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MITIGATION OF MICROBIOLOGICALLY INDUCED CORROSION DUE TO SULPHATE REDUCING BACTERIA BY CHEMICALS, COATINGS, AND CATHODIC PROTECTION

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ABSTRACT

Microbiologically induced corrosion (MIC) causes significant damages in industries. Combating MIC, in particular the one caused by sulphate reducing bacteria, can be a huge challenge to corrosion engineers due to complexity of behavior and nature of the bacteria. Over the past five decades, extensive research and development have led to new discovery of mitigating MIC and to growing consciousness from various industries. This article offers brief review on recent progress or development in research on combating MIC using chemicals or biocides, coatings, and cathodic protection.

Keywords: *Microbiologically induced corrosion, mitigation, chemical protection, coating, cathodic protection*

1.0 INTRODUCTION

Microbiologically induced corrosion (MIC) occurs in the presence of bacteria. Historically, MIC has contributed to 20% of damage due to corrosion worldwide, costing about USD 44 billion annually [1]. One type of bacteria causing MIC is Sulphate Reducing Bacteria (SRB). This bacteria is considered among the most notorious [1]. SRB lives in colony under the formation of biofilm and can survive without the presence of oxygen, which means it is an anaerobic bacteria. SRB can survive only on the consumption of sulphate (SO_4^{2-}) in the environment it lives, reducing it into sulphide (S^{2-}), and consequently forming the corrosion product, iron sulphide (FeS).

Due to its nature that can adapt to the environment where it lives in and its dynamic behaviour, SRB is considered challenging to mitigate. Mitigation techniques with respect to chemical usage, coating applied, and cathodic protection application are presented based on latest development or latest technologies to combat MIC, especially SRB, from recent reports.

2.0 MITIGATION BY CHEMICALS

Mitigation by chemical usage or sometimes called antimicrobial agent or biocide is widely used especially in oil and gas industry, especially in transporting oil and gas via pipelines if the pipelines are prone to bacteria attack. The chemical is injected into the pipeline either by batching or continuous injection.

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However, it should be noted that most of the chemicals used are only effective to combat planktonic bacteria and not the sessile bacteria in its biofilm [2-3]. The chemical reactions for MIC can only happen if the bacteria are in contact with metal by the formation of biofilm. As such, these sessile bacteria, once it colonized and biofilm is formed, the chemical used cannot penetrate easily into the biofilm to control or kill them in order to prevent MIC.

In order to overcome the issue of controlling or killing sessile bacteria, the formation of biofilm has to be eliminated first. The study on the usage of chemical known as dodecyl dimethyl ammonium bicarbonate (DDABC) through batch treatment (four hours, twice a week) in a dynamic flow loops reported that this chemical is able to reduce the formation of biofilm and, hence, is able to prevent MIC from happening [2]. Figure 1 shows the result by using DDABC and other chemicals to reduce the formation of biofilm, i.e. glutaraldehyde and tetrakis (hydroxymethyl) phosphonium sulfate (THPS).

