Microbiologically influenced corrosion in petroleum product pipelines — A review

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Microbiologically influenced corrosion is responsible for most of the internal corrosion problems in oil transportation pipelines and storage tanks. One problematic area in treating gas lines is the occurrence of the stratification of water in the line. Under these conditions, corrosion inhibitors do not come into contact properly and oil and inhibitors undergo degradation. The role of bacteria on oil degradation, the consequences of oil degradation in fuel systems and its influence on corrosion have been explained in detail. Besides, factors influencing on degradation of oil and corrosion inhibitors have also been discussed. Mechanism of microbiologically influenced corrosion in oil pipeline has been explained. Many of the misapplication of biocides/inhibitors occur mainly because the characteristics of biocides/inhibitors are not considered before use in pipeline industry. List of biocides and monitoring programme have been collected from literature and presented.

Keywords: Biocides, Corrosion, Degradation of oil, Microbial corrosion, Oil pipelines, Petroleum product, Storage tanks

Corrosion refers to the deterioration of the materials (metallic and non-metallic) due to their reaction with the environment. Rusting of iron with the formation of iron oxide is a typical example of corrosion. Corrosion of metals and alloys leads to enormous losses to the country. Large amount of coating materials like paints, as well as corrosion resistant alloys are needed for controlling corrosion. By understanding the mechanism of corrosion and the principle involved in the methods of protection of the same, the country would be able to save at least 15-20% of the total loss, amounting to about Rs.15,000 crores annually.

Microbiologically influenced corrosion (MIC)

Microbial corrosion is recognized as one of the major problems in various fields. The biological growth causes fouling and corrosion problems. A large variety of bio-organisms can enhance the corrosion rate of metals through their metabolic processes. The ways in which these organisms influence corrosion have been described in the literature. Particularly it has been shown that the presence of bio-organisms in any environment results in localized rather than general corrosion. However, the ability of these bio-organisms in deposits, relatively in large amounts with metal ions, suggests that they participate in corrosion processes. Microbiologically influenced corrosion (MIC), is responsible for most internal corrosion found in oil transmission pipelines. The type of corrosion caused by microbes results in sharp-sided rounded pits and often with pits within the pits. These are typically scattered randomly along the pipe whenever the line has become water-wet, either when low velocities result in water lying in low spots in the line, or when the water is more than about 30% of the liquid phase. The pitting occurs in the bottom of the line, and often occurs as linear strings of pits associated either with the oil-water contact phase or along the edge of sediment deposits. Water can stratify and collect in pipelines when the velocity is too slow, typically below 3-4 ft/sec, or if the pipeline is operated in a 'stop-start' mode.

When bacteria grow on the walls of the pipe, they develop into colonies containing many types of bacteria, which help each other in life. Well-known types, which cause corrosion, include acid-producing bacteria (APB), sulphate-reducing bacteria (SRB), iron bacteria (IB) and manganese oxidizing bacteria (MoB). SRB and acid producing bacteria are the two types of bacteria commonly found in oil and gas pipelines. SRB produce hydrogen sulphide, while APB generate acetic acid/sulphuric acid, both of

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which are highly corrosive to the pipe. Many other types of bacteria like manganese oxidizing bacteria and heterotrophic bacteria are present. Iron bacteria precipitate the iron present in solution arising from corrosion and form a tubercle on the top of the corrosion pit.

The present review deals with two parts: (1) role of oil degradation on microbiologically induced corrosion and (2) oil degradation due to microbes.

Microbial corrosion is one among the many forms of corrosion that contributes to substantial losses to the economy. This is an interdisciplinary subject, which requires at least a basic understanding in the field of microbiology, chemistry, biochemistry and metallurgy. By definition, it refers to the degradation of metallic structures resulting due to the activity of a variety of microorganisms, which either produce aggressive metabolites to render the environment corrosive or able to participate directly in the electrochemical reaction occurring on the metal surface.

Microorganisms present in aqueous environment form biofilm on solid surfaces. Biofilm consists of populations of microorganisms and their hydrated polymeric secretions. Numerous types of organisms may exist in any particular biofilm, ranging from strictly aerobic bacteria at the water interface to anaerobic bacteria such as sulphate reducing bacteria (SRB) at the oxygen depleted metal surface. The presence of biofilm can contribute to corrosion in three ways:

1. Physical deposition, 2. Production of corrosive by-products, and 3. Depolarization of the corrosion cell caused by chemical reaction.

