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**Research Article**

# BIOCIDAL EFFICIENCY OF ORGANIC INHIBITOR IN COOLING WATER SYSTEMS

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**ABSTRACT**

The inhibiting action of phenol and biocides towards corrosion of carbon steel in open recirculating cooling systems has been studied in presence of $Zn^{2+}$ (as $ZnSO_4$. $7H_2O$) by weight loss and potentiodynamic polarization methods. Open recirculating cooling water systems are commonly used for industrial cooling purposes to dissipate heat. The main problems associated with this system are scaling, corrosion, fouling and microbiological growth which if left untreated can lead to various problems. Microbiologically influenced corrosion is emerging as a serious problem in cooling systems. Once a biofilm forms, the local environment at the metal /biofilm interface undergoes drastic changes in terms of pH, dissolved oxygen content and concentration of the ionic species. To eliminate the threat of such potential problems, a suitable biocide must be added. A biocide must successfully control a broad spectrum of microbial contamination, provide cost-effective performance and prove compatible with other system components, while at the same time meeting stringent environmental, health and safety standards.This paper is concerned with the study of biocidal efficiencies of CTAB, CPC and SDS in the presence and absence of the inhibitor phenol in carbon steel..

**Keywords:**Biocide, Biofilm, carbonsteel, CTAB (N-cetyl-N,N,N-trimethyl ammonium bromide), CPC Cetylpyridinium chloride) SDS (Sodium dodecyl sulphate).

## INTRODUCTION

In open recirculating cooling water system (ORCS) of a petroleum refinery, carbon steel corrosion is a major problem. The makeup water used in (ORCS) are either from river, sea or underground sources. The presence of large amount of total dissolved solids, total suspended solids, total hardness, microorganism and dissolved gases, such as $O_2$ and $CO_2$ in the makeup water are responsible for scaling, fouling, under deposit and microbiological corrosion in the various equipments of cooling water system. Due to such corrosion the tubes of heat exchanger, an important part of ORCS get damaged easily, which affect the productivity and profitability. To minimize the adverse effect of corrosion, various productive methods have been adopted, one of the frequency used measure is the use of organic compounds containing nitrogen and sulphur atoms [1-3]. These compounds either can form strong co-ordination bond with metal atom or form passive film on the surface [4]. There is still a continuous search for better inhibitors or blend of inhibitors to meet the demand of the industry. The selection criteria for various inhibitors include low concentration, stability in recirculation, cost effectiveness and low operational hazard. Many studies have also been done for preparation of corrosion inhibitors having biocide properties. Microbiologically induced corrosion (MIC) has been identified as one of the major causes of corrosion of cooling water systems [5]. Technically, biocide is any substance that is poisonous to organisms and can inhibit their metabolism or annihilate them. The objective of this work seeks to investigate the efficacy of biocide in the treatment of internal corrosion of mild steel in cooling water pipelines [6]. Rajendran et al[7] have studied the influence of CTAB on the corrosion inhibition of mild steel by ATMP-$Zn^{2+}$ system, and also the biocidal efficiency of CTAB in the presence of various phosphonic- $Zn^{2+}$ system and reported that CTAB acts as an excellent biocide as monomer and also as micelle. It is

reported that most of the biofilms are sensitive to the detergent biocide SDS [8,9]. Iwalokun et al[10] have suggested to use urea and SDS in the laboratory to reduce the risk of infection with virulent proteus strains. Richard et al[11] have investigated the effect of the surfactants such as alcohol ethoxylates, amine ethoxylates, amine oxide and SDS on bacterial cell membranes using EPR spectroscopy. The purpose of the present investigation is to assess the biocidalefficiency of SDS, CTAB and CPC in well water in the presence and absence of the inhibitor systems.

**EXPERIMENTAL**

**Preparation of the specimen**

The carbon steel specimens were chosen from the same sheet of the following composition:

| Elements | S | P | Mn | C | Fe |
|---|---|---|---|---|---|
| Composition (%) | 0.026 | 0.06 | 0.4 | 0.1 | 99.365 |

Carbon steel specimens of the dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for weight-loss and surface examination studies. The environment chosen is well water and the physico-chemical parameters of well water is given in Table 1.

