use of these is restricted due to the problem of environmental pollution.

The awareness of environment in the recent years paved way to the development of alternate coatings and new procedures for fouling control. Considering current antifouling regulation in different countries, the use of coatings requires clearance from the Government. In general, TBT based antifouling paints must not be applied to vessels of < 25 m in length and they must have biocide release rates less than $4 \mu\text{g TBT cm}^{-2} \text{ day}^{-1}$. All copper based coatings must have a copper release rate of less than $40 \mu\text{g cm}^{-2} \text{ day}^{-1}$. Tin free coatings using chemicals such as ammonium quaternary compounds and polymeric silicones bonded to polymeric chain are reported to obtain a low bio-adherence. Development of a system that uses non-stick mechanism to give a glossy surface without biocides is also under study. The incorporation of natural products of plant or animal origin, which have antifouling properties in the antifouling coatings, is a new area of study.

Microbial Corrosion

Seawater is a well-known corrosive environment and any biological activity can enhance its aggressiveness. The involvement of microorganisms in metal corrosion process was suggested as early as in late 1890s. It was reported that the corrosive action of water on lead could be due to ammonia, nitrites and nitrates produced by bacteria. The interaction of a biofilm and the substratum produces a new physical and chemical environment. The conditions at the substratum will be quite different to that in the bulk phase or in the unfouled surface and the activity of microorganisms within biofilms will result in a range of consequences.

Microbial action may bring about metallic corrosion by one or more of the following mechanisms: (a) production of corrosion metabolic products (b) production of differential aeration cells, (c) disruption of protective films (natural and applied) and breakdown of corrosion inhibitors. Most of the time corrosion occurs as a result of more than one mechanism either simultaneously or successively. Differential aeration cells can be created between normally highly oxygenated surface and metal under macro fouling or even under a thin layer of biofilm.

The formation of various corrosion products on the metal slows down the corrosion process. But organisms disrupt these films and stimulate corrosion process. Hydrogen sulphide produced by sulphate-reducing bacteria under anaerobic conditions cause serious corrosion problems. There are several groups of bacteria, which are strongly associated with corrosion. Sulphate reducing bacteria, iron bacteria, slime forming bacteria, sulphur oxidizing bacteria and nitrogen utilizing bacteria are the important ones. Sulfate reducers of the genus *Desulfovibrio* are commonly reported groups.

Assessment of Biodeterioration

There are standard methods for assessing/testing Biodeterioration that can be grouped into two: destructive testing and non-destructive testing.

Destructive testing- includes test procedures, which destroy the test sample under assessment. Mechanical strength testing and cutting opening the sample to see the internal damage especially in natural materials like wood come under this.

Non-destructive testing - include procedures like X-ray radiographs and visual observation of the surface of the test sample. These methods do not destroy the test sample and have the advantage of using the same sample for further study.

Prevention

In the ocean where there are continuously changing physical, chemical and biological parameters it is often difficult to predict biological corrosion. Most often it is unexpected and is difficult to control, once established in the system.

To prevent or control the problem, the following methods are used.

- i. Use of biocides to control the biological activity.
- ii. Use of anticorrosive coatings and application of Cathodic protection procedures
- iii. Upgradation of material
- iv. Use of physical barriers/wrappings