Many of the by-products of microbial metabolism including organic acids and hydrogen sulphide are corrosive. These materials can concentrate in the biofilm causing accelerated metal attack. Corrosion tends to be self-limited due to the build-up of corrosion reaction products. However, microbes can absorb some of these materials in their metabolism, thereby removing them from the anodic and cathodic sites. The removal of reaction products, termed depolarization, stimulates further corrosion. The surface exhibits its scattered areas of localized corrosion, unrelated to the flow pattern.

Microorganisms associated with corrosion

Fungi

Two forms of fungi that are commonly associated with corroding metal are filamentous forms (mould) and unicellular forms (yeasts). The filamentous forms are branched and a tangled mass referred to as mycelium. This releases organic acids as metabolites, which enhances corrosion. Fungi are the most desiccant resistant microorganisms and can remain active down to a$_w$ = 0.60. Most of the fungi are aerobes and are only found in aerobic habitats. Fungi are non-photosynthetic organisms, having a vegetative structure known as hypae. The outgrowth is a single microscopic reproductive cell or spore. A mass or thread like hypae make up a mycelium, mycelia are capable of almost wide finite growth in presence of adequate moisture and nutrients so that fungi often reach macroscopic dimensions. Spores, the non-vegetative dormant stage, can survive long periods of unfavourable growth conditions e.g. drought and starvation. When conditions are favourable, spores germinate. Fungi ubiquitous in atmospheric and aquatic environment where they assimilate organic material and produce organic acids including oxalic, formic, acetic and citric acid. Fungal contamination and decomposition of hydrocarbons are well documented. Cladosporium resinae, the kerosene fungus, grew in 80mg water per litre of kerosene.

Little and Ray demonstrated metal ion binding by fungal mycelia, resulting in metal ion concentration cells on the metal surface. Differential aeration caused by the adhesive or fungal mats can cause crevice corrosion. Besides the decrease in bulk pH also accelerates corrosion due to metabolites produced during the growth by fungi.

Bacteria

These organisms can either be autotrophic or heterotrophic and either aerobic or anaerobic. Heterotrophic bacteria derive their energy and carbon requirements from organic sources. Autotrophs are bacteria, which obtain their energy from the light or by the oxidation of inorganic materials and the carbon by assimilation. Anaerobic bacteria do not require oxygen for their growth. It is the major group in moist soil and water contributing to corrosion process. Sulphate reducing bacteria (SRB), sulfur-oxidizing bacteria are the major group involved in microbial corrosion.

Sulphate reducing bacteria (anaerobic corrosion)

The role of hydrogenase activity in SRB related corrosion of mild steel is unclear. Hydrogenase positive SRB can oxidize the molecular hydrogen generated at the cathodic sites to facilitate 'cathodic
depolarization. In this mechanism, the combination of adsorbed H-atoms produces H₂S gas and this is considered to be the rate-controlling step. Bacteria effectively increase the hydrogen evolution rate and thereby the activity increases the corrosion rate. Besides, stimulation of anodic reaction by bacterially produced sulphide has also been suggested. Moreover, the initial corrosion rate that was accelerated by iron sulphide in a biofilm system, has been attributed to both “anodic and cathodic depolarization”. However, corrosion engineers consider the role of corrosion process in oxygen-free environment that is principally dependent on their ability to produce ferrous sulphide as suggested by King et al. Besides these sulphides have been claimed as semiconductors.

**Acid producing bacteria**

The most corrosive metabolites produced directly by microorganisms seem to be acid producers. Acetic and butyric acids are examples of such corrosive microbial products. The sulfur oxidizing bacteria e.g. *Thiobacillus* sp. produce sulfurous acid from sulfur or sulfide. They occur commonly in solids, soils and water that contain sulfide minerals. In some buried pipelines, production of sulfuric acid has been reported. Corrosion of concrete and steel pipes carrying municipal water has also been related to localized production of sulfuric acid by *Thiobacillus* sp.