**Table 1- Physico-chemical parameters of well water**

| Parameters | Value |
|---|---|
| pH | 8 |
| TDS | 2018 ppm |
| Chloride | 665 ppm |
| Sulphate | 14 ppm |
| Total Hardness | 1100 ppm |
| Conductivity | 3110 µmhos/cm |

**Weight Loss Method**

Three carbon steel specimens were immersed in 100ml of the solutions containing well water and various concentrations of the inhibitor in the absence and presence of Zn2+ for a period of seven days. The corrosion product is cleaned with Clark's solution [10]. The weights of the specimens before and after immersion were determined using a Shimadzu balance AY62. Inhibition efficiency (IE) was calculated from the relationship:

$$IE = (1-W2/W1) \times 100\ \%$$

where

W1 = corrosion rate in the absence of inhibitor and

W2 = corrosion rate in the presence of inhibitor.

**Preparation of inhibitor and biocide(CTAB/CPC/SDS)**

A stock solutions of phenol (inhibitor) and CTAB/CPC/SDS (biocide) was prepared by dissolving 1g of respective compounds in 100 ml of double distilled water and then made up to 100 ml in a standard measuring flask. zinc sulphate solution was prepared by dissolving exactly 1.1g in double distilled water and made up to 250 ml in a 250 ml standard measuring flask. A hundred- fold dilution yields exactly 10 ppm of $Zn^{2+}$ concentration.

**Zobell medium**

Zobell medium was prepared by dissolving 5g of peptone, 1g of yeast extract, 0.1g of potassium dihydrogen phosphate and 15g of agar-agar in 1litre of double distilled water. The medium was sterilized by applying 15 pounds per square inch for 15 minutes in an autoclave.

**Influence of N-cetyl-N,N,N-trimethylammonium bromide [CTAB] on the IE of Inhibitor - Zn2+ system**

Influence of N-cetyl-N,N,N-trimethylammonium bromide [CTAB] on the corrosion inhibition efficiency of phenol - Zn2+ system is given in Table 2.

It is inferred that, the addition of various concentrations of CTAB to the inhibitor formulation (150 ppm of phenol + 100 ppm of Zn2+) reduces the IE gradually from 98 % to 71 %. Addition of 50 ppm of CTAB to the inhibitor formulation shows better IE (i.e.) 95 %. This may be due to the corrosion inhibiting property of CTAB [30] and that is when CTAB exists as a monomer, a synergistic effect is observed between Zn2+ and CTAB. Further addition of CTAB gradually decreases the IE. This is because at the critical micelle concentration (CMC), CTAB molecules aggregate to form micelles. These micelles do not show inhibition efficiency in the presence of Zn2+. There may be a competition between Zn2+ and Fe2+ for the counter ion namely Br-. It seems that Zn2+ wins over Fe2+ ions [12]. The micelles formed prevents the reach of inhibitor - Zn2+ complex to the surface of the metal. Hence a fall in IE is noticed after critical micelle concentration.

 

**Influence of N-cetylpyridinium chloride [CPC] on the IE of phenol - $Zn^{2+}$system**

Influence of N-cetylpyridinium chloride [CPC] on the corrosion inhibition efficiency of phenol-Zn2+ system is given in Table 3. A steep fall in IE of the formulation is observed on introducing 50 ppm of CPC to the inhibitor system i.e. from 98 % to 39 %. It is observed that as the concentration of CPC increases, the IE decreases. It is due to the fact that as the concentration of CPC increases, the chloride ion concentration (due to the ionization of CPC) also increases and hence IE decreases, which resulted in the breaking of the protective film formed [13]. Further additions of CPC, decreases the IE rapidly to 2 %. This shows that CPC shows antagonistic effect with phenol at low and high concentrations of CPC.

**Influence of sodiumdodecyl sulphate [SDS] on the IE of phenol - $Zn^{2+}$system**

Influence of sodiumdodecyl sulphate [SDS] on the corrosion inhibition efficiency of phenol-Zn2+ system is given in Table 4. Addition of 50 ppm of SDS to 150 ppm of phenol and 100 ppm of Zn2+ reduces the IE to a small extent, i.e., from 98 % to 92 %. Addition of 100 ppm of SDS achieves 98 % IE. This is due to the corrosion inhibiting property of SDS [14-15]. However, the IE does not alter much by further addition of SDS. Hence, it is concluded that SDS does not alter the corrosion behaviour of steel in the presence of the inhibitor system. This shows that monomers of SDS are responsible for the corrosion inhibition at medium concentration in controlling the corrosion of carbon steel. In corrosion inhibition with surfactant inhibitors, the critical micelle concentration (CMC) is the most important parameter. When the concentration of surfactant adsorbed on the solid surface is high enough, organized structures (hemi-micelles such as bi or multilayer) are formed, which decrease the corrosion reaction by blocking the metal surface [35].