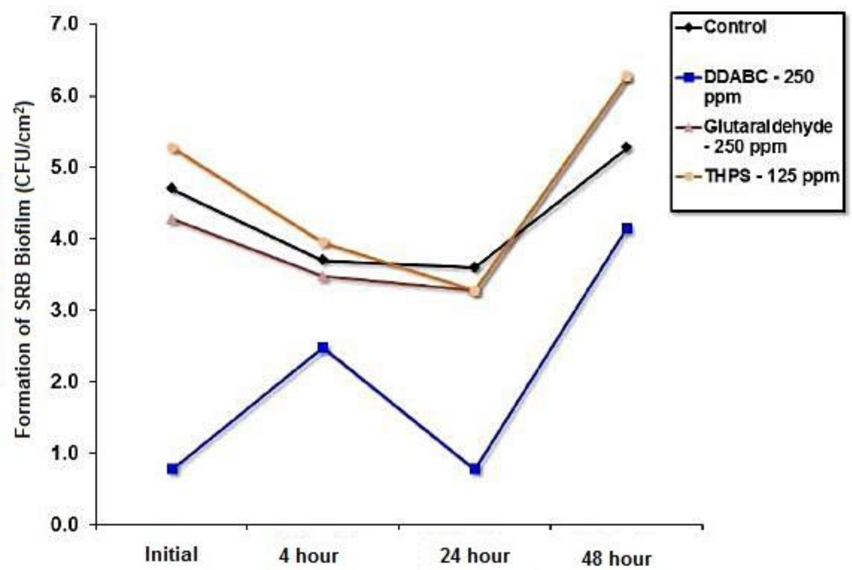

Figure 1: Prevention of SRB biofilm re-growth following DDABC batch treatment vs. alternate biocide treatment programs [2]

Also, the formation of biofilm can be prevented by addition of cleaning agent with the usage of normally used chemical to kill bacteria [3]. Although the type of cleaning agent was not specifically mentioned in the dynamic flow loops experiment, the usage of this cleaning agent, used together with chemical was able to reduce the thickness of biofilm which later easier for chemical to penetrate into the film to kill the sessile bacteria and consequently, reducing the MIC. This experiment may lead to new research of finding new cleaning agent to be used together with chemical in preventing MIC.

Besides the use of chemical to prevent the formation of biofilm only, the use of heterocyclic bisquats named MDHTD (N-Metronidazole-N-(Dodecane Dimethyl)-2-Hydroxy-1,3-Thirddil-ammonium Dichloride) could decrease the corrosion reaction caused by bacteria by killing them and limiting the formation of biofilm [4]. MDHTD, when added into a culture medium with bacteria inside, it functioned as a sterilizer, which killed the bacteria and at the same time, formed a protective layer on the metal surface which preventing bacteria from settling on the metal surface to create biofilm. Table 1 shows the number of bacteria with and without the addition of MDHTD, where the number of bacteria was reduced with the addition of MDHTD. Also, the biofilm became loose with the addition of MDHTD, which could prevent the MIC corrosion by sessile bacteria.

Table 1: Variation of SRB number in culture medium with cultured time (T = 40±1^{o}C) [4]

Culture time (days)	**1**	**3**	**5**	**7**
SRB number in culture media (cells/m**L)**	3.5×10^{5}	2.6×10^{7}	3.2×10^{6}	2.3×10^{6}
SRB number in culture media + 0.1 g.L MDHTD **(**cells/m**L**$^{-1}$**)**	3.2×10^{2}	1.5×10^{2}	25	12

3.0 MITIGATION BY COATING APPLICATION

Mitigation by coating is by an application of a barrier between bacteria and metal surface. By segregating the contact between these two, MIC can be prevented from happening. The mechanism of coating can be either as poisonous coating, sacrificial coating, or immune coating.

One of the coating applications to mitigate MIC is by using nickel-cobalt (Ni-Co) coating. Nickel (Ni) has been widely used in many industries because of the electrochemical properties of nickel which exhibits good corrosion resistance in aggressive solution and high catalytic activity for many electrochemical processes. Ni-Co coating was introduced into a medium containing bacteria (*aeromonassalmonicida* and *clavibactermichiganensis*) and results show that there is a decrease in value detected for E_{corr} and I_{corr} (and consequently the corrosion rate) once the introduction of the coating to bacteria [5]. Table 2 shows the result of the experiment in medium with and without bacteria.