**Iron reducing bacteria**

Various *Pseudomonas* sp. have been implicated in the reduction of ferric (Fe³⁺) to ferrous ion (Fe²⁺). As ferric salts protect the metal surface from further corrosion due to chemical activity. Ferrous salts are mostly soluble and therefore reduction of ferric salts results in the removal of the protective layer. Thus, iron reducing *Pseudomonas* sp. promotes corrosion directly.

**Iron oxidizing bacteria**

The aerobic iron oxidizing bacteria namely *Pseudomicrobium* sp. and *Gallionella* sp. oxidize ferrous (Fe²⁺) to ferric ion. Tubercles are initially formed by the deposition of iron and manganese oxide. The tubercles have a steep pH gradient, the pH inside being very low.

**Manganese oxidizing bacteria**

It has been found that the actively metabolizing manganese oxidizing bacteria deposit MnO₂ creating an anaerobic arena that would favour the growth of sulfur reducers whose activity at low values of electrochemical potential might further stimulate the corrosion process initiated by the MnO₂ ennoblement. Xu et al. proposed that the loss of passivity or interference with repassivation might arise from the production of strong environmental oxidants such as Mn(III) complexes, which may initiate localized corrosion of passive metals.

SRB stimulates a pre-existing active corrosion in mild steel and the biogenic sulfide reacts with ferrous ions already solubilized from the metal substratum. The biominalized MnO₂ arises from the oxidation of soluble manganese in the bulk medium and makes corrosion possible that would not otherwise occur. SRB sews to initiate a series of reactions that are therefore autocatalytic. In the case of MnO₂ it is reduced as the cathodic reductant and must, therefore, be continuously replenished by ongoing microbial activity. The two microbially influenced cathodic reactions occur at different electrochemical potentials but the essential redox characteristics remain as such. This considerably strengthens the electrochemical/physiological electron transfer hypothesis in a microbially influenced corrosion by extending its validity to active, mild and passivated stainless steels.

**Role of microbes on oil degradation**

ZoBell reviewed the action of microorganisms on hydrocarbons. He recognized that many microorganisms have the ability to utilize hydrocarbons as sole source of energy and these microorganisms are widely distributed in nature. He further recognized that microbial utilization of hydrocarbons was highly dependent on the chemical nature of the compounds within the petroleum mixtures and on the environmental determinants.

Twenty-one years after ZoBell’s classic review, the super tanker Torrey Canyon sank in the English Channel. With this incident, attentions of the scientific community were dramatically focused on problems of oil pollution. After this event, several studies were initiated on the fate of problems of oil pollution. Several studies were also initiated on the fate of petroleum in varied ecosystem. Biodegradation of petroleum in natural ecosystem is complex. The evolution of the hydrocarbon mixture depends on the nature of the oil, the nature of the microbial community, and a variety of environmental factors, which influence microbial activities.

**Hydrocarbon utilizing microorganisms**

The ability to degrade petroleum hydrocarbons is not restricted to a few microbial genera. A diverse
group of bacteria and fungi have been shown to have this ability. Zobell in his review noted that more than 100 species representing 30 microbial genera had been shown to be capable of utilizing hydrocarbons. In a review, Bartha and Atlas listed 22 genera of bacteria, 1 algal genus and 14 genera of fungi, which had been demonstrated to contain members, those utilize petroleum hydrocarbons. All of these microorganisms had been isolated from aquatic environments. The most important (based on frequency of isolation) genera of hydrocarbon utilizers in aquatic environments were Pseudomonas sp., Achromobacter sp., Micrococcus sp., Nocardia sp., Candida sp., Vibrio sp., Acinetobacter sp., Brevibacterium sp., Rhodotorula sp., Sporobolomyces sp., Corynebacterium sp., and Flavobacterium sp.