**Determination of biocidal efficiency of the system**

Inhibitor-Zn2+ formulation that offered the best corrosion inhibition efficiency was selected. The biocidal efficiency of biocides such as N- cetyl –N, N, N-trimethyl ammonium bromide (CTAB), N-cetylpyridinium chloride (CPC) and sodiumdodecylsulphate (SDS) was determined.

Various concentrations of CTAB, CPC and SDS namely 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm were added to the formulation consisting of the inhibitor system. Polished and degreased carbon steel specimens in duplicate were immersed in these environments for a period of seven days. After seven days one ml each of test solutions from the environments was pipetted out into sterile petri dishes containing about 20 ml of the sterilized Zobell medium kept in a sterilized environment inside the Laminar flow system. Then the Petri dishes were kept in an incubator at 30ºC in an inverted position for 2 days. Distinct colonies of bacteria were developed. Such colonies may be easily isolated. The number of colony forming units (CFU/mL) present in the above formulations were determined by Step dilution technique [16]. Each organism grows and reproduces itself. To determine the number of colonies, plate count technique [17] was applied.

**Biocidal efficiencies of biocides in well water**

The biocidal efficiencies [BE] of CTAB , CPC and SDS in the presence and absence of phenol + Zn2+ formulation in well water after suspending the specimen samples for 7 days are given in Tables 5-7.. The visuals of the bacterial colonies formed in the presence and absence of inhibitor system, biocides namely CTAB, CPC and SDS after immersing the specimens for one day are shown in Fig. 1.

Table 5-7 points out that the inhibitor formulation (phenol + Zn2+) offers 99.5 % BE in the absence of the biocide and 50 ppm of CTAB [17] is needed to achieve 99.9 % biocidal efficiency (BE) in the absence of inhibitor formulation. However, in the presence of the inhibitor formulation 100 % BE is achieved with 10 ppm of CTAB itself. This is due to the fact that CTAB itself is a biocide [18-20]. It kills the microbes. Hence the corrosion caused by the microbes is reduced and hence the BE increases. The corrosion inhibition study of phenol + Zn2+ + CTAB shows that a maximum IE of 95 % is obtained with 50 ppm of CTAB. Hence a combination of 100 ppm of Zn2+, 150 ppm of phenol, 50 ppm of CTAB gives 95 % IE and 100 % BE. Similarly, a combination of 100 ppm of Zn2+, 150 ppm of phenol, 150 ppm of CPC could give only 39 % IE and 100 % BE.

The study of corrosion inhibition of Zn2+, phenol and CPC / CTAB system reveals that the addition of CPC / CTAB, reduces the IE drastically and hence it is inferred that CPC is not a good additive as biocide for Zn2+/phenol formulation.

 

