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CONTROL OF MICROBIOLOGICALLY INDUCED CORROSION

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Mircrobiologically influenced corrosion (MIC) of metals is a highly documented hazard that baffles almost all the metal using industries. Several failures of this sort have been reported in the literature, especially in cooling towers, oil well explorations, alcohol industries, drainage pipes, underground tanks, nuclear power stations, heat exchangers, etc. This article briefs some keys for the field identification of microbial groups involved, explains a MIC monitoring program and analyses the physical, biological and chemical measures for MIC control.

Key words: Microfouling, microbial corrosion, mildewcides

INTRODUCTION

The increasing awareness towards microbiologically influenced corrosion (MIC) can easily be understood through increasing research work available on MIC and allied problems [1-5]. Microbial corrosion does not involve any new form of corrosion, but it provides a different path to an already existing process. The microbial involvement in corrosion processes may be either direct, by the intrusion into the electrochemical reactions, or indirect, by virtue of their metabolic products and other physiological activities.

Microbes can induce corrosion by creating differential aeration/concentration cells [6], retaining water, disturbing passive films [7], changing pH [8], synthesising or depleting oxygen [9], utilizing cathodic hydrogen [10] (thereby depolarizing cathode) or by producing hydrogen [11], removing metallic atoms from metals [12], oxidizing [13] or reducing [14] corrosion inhibitors, setting up of galvanic cells, disturbing or feeding upon protective organic coatings [15] and by their metabolic products [16].

The present article deals with the field identification, monitoring and eradication of the microbial culprits involved in this unique form of corrosion.

In situ detection of MIC

In general, each group of microbes has certain apparent pattern of attack on metals. This attack may be brought about by microbes either individually or by working in a cyclic fashion. This character of microbes is helpful to identify the groups of microbes involved in MIC.

Some of the keys to identify the groups involved are:

1.	Tuberculation/blistering	May be due to IB
2.	Unexpected increase in H_2S odour/black deposits	May be due to SRB
3.	Delicate scummy products in different colours	May be due to SFB
4.	Slimy, brown coloured (like rust) or rose coloured colonies	May be due to Thiobacilli
5.	Generally green delicate scums; almost uniformly distributed	May be due to algae
6.	Generally dry, appear like cotton or wool; or in dot like colonies	May be due to fungi
7.	Decreased pH; increase in turbidity in site water	May be due to acid producing bacteria
8.	Increased organic acid concentration	May be due to *Flavobacterium* sp. or *Lactobacillus* sp.
9.	Presence of sulfur, when there is no other source for it in the site	May be due to Thiobacilli
10.	Creation of anaerobic conditions or decrease in dissolved oxygen	May be due to SRB

If the major groups are identified using these keys, then microbiological analysis can be made to predict the exact genus/species involved in MIC, which would be more helpful to select a species-specific micro-biocide.

Also, perhaps these are the apparent symptoms of MIC, and it should be kept in mind that the above characters can be created by nonbiological factors also.

MIC MONITORING PROGRAM

Initial and continuous care is better than later prevention in the case of MIC, because once the metal is microfouled, the film can be eradicated only with the addition of microbiocides at very strong doses or by scrapping, which usually involves much trained labour and high operational costs. Hence, it is necessary to formulate a continuous monitoring program by weight loss assessments and by microbiological analyses, if untreated water is used. A simple monitoring program is given below:

1. Chemical analysis of the water used.
2. Sampling and identification of the microbial populations in the water.

3. Identification of microbes that form sessile consortia on the metals used in the site.
4. Identification of the microflora present in and around the welds/joints.
5. A thorough study on the metabolites of the prevailing microbial communities
6. Detection of low velocity/stagnant points in the flow lines.
7. Selection of specific microbiocides (e.g. CPBr for SRB) with respect to the exact populations encountered in the site.
8. Determination of exact concentration of microbiocide at which it ensures cent percent efficacy over sessile bacteria.
9. If needed, a dispersant can also be supplemented with the microbiocide.
10. After cleaning the system, a higher concentration of the microbiocide can be added followed by periodical additions at lower concentrations (shock treatment). The quantity added should not be below the prescribed level, since a macrobiocide at insufficient concentrations promotes the microbial growth.
11. Monitoring the magnitude of bacteria before and after every four hours of biocide addition (API time-kill test) [17].
12. Periodical monitoring of MIC by weight loss method.

CONTROL OF MIC

Control of MIC can be achieved by several means. Each and every control measure has its own merits and demerits, naturally. Besides, there are certain limitations for each and every method. Some types of protection can be applied to certain systems whereas some others fit for the rest, e.g. antifouling paints cannot be applied to control MIC in internal pipewalls, whereas biocides can achieve good results in that case. But biocides cannot be directly applied to the outer walls of any underwater equipments, unless they are complexed with a suitable paint substance.

Broadly control measures of MIC can be classified into control by physical means, biological and control using chemicals.

Physical

Scrapping

The conventional way of cleaning, which is impossible in the case of internal fouling of pipelines, also involves experienced labour, lot of expenditure as well as lock-down losses during the period of cleaning. Complete disinfection is not possible in this method.

U.V. disinfection

A recently identified sophisticated technique, in which cent per cent kill can be achieved by placing high pressure U.V lamps internally in the middle of the pipeline and also in the hulls of the seagoing vessels. But as high investment is required for this sort of MIC control, only larger sectors can step into this.