Walker et al. compared the abilities of bacteria and fungi in the degradation of hydrocarbons. The following genera were included in their study Candida sp., Sporobolomyces sp., Hansenula sp., Rhodotorula sp., Cladosporium sp., Penicillium sp., Aspergillus sp., Pseudomonas sp., Vibrio sp., Nocardia sp., and Rhodobium sp. Walker et al. isolated Vibrio sp., Pseudomonas sp. and Acinetobacter sp. from oil-contaminated sediments and Pseudomonas sp. and Coryneform sp. from oil-free sediment. A large number of Pseudomonas sp. have been isolated that are capable of utilizing petroleum hydrocarbons. The genetics and enzymology of hydrocarbon degradation by Pseudomonas sp. have been extensively studied. The genetic information for hydrocarbon degradation in these organisms generally has been found to occur on plasmids. Numerical taxonomy has also been used to examine petroleum-degrading bacteria. Recently Rahaman et al. reported 130 bacterial culture as crude oil degrades in Bombay high.

**Factors influencing oil degradation**

**Nitrogen and phosphorous**

There is some confusion and considerable apparent conflict in the literature regarding the limitation of petroleum biodegradation by available concentrations of nitrogen and phosphorous. Lepeit and Barthelemy reported that the concentration of available nitrogen and phosphorous in water are severe limiting factors for microbial hydrocarbon degradation. Kinney, however is of the opinion that nitrogen and phosphorous are not the limiting factor, since microorganisms require nitrogen and phosphorous for their incorporation into biomass and that the availability of these nutrients within the same area as that of hydrocarbon is critical. Colwell et al. concluded that Metula oil was degraded slowly in the marine environment most probably because of the limitations imposed by the relatively low concentrations of nitrogen and phosphorous availability. The cultures studies have indicated that the available concentrations of nitrogen and phosphorous severely limit the extent of hydrocarbon degradation of the most major oil spills. Rates of nutrient replenishment generally are inadequate to support rapid biodegradation of large quantities of oil. The addition of nitrogen and phosphorous containing fertilizers can be used to stimulate microbial degradation of hydrocarbon.

**Oxygen**

As with nutrients, there has been controversy over whether oxygen is absolutely required for hydrocarbon degradation or whether hydrocarbons are subject to anaerobic degradation. The recent literature by Grishchenkov and Zinjarde supports the view that anaerobic degradation by microorganisms at best proceeds at negligible rates in nature. The existence of microorganisms, which are capable of anaerobic hydrocarbon metabolism, has not been excluded. During storage of oil products, underground conditions are usually limited in oxygen and it is of special concern if hydrocarbon degradation is possible under anaerobic conditions. The initial attack on hydrocarbon requires oxygen, but for the subsequent steps, anaerobic processes may degrade partially oxygenated intermediates further. Under oxygen limited conditions and accumulation of degradation products in the form of fatty acids occur. It has been shown that the sulphate-reducing bacteria in the fuel, and even in a relatively static system. The microbes themselves can produce biosurfactants and gaseous by-products which carry up into fuel, increasing the surface area available for microbial activity.

In fact, there have been several reports of isolated microorganisms, which are capable of alkane dehydrogenation under anaerobic conditions. These organisms have enzymatic mechanisms, which should permit addition of water across the double bond, forming a secondary alcohol, and therefore permit anaerobic growth. In the case of Pseudomonas sp. strain studied by Senez and Azouly, the organisms consumed oxygen when grown on heptane even though it had an n-heptane dehydrogenase enzyme. The importance of oxygen for hydrocarbon degradation is well indicated by the fact that the major degradative pathways for both saturated and aromatic
Degradation of hydrocarbons has been reviewed by Atlas\textsuperscript{35} and SRB can use a wide range of fatty acids including acetate, lactate, propionate, butyrate and fatty acids up to C\textsubscript{16} and some phenyl substituted acids\textsuperscript{34}. The generally accepted view is that anaerobic degradation of hydrocarbons is a very slow process as compared to aerobic degradation. Over very long periods, however, it might be significant. Reports on the anaerobic degradation in natural ecosystems have suggested that nitrate or sulphate could serve as electron acceptors in place of oxygen\textsuperscript{19}.  