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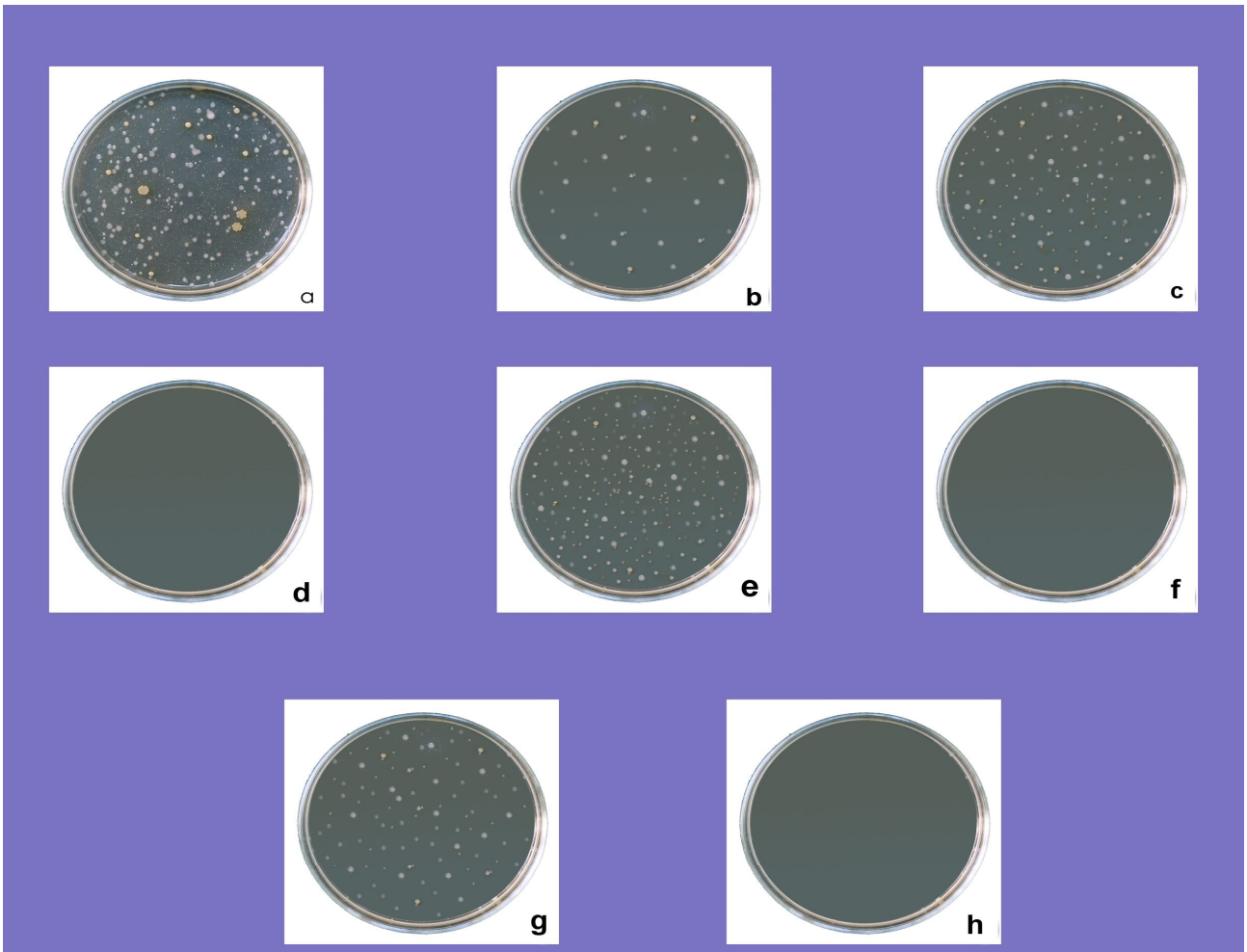


**Fig v.1.7 Bacterial colonies formed in**

**a) Well Water**

**b) 150 ppm Phenol + 100ppm $zn^{2+}$ + well water**

**c) 10 ppm C TAB.**

**d) 150 ppm phenol + 100ppm $zn^{2+}$ + well Water + 10 ppm C TAB**

**e) 10 ppm CPC**

**f) 150 ppm phenol + 100ppm $zn^{2+}$ + well Water + 150 ppm CPC**

**g) 10 ppm SDS**

**h) 150 ppm phenol + 100ppm $zn^{2+}$ + well Water + 150 ppm SDS**

**Figure1. Bacterial colonies formed in well water and for the various concentrations of inhibitor and biocides**

**Table 2. Corrosion rates of carbon steel in well water containing phenol - Zn2+ inhibitor formulation for various conc. of CTAB**

| Phenol (ppm) | $Zn^{2+}$ (ppm) | CTAB (ppm) | Corrosion Rate (mpy) | Inhibition Efficiency % |
|---|---|---|---|---|
| 0 | 0 | 0 | 55.43 | - |
| 150 | 100 | 0 | 1.10 | 98 |
| 150 | 100 | 50 | 2.77 | 95 |
| 150 | 100 | 100 | 7.76 | 86 |
| 150 | 100 | 150 | 8.31 | 85 |
| 150 | 100 | 200 | 13.85 | 75 |
| 150 | 100 | 250 | 16.07 | 71 |

**Table 3.Corrosion rates of carbon steel in well water containing phenol - Zn2+ inhibitor formulation for various conc. of CPC**

| Phenol (ppm) | $Zn^{2+}$ (ppm) | CTAB (ppm) | Corrosion Rate (mpy) | Inhibition Efficiency % |
|---|---|---|---|---|
| 0 | 0 | 0 | 55.43 | - |
| 150 | 100 | 0 | 1.10 | 98 |
| 150 | 100 | 50 | 33.81 | 39 |
| 150 | 100 | 100 | 38.24 | 31 |
| 150 | 100 | 150 | 47.60 | 14 |
| 150 | 100 | 200 | 53.76 | 3 |
| 150 | 100 | 250 | 54.32 | 2 |