Antifouling paints

In India, the conventional cuprous oxide paints alone are available. Development of an economic antifouling paint is an undergoing venture at CECRI. Complexing a microbiocidal chemical into a resin can give an antifouling paint. The conventional coal tar or cashew nut shell liquid is also effective in the control of MIC.

Insitu electrolysis of sea water

This method is purely meant for marine conditions. By immersing a typical electrolytic cell with an anode and cathode into the sea water, the chlorides dissolved can be made to evolve as chlorine, which is a general purpose biocide.

Biological

Adequate literature is available, which describes the antibacterial, antifungal and antialgal substances that are secreted by many organisms like cyanobacteria. Also some species of Thiobacilli are known to produce anti SRB compounds. Hence by employing such harmless biological species, e.g. noncorrosive cyanobacteria, acid negative Thiobacilli, etc. the biological control of MIC can be achieved.

Chemical

Wide spectrum of chemicals, possessing antimicrobial or microbiocidal activities can be easily purchased nowadays. These chemicals can be classified as (i) Mildewcides/microbicides (chemicals that kill microbes) (ii) Mildewstats/microbistats (chemicals that inhibit only the growth of the microbes). The decision, whether to use a mildewcide or mildewstat is dictated by the bacteria involved, nature of fouling and by the nature of functioning of the equipment reported to be fouled, etc.

For example, (i) SRB requires a microbiocide, whatever may be the structure (ii) If the microfouling is uniform over the plant it is actually protective for some period. So a mildewstat can be preferred. (iii) Whatever may be the nature of fouling in a cooling tower, or any other heat transfer system, a total kill is desired; so a microbiocide can be applied.

Classification of biocides (based on their mode of action)

In general, biocides achieve their targets in three different ways. They are classified accordingly.

Oxidizing biocides

Examples are chlorine, bromine, iodine. Chlorine combines with bacterial protoplasm and forms stable nitrogen-chlorine bonds with proteins. Conventionally these are used for swimming pool sterilization. Also chlorine derivatives such as chloramine-T, calcium hypochlorite, etc. are also used as biocides. Their effectiveness is enhanced by low pH, high temperature and concentration and decreased by the presence of organic matter.

Enzyme poisons

These cause microbial mortality by blocking the transfer of electrons in the respiratory systems of microbes e.g. methylene bisthiocyanate, acrolein, heavy metals.

Toxicants that distrupt the cell wall and cytoplasm

These are the surface active poisons. There are two types of biocides in this group, one is anionic and the other is cationic. Anionic biocides are effective over Gram positive bacteria and the cationic biocides are used to control Gram negative bacteria, e.g. dodecyl guanidine HCl, chlorophenol, quaternary ammonium compounds.

Efficacy of some microbiocides

Typical microbiocides	*Comments on their efficacy*
Inorganic biocides	
Chlorine gas	Universal, least effective, induces electrochemical corrosion
Sodium hypochlorite	Effective for SFB
Calcium hypochlorite	
Hydrogen peroxide	General biocide
Copper sulfate	General biocide
Organic biocides	
Dichloro dimethyl hydantoin	Slow chlorine donor, effective for SFB
Chlorinated isocyanurates	Fast chlorine donor, effective for SFB
Acrolein	Competitive with chlorine, excellent where chlorine and/or nonoxidizing biocides are ineffective
Chlorinated phenols, e.g. penta chlorophenol	General purpose biocides, effective against fungi and SRB
Quaternary ammonium compounds e.g. Cetyl pyridine chloride Cetyl pyridinium bromide	Relatively ineffective against fungi; Good against algae and SRB
Methylene bisthiocyanate	Very good for SFB control. Not effective
Hexachlorodimethyl sulfone	under high pH
Alkyl dithiocarbamates	Excellent SFB-cide Good general biocides; effective in high pH systems
Gluteraldehyde	Very good SRB-cide
Formaldehyde	Good general biocide

Apart from the general considerations in mildewcide selection, i.e. species specificity, etc. the microbiocide should get through some other tests also as below.

Compatibility

The microbiocide is generally injected along with some other additives such as oxygen scavengers, corrosion inhibitors, clay stabilizers, etc. So, microbiocide may react with the other additives and may lose their biocidal efficacy or may make the other additives useless. So a laboratory set up can be run for testing the restoration of the properties of each additive, when mixed.

Besides, there are also some situations, where biocide is not compatible with the system to be treated. Some examples are: (i) treatment of a low pH system with a chlorophenate type compound (ii) treatment of high sulfate containing system with a quaternary type compound (iii) treatment of a system containing H_2S with a heavy metal compound containing Ag (iv) treatment of any system by chlorine compounds may aggravate corrosion (v) treatment by oxygen scavenger enhances the activity of SRB (vi) treatment of a system containing sulfides, by chlorination results in the formation of elemental sulfur, which plugs permanently.

Corrosivity

Also, before use, the microbicides should be tested for their corrosive nature, because most of mildewcides that are readily available in the market, have 100% efficiency in the control of bacteria, but corrodes the metal directly e.g. alkyl trimethyl ammonium chloride (ATAC) actually passes through the time-kill tests for SRB, but induces corrosion two times more than the electrochemical corrosion and one and half times more than the SRB induced corrosion in the case of mild steel.

CONCLUSION

In general, applied works towards the control of MIC in the literature is very much limited. Industries require immediate solution to their problems on MIC rather than the mechanisms involved. More research work on the insitu identification of MIC and also the ways to control MIC instantaneously are the need of the hour. A continuous monitoring program must be established in the industries which would be helpful in knowing the alarming concentration of microbes present in cooling water.

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