**Temperature and pressure**

Schwarz \textit{et al.}\textsuperscript{35} examined the growth and utilization of hydrocarbons at ambient and in \textit{sinu} pressure for deep-sea bacteria. The rate of hydrocarbon utilization at high pressure and ambient temperatures were found to be significantly lower than the rates found under conditions of ambient temperatures and atmospheric pressure, whereas 94\% hexadecane was utilized within 8 weeks at 1 bar while at 500 bars it took 40 weeks for similar degradation. It appears that oil, which enters deep-ocean environments, will be degraded very slowly and persist for long periods of time. Biodegradation can occur over a wide range of temperatures from below 0\(^\circ\)C to 70\(^\circ\)C\textsuperscript{19,20}.  

Most hydrocarbon degrading microorganism prefers a near neutral pH while source organism can tolerate extreme values.

**Consequences of oil degradation in fuel systems**

**Physical debris**

The most obvious and recognizable consequence of microbial activity is the formation of visible solids. These are the combinations of living and dead cellular material, inorganic by-product and extraneous debris and biologically generated membranous material. The "classic" historical problems are centered on 

\textit{Cladosporium resinae}, but many yeasts and bacteria can contribute significantly too to this physical load. This material may block fuel lines, injectors, pipes, filters and oil/water separators as well as adding potential corrosion problems.

**Fuel turbidity/cloudiness**

For a fuel to be of marketable quality, it must be clear and bright (C+B). Microbial growth can often cause severe turbidity and cloudiness. This arises in one of two ways. Any mixing of interfacial growth can often produce particles of such a density that they remain in components. The hydrocarbon range of gasoline, C\textsubscript{3}–C\textsubscript{5} is less likely to be degraded, but kerosene with a hydrocarbon range of C\textsubscript{10}–C\textsubscript{18} is more susceptible\textsuperscript{36}. The preferential removal of C\textsubscript{15}–C\textsubscript{35} n-alkanes relative to branched and cyclic alkanes is recognized as standard feature in biodegradation of crude oils\textsuperscript{35,36}. Degradation normally proceeds by a monoterminal attack wherein usually a primary alcohol is formed followed by aldehyde and a mono carboxylic acid.

**Chemical alteration of fuels**

Often linked with the increased corrosivity as mentioned above are microbiologically produced by-products that can often change the actual chemical properties of fuels in storage tanks and transporting pipelines. Gaseous by-products from microbial metabolism such as H\textsubscript{2}S, SO\textsubscript{2} and CO\textsubscript{2} are often generated in such quantities that they can dissolve in the fuel, increasing the silver strip corrosion index. The H\textsubscript{2}S generation can also be a severe health hazard to the operating staff. Other metabolites, such as biosurfactants, can increase the emulsification of fuels.

**Control of biodegradation of fuels**

**Physical control**

Apart from maintaining fuels at temperatures unsuitable for microbiological growth, which is often very difficult, the more obvious method of control is to eliminate water, by good house keeping techniques, but this is often very difficult to achieve for the following reasons:

- Many fuels contain a degree of dissolved or chemically bound water, which can later condense out during temperature changes and form free microbiologically available water.
- Atmospheric moisture may often enter the storage systems through breather vents, floating tank tops, ineffective seals etc.
- Other systems may actually purge delivery lines with various sources of water, for example cleaning of pig on muck collecting tanks.
- Complete water removal may be very difficult due to tank design etc. Thus, given that temperature control and water elimination, which is often impractical or costly to implement, the alternative is to look for some means of chemical control for
the growth of fungi, yeasts and bacteria, i.e., a microbicide or microbiostat.

**Chemical control**

One of the main considerations in choosing microbicide is whether the aim is to treat the water phase, fuel phase or both. There are advantages and disadvantages of treating either the water-fuel phase, but for long-term protection, a biocide that can treat the whole system appears to be an ideal solution.

Generally the bacterial physiology in oil pipeline undergoes in two ways:

1. Conversion or storage or deposition of metals. Since these two processes are interlinked and dependent during the physiological activity of microbes, the corrosion action will be high in oil pipelines. Hence, MIC is an important aspect in oil industry and it should be considered as a major factor by maintenance engineers.

**Role of oil degradation on corrosion**

The biodegradation of aliphatic and aromatic hydrocarbons present in diesel oil by *Pseudomonas* sp. was studied by Trzesicka-Mlynarz and Ward, and reported that degradation of aliphatic than aromatic compounds occurred within 20 days of incubation. Identically, CECRI has noticed that the rates of degradation of aliphatic hydrocarbons were found to be high when compared to the rates of degradation of aromatic hydrocarbons. The rate of addition of oxygen (consumption of hydrogen) to various strains is given below by Muthukumar et al., which was collected from an oil pipeline in Northern India.