**Table 4. Corrosion rates of carbon steel in well water containing phenol - Zn2+ inhibitor formulation for various conc. of SDS**

| Phenol (ppm) | $Zn^{2+}$ (ppm) | CTAB (ppm) | Corrosion Rate (mpy) | Inhibition Efficiency % |
|---|---|---|---|---|
| 0 | 0 | 0 | 55.43 | - |
| 150 | 100 | 0 | 1.10 | 98 |
| 150 | 100 | 50 | 4.43 | 92 |
| 150 | 100 | 100 | 1.10 | 98 |
| 150 | 100 | 150 | 3.32 | 94 |
| 150 | 100 | 200 | 4.98 | 91 |
| 150 | 100 | 250 | 5.54 | 90 |

**Table 5 Biocidal efficiencies of CTAB in various environments**

| Phenol (ppm) | $Zn^{2+}$ (ppm) | CTAB (ppm) | Colony Forming units/ml | Biocidal Efficiency % |
|---|---|---|---|---|
| 0 | 0 | 0 | 9537 | - |
| 0 | 0 | 10 | 301 | 96.8 |
| 0 | 0 | 25 | 127 | 98.6 |
| 0 | 0 | 50 | 1 | 99.9 |
| 150 | 100 | 0 | 40 | 99.5 |
| 150 | 100 | 10 | nil | 100 |
| 150 | 100 | 50 | nil | 100 |
| 150 | 100 | 75 | nil | 100 |
| 150 | 100 | 100 | nil | 100 |
| 150 | 100 | 150 | nil | 100 |

**Table 6Biocidal efficiencies of CPC in various environments**

| Phenol (ppm) | $Zn^{2+}$ (ppm) | CPC (ppm) | Colony Forming units/ml | Biocidal Efficiency % |
|---|---|---|---|---|
| 0 | 0 | 0 | 9537 | - |
| 0 | 0 | 10 | 1346 | 86 |
| 0 | 0 | 25 | 890 | 91 |
| 0 | 0 | 50 | 381 | 96 |
| 150 | 100 | 0 | 40 | 99.5 |
| 150 | 100 | 10 | 602 | 93.6 |
| 150 | 100 | 50 | 635 | 93.3 |
| 150 | 100 | 75 | 9 | 99.9 |
| 150 | 100 | 100 | 1 | 99.9 |
| 150 | 100 | 150 | nil | 100 |

**Table 7Biocidal efficiencies of SDS in various environments**

| Phenol (ppm) | $Zn^{2+}$ (ppm) | SDS (ppm) | Colony Forming units/ml | Biocidal Efficiency % |
|---|---|---|---|---|
| 0 | 0 | 0 | 9537 | - |
| 0 | 0 | 10 | 100 | 98.9 |
| 0 | 0 | 25 | 50 | 99.4 |
| 0 | 0 | 50 | 9 | 99.9 |
| 150 | 100 | 0 | 40 | 99.5 |
| 150 | 100 | 10 | 1907 | 80 |
| 150 | 100 | 50 | 1771 | 81.4 |
| 150 | 100 | 75 | 12 | 99.8 |
| 150 | 100 | 100 | 1 | 99.9 |
| 150 | 100 | 150 | nil | 100 |

The Table 6 points out that SDS offer 99.9 % BE when 50 ppm of SDS was added to well water in which the test specimens were immersed for 7 days. The inhibitor formulation gives 99.5 % BE in the absence of SDS. The inhibitor formulation consisting of 150 ppm of phenol, 100 ppm of Zn2+ ions and 100 ppm of SDS gives 100 % BE. Therefore, a minimum of 100 ppm of SDS is required for the complete eradication of microbes. Interestingly, the same formulation offers a maximum inhibition efficiency of 98 %. As the combination of 150 ppm of phenol, 100 ppm of Zn2+ions and 100 ppm of SDS offer 100 % BE and 98 % IE, it is ideal to use this combination for cooling water system to control corrosion as well as microbial growth.

**CONCLUSION**

Among the three biocides, SDS offers 99.9 % BE when 50 ppm of SDS was added to well water in which the test specimens were immersed for 7 days. The inhibitor formulation gives 99.5 % BE in the absence of SDS. The inhibitor formulation consisting of 150 ppm of phenol, 100 ppm of Zn2+ ions and 100 ppm of SDS gives 100 % BE. Therefore, a minimum of 100 ppm of SDS is required for the complete eradication of microbes. Interestingly, the same formulation offers a maximum inhibition efficiency of 98 %. As the combination of 150 ppm of phenol, 100 ppm of Zn2+ions and 100 ppm of SDS offer 100 % BE and 98 % IE, it is ideal to use this combination for cooling water system to control corrosion as well as microbial growth.

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