Table 2: Electrochemical parameters of Ni-Co coating corrosion inhibition in medium with and without bacteria [5]

	E_{corr}, Vvs Ag/AgCl	**I_{corr} (mA)**	**$I_{corr.}$ (μA cm^{-2})**	**η_p (%)**	**Anodic Tafel Slope β_{a1} (V dec^{-1})**	**Anodic Tafel Slope β_{c1} (V dec^{-1})**	**Corrosion rate (mm/year)**	**QCM mass loss (μg/cm^{2})**
Medium	-0.61	2.50	12.29	-	0.29	0.23	132.61	96.9
A. salmonicida	-0.60	1.06	5.20	57.6	0.06	0.19	56.15	6.10
B. michiganensis	-0.59	0.48	2.36	80.8	0.08	0.11	25.42	2.14

Besides Ni-Co coating, Yuan et al. [6] reported that Ag/SiO_2 core–shell nanoparticles coating could enhance long-term corrosion protection in comparison with Cu_2O coating. Silver (Ag) is an effective inhibitor for MIC while silica shell can provide slow release of the Ag blocking the initial corrosion processed and its –Si–O–Si– skeleton and partial ionic character which always resist bacteria and other organisms by its surface-active properties. A comparison of Ag/SiO_2 and Cu_2O coatings shows Ag cores would release Ag ions slowly through the outer porous silica shell; as a result, leaching of the Ag was more efficiently controlled. In contrast, higher loads of Cu_2O lead to a higher leaching of Cu ion. The large active surface area and core–shell structure offered by the Ag/SiO_2 nanoparticles make it possible to reduce the load and provide better leaching control, and consequently, long term corrosion protection against bacteria.

Although Ag is proven to be a good resistance element to MIC, leaching out tribulations of Ag into the environment is a serious problem which causes environmental risk and has serious adverse effects on the durability of the treated material [7-9]. Akram, et al. [7] developed organic-inorganic hybrid polyurethane silver nanocomposite (Ag/LPOSiPU) coating and antibacterial activity of the coating was evaluated using *S. aureus* and *E. coli* bacteria. Ag/LPOSiPU coating enhanced antimicrobial efficacy and it has potential to be considered as effective and long-lasting bactericidal surface coating material.

Another alternative for environmental-friendly coating is utilizing zeolite coating [8-9]. The use of bio-toxic metals functionalized zeolites as antimicrobial agents in liquid media has been studied extensively and coating of as-synthesized zeolite ZSM-5 imparted a good anti-microbial property against *E. coli* and *S. aureus*species of bacteria [8]. As per Table 3, it seems that microbial activity quite in acceptable range. ZSM-5 showed to possess higher efficiency to inhibit the growth of Gram negative bacteria as compared to the Gram positive bacteria (*S. aureus*). One of the reasons for such variation in antimicrobial activity could be due to difference in bacterial cell wall of Gram positive- and Gram negative-bacteria.

Table 3: Anti-microbial activity of ZSM-5 against standard drug [8]

Bacteria	**Minimum inhibition concentrations (µg/mL)**	
	Zeolite	**Ampicillin**
Escherichia coli, MTCC 443	125	100
Psuedomonas, MTCC 10053	100	-
Staphylococcus aureus, MTCC 96	250	200
Salmonella entericatyphi, MTCC 98	100	125

Another type of coating to fight MIC is 4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT). DCOIT, an antifoulant, is widely used in marine antifouling applications as an alternative for tributyltin (TBT), which is prohibited from use because of its toxic effects on the marine environment. Study by Xiaofan et al. [10] showed adding DCOIT in galvanizing coating can inhibit the growth and metabolism of *Desulfovibriocaledoniensis* bacteria. DCOIT successfully adsorb on the surface of coatings with efficient organic structures and modified the surface morphology of the coatings to fluffy and rough but shiny.

4.0 MITIGATION BY CATHODIC PROTECTION

Mitigation by cathodic protection (CP) is by supplying current to a substrate which required to be protected from corrosion. There are two types of CP mechanism which are impressed current CP (ICCP) and sacrificial anode CP (SACP). ICCP is where current is supplied by external power source while SACP is by its own metal degradation (normally zinc (Zn) or aluminium (Al) based on galvanic series to protect metal from corrode.

In combating MIC by CP, mixed reviews are found based on latest journal publications. Medihala et al. [11] stated that bacteria communities or biofilm can either be inhibited or stimulated by the application of CP regardless the location of the CP is applied (Figure 2).