- *Brucella* sp. < Sulfolobus sp. < Thiobacillus sp. < *Moraxella* sp. < *Gallionella* sp.

CECRI also observed that, *Brucella* sp. was the most prevalent and dominant aromatic hydrocarbon degrading bacteria. Similarly, the works of Daughter et al. on the polynuclear aromatic hydrocarbon (PAH) degrading bacterial strains showed *Pseudomonas putida*, *P. fluorescens*, and *P. aeruginosa* isolated from the oil contaminated soil, which were further characterized for specific features regarding PAH degradation. The soil fungus *Chadophialaphora* sp. was also capable of degrading alkylated benzenes (toluene, ethyl benzene, xylenes) by a combination of assimilation and cometabolism. Toluene and Ethyl benzene were used as sources of carbon and energy. The ethyl benzene was degraded by monooxygenase enzyme. Besides *Rhodococcus rhodochrous* S-2 produces extra cellular polysaccharides that help to sustain in aromatic fraction. Since *Gallionella* sp. oxidizes ferrous ions into oxide in presence of oxygen, it utilizes energy from carbon and hydrogen during oil degradation. Besides, it can be assumed that *Brucella* sp. help for the formation of more aliphatic protons in diesel which may be utilized by *Gallionella* sp.

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\text{Fe}^{2+} + \text{O}_{2} \rightarrow \text{Fe}^{3+} + \text{O}_{2}^{-} \text{Bacterial metabolism}
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**Internal corrosion control in oil pipelines**

Enormous amount of money is being spent every year on prevention, monitoring, inspection, and land repair of the corrosion-related damages. Internal corrosion control programmes usually involve chemical treatment with corrosion inhibitors. Corrosion inhibitors are marketed in several basic types, such as oil-soluble, water-dispersible, water-soluble, limited-solubility (gunkers), and volatile, etc., and each performs uniquely in different pipeline conditions. It can be applied in a batch procedure where the persistent nature of a heavy protective film may last for weeks or months. Or they can be continuously metered into the pipeline in low concentrations through a continuous injection programmer, in which a thin film is gradually laid down and maintained overtime. The chemicals work very well, provided that they can reach the wall of the pipe and form an effective film.

Corrosion inhibitors are based on cationic surfactant chemicals, which chemically bind to any negatively charged surface. Included in this grouping are metal and corrosion products such as iron carbonate, iron sulphide, iron oxide, sand and clay. If deposits of dirt, corrosion products, and bacteria are inside the pipe, they can both consume chemicals meant to treat the walls of the pipe, and prevent the chemical from contacting the walls of the pipe beneath the deposits. For these reasons, pipelines should be as clean as possible when corrosion inhibitors are applied.

A pigging programme is the most cost-effective and efficient method of cleaning the pipe surface, for the application of liquid inhibitors.

**Degradation of inhibitors/biocides in petroleum pipeline**

In general, organic films are used in oil and gas production, transport and storage systems.
could be susceptible to microbial degradation during their use with a consequent loss in their efficiency for corrosion inhibition. Many of the misapplications of biocides/inhibitors occur because of the characteristics of the biocide/inhibitors that are not considered before use. Genetic diversity and molecular evolution among microbial consortia make them more potent and competent enough to transform or utilize the hydrocarbon/inhibitors.

Benzoin acid is readily decomposed by the microorganism Actinobacter calcoaceticus, among others. The biodegradation of both n-alkane and several carboxylated cyclo alkanes in oil sand tailings are also reported. Ingrum described yeast, that could degrade benzoin acid but only with the concomitant degradation of sugars. None of the organisms were able to utilize methyl p-hydroxybenzoate for growth but Hugo and Foster showed that Pseudomonas aeruginosa NCTC 7244, an organism not examined by Beveridge and Hugo was able to do so. Beveridge and Hart made further investigations on the decomposition of esters of p-hydroxybenzoic acid by microorganisms. They found that Alcaligenes sp., Aeromonas sp., Pseudomonas aeruginosa, P. fluorescens and Bacillus sp. were isolated from a variety of environment that could degrade the esters. Sokolski et al. demonstrated the hydrolysis of methyl p-hydroxybenzoate by Clostridium resinae (now Hormonicon resinae). The parent acid was decomposed by all but one of the nine organisms tested by Beveridge and Hugo but these workers found no attack upon the methyl ester. Sorbic acid is used as a preservative in the food and oil industry. It can be degraded to 1, 3-pentadiene by certain moulds of the genus Penicillium.