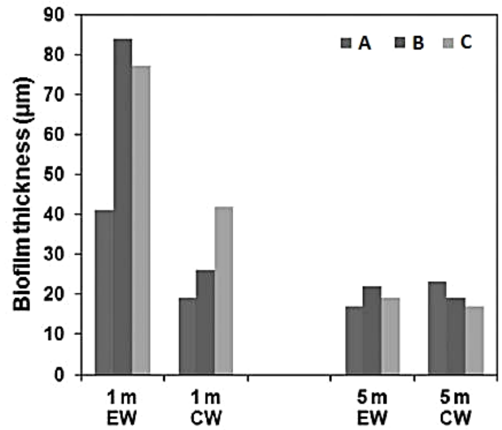

Figure 2: Biofilm thickness at electrified well (EW) and controlled well (CW) at different depths and positions of coupons (A, B, and C, i.e. bottom, middle, and top position) [11]

However, another research shows if the environment which bacteria live in was protected by CP at a more negative potential value (less than -850mV), the corrosion rate will be reduced [12] (Figure 3). It should be noted that this experiment was done for bacteria in soil only, which might produce different result if the experiment is performed in other environment containing bacteria.

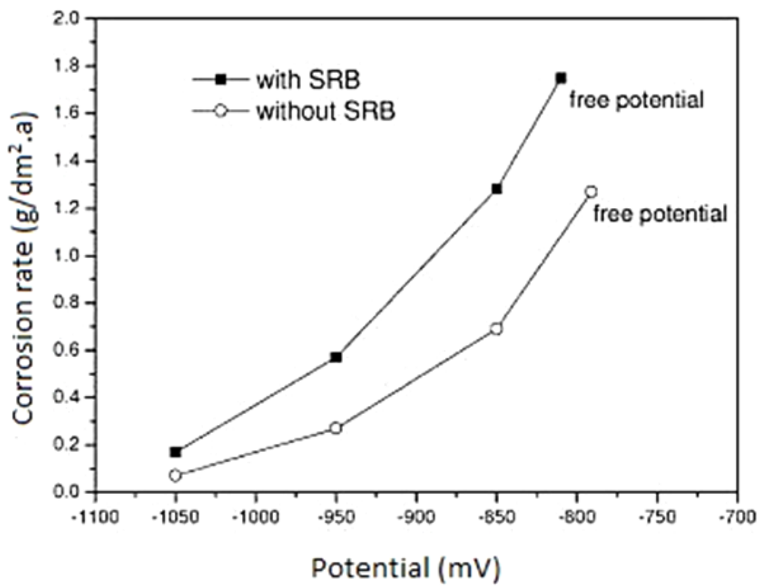

Figure 3: Corrosion rate of Q235 steel with cathodic potential in soil [12]

Although CP could reduce the corrosion rate of metal in bacteria environment as stated above, one need to consider the consumption rate of sacrificial anode in the present of bacteria. Consumption rate of anode, be it Zn or Al was found to be increased when it was used to protect metal in the environment containing bacteria [13-14]. Regardless the temperature, flow rate or time, whenever there is a presence of bacteria, the consumption rate of anode increases. As such, economically, when designing CP in the presence of bacteria, the cost for producing CP would be higher since the amount of sacrificial anode required to combat bacteria will be a lot.

5.0 CONCLUSIONS

Bacterial corrosion or MIC attracts more and more attention since its effects contribute to a greatly damage to component, structure and many more. This review focuses on MIC that is caused by SRB. Many latest researches and developments have been put to combat MIC, be it by using chemicals, coatings, or cathodic protection, with some of them are summarized in this review. Initially, the understanding of mitigating bacteria by usage of chemical was cleared out between combating sessile and planktonic bacteria. Also, environmental impact due to usage of chemical and coating need to be highlighted in designing new chemical or coating. With regards to cathodic protection, further developments and researches need to be performed more due to some inconclusive results.

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