The pathways discussed so far have all dealt with the decomposition of preservatives under aerobic conditions. In fact, many of the studies and ancillary biochemical investigations were carried out in air by Warburg respirometry. The anaerobic degradation of aromatic compounds could be of importance in preserved preparations packed in airtight containers. Anaerobic metabolism of these compounds has been reviewed by Sleat and Robinson. Of the compounds decomposed anaerobically, the following preservatives were identified: benzoate, benzoic alcohol, phenol, cresols, cinnamic acid and vanillin acid. The o-, m- and p-hydroxybenzoic acids are also known to be metabolized and it would be interesting to see if their alkyl esters suffered decomposition. It is clear that the ability to decompose compounds traditionally regarded as preservatives is a property of many microorganisms ranging from bacteria to fungi and this facet of microbial activity cannot be ignored during formulation as a possible causative factor for microbiological spoilage.

One problematic area in treating gas lines is that stratification of liquids in the line may occur. Therefore, the flow pattern or regimes must be considered when applying corrosion inhibitors. When multiphase conditions exist, liquids stratify along the pipe bottom, with water forming a separate layer beneath the hydrogen liquids. Under these conditions, certain corrosion inhibitors do not come into contact properly with upper walls of the pipes, thereby leaving a good portion of it unprotected. The changes in flow regimes that develop due to changes in pipeline elevation or hindrance to the stratified flow or slug flow when fluids start flowing uphill or downhill often result in the failure of inhibitor contacting the pipe walls.

Corrosion failure can occur when stratification of pipeline liquids prevents the corrosion inhibitor from reaching the upper walls of the pipe. In oil lines, water can stratify also at the bottom of the line with velocity is less than required to entrain the water and sweep it through the system. Using oil soluble, water dispersible, filming amine-type corrosion inhibitors that can disperse sufficiently into stratified water layers to prevent corrosion beneath the water best inhibits oil lines. Control of bacteria and bacterially induced corrosion in pipelines is another area where chemical application is enhanced greatly when used in conjunction with pigging. Organic corrosion inhibitors function by chemisorption of the molecule on a metallic substrate, complexing of the molecule with the metal ion that remains in a solid lattice, neutralizing corrosive and or absorbing the corroding agent. Biocides reduce the proliferation of bacteria in the product and on metals. Many of the misapplications of biocides/inhibitors occur mainly because the characteristics of biocides/inhibitors are not considered before use and this plays an important role of MIC.

The petroleum industries are universally facing a tough time due to corrosion in the pipeline transporting the petroleum product. Many pipeline users like Indian Oil Corporation, Bharath Petroleum Corporation and Oil and Natural Gas Commission are using many inhibitors/biocides (Figs 1 & 2) to overcome the microbial corrosion in the storage tanks and in the pipeline transporting petroleum products. Many oil pipelines in India employing biocide/inhibitors are facing severe corrosion and microfouling problems in their pipeline due to degradation of preservatives.
This article also presents the MIC and control measures associated with the selection of various inhibitors/biocides to make the oil field personnel, especially the non-biologists aware of the problems associated with the applications of biocides even though the chemicals selected have been reported by biologists, to be effective against corrosion.

Volatile inhibitors, such as diethylamine, can also be injected at the same time in order to prevent corrosion in condensing liquids at the top of the pipe. This can provide protection to the initial portion in the line where condensation rates are high, although volatile inhibitors are generally considered for their limited travel ability not going very far down the line.

**Biocides**

Biocides are the most underused, misunderstood, and misapplied chemical products in the petroleum industry. They are most effective when properly selected and applied. This article presents the MIC and control measures associated with the selection of various inhibitors/biocides to make the oil field personnel, especially the non-biologists aware of the problems associated with the applications of biocides even though the chemicals selected have been reported by biologists, to be effective against corrosion.

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**Fig. 1 — Oil field corrosion inhibitors — Cationic molecular structures**
industries for many reasons. Biocides are used to combat a problem that is subtle and difficult to detect. In general, biocides are needed to control the activity of the bacteria in a system. However, biocides alone cannot solve a microbiological problem.

Very few sample and reliable means of monitoring are available to the supplier or the end user, and the benefits of biocide use take a long time to become evident. Finally, once bacteria are well established it is nearly impossible to control without drastic measures.

![Chemical structures](image)

**Dimer-trimer acids**

- **Fatty acids**

- **Naphthenic acids**

- **Dodecyl benzene sulfonic acids**

**Petroleum oxides**

- **Petroleum-derived oxides** (from petroleum, paraffin wax, lubricating oil, or fuel distillate) are complex mixtures composed primarily of organic acids and esters, but also contain alcohols, ketones hydroxy and keto acids, estolides, lactides, and lactones.

**Phosphate Esters of Ethoxylated alcohol**

**Other organic Acids**

1. Acetic
2. Hydroxyacetic
3. Benzoic

**Fig. 2.— Oil field corrosion inhibitors — Anionic molecular structures**
measures\textsuperscript{54}. Hence, identification of microbes and also the role of inhibitors on microbial growth are to be studied in detail.

Examples of chemicals used as fuel system biocides (fuel- or water soluble)
- Methylene bithiocyanate
- Hexahydrido-1,3,5-tris (2-hydroxyethyl)-S-triazine
- Mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazoline-3-one
- Ethylene or diethylene glycol monomethyl ether
- Mixture of 4-(2-nitrobutyl) morpholine and 4,4′-(2-ethyl-2-nitromethylene-dimorpholine
- Mixture of 2′-s-oxy-bis(4,4,6-trimethyl-1,3,2-dioxaborinane) and 2, 2′-(1-methyl-trimethylene di-oxy) bis-(4-methyl-1,3,2-dioxaborinane)
- Methyl-1-(butylcarbamoyl)-2-benzimidazole carbonate-1-(2-hydroxyethyl)-2-alkyl-(C-18)-2-imidazole etc.

Monitoring program
Initial and continuous care is better than later prevention because once metal is microfouled, the film can be eradicated only with the addition of a biocides at very strong doses of or by scraping, which usually involves much trained labours and high operational costs. Hence, it is necessary to formulate a continuous monitoring programme by weight loss assessments and by microbiological analyses, if untreated water is used. A simple monitoring programme is given below:
- Chemical analysis of the water/oil used.
- Sampling and identification of the microbial population in the water/oil.
- Identification of microbes that form sessile consortia on the metals used in the site.
- Detection of flow lines and stagnant points in the flow lines.
- The quantity and the nutrient contents of the water, the interface between inhibitor and biocide, the degradation of inhibitors have to be analysed for effective usage of biocides.
- Selection of specific biocides with respect to the exact populations encountered in the site.
- Determination of exact concentration of biocide at which it ensures highest percent efficiency over sessile bacteria.
- If needed, dispersant can also be supplemented with the microbeicide.
- Immediately after pigging the line, a higher concentration of the microbeicide can be added followed by periodical additions at lower concentration (shock treatment). The quantity added should not be below the prescribed level, since a microbeicide at insufficient concentration promotes the microbial growth.
- Monitoring the magnitude of bacteria before and after every four hours of biocide addition has to be carried out.
- Periodical monitoring of MIC by weight loss method/electrochemical probe technique is to be followed.
- The persistency and the level of the inhibitor/biocide should be checked by taking samples periodically at various pumping stations.

In general, applied work towards the control of MIC in oil pipeline is very much limited. Oil pipeline industries require immediate solution to their problems of MIC rather than the mechanisms involved. More research work on the \textit{in situ} identification of MIC and also the ways to control MIC instantaneously is the need of the hour. A continuous monitoring programme must be established in the industries, which would be helpful in knowing the alarming concentration of microbes present in oil pipelines.

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