Scale and Corrosion Prevention in Cooling Water Systems Part I: Calcium Carbonate

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Abstract: This paper presents the results of study that was undertaken to investigate the ability of a new antiscale, polyacrylamide in solving problems found in cooling water systems. The effects of the polymer on C-steel and copper dissolution in synthetic cooling water environment were studied through scale, Tafel, and Linear polarization measurements. The results obtained from this study showed that the new antiscale polymer can decrease scale build-up growth under experimental conditions. Both linear and Tafel polarization studies indicate that the polymer acted as an anodic type corrosion inhibitor on C-steel and mixed-type on copper, thus reducing metal dissolution. Morphological investigations of calcium carbonate deposits on both C-steel and copper surfaces were studied by optical microscopy. The polymer used in this study appears to have an excellent crystal modification effect on reducing calcium carbonate scale. The antiscale effect results from changes in crystallization behavior promoting bulk solution precipitation rather than formation of adherent scale.

Keywords: Scale inhibition, cooling water treatment, polyacrylamide, calcium carbonate, electrochemical polarization, optical microscopy.

1. INTRODUCTION

Water is the most commonly used cooling fluid to remove unwanted heat from heat transfer surfaces. At the present time, some of the demand for better utilization of the limited water supplies is due to population growth and increasing development. Due to this, open recirculating cooling water systems that reuse cooling water are frequently used at large central utility stations at chemical, petrochemical, and petroleum refining plants in steel and paper mills, and at all types of processing plants [1].

The build-up of scale formation in water systems is a serious problem, whose solution normally requires costly chemical softeners. Calcium carbonate is the predominant component of scales deposited from natural water, especially in cooling and in heating water systems.

Scale formation, which impairs heat transfer and reduces flow velocities inside the condenser tubes of desalination plants, is a major operational problem. Alkaline scales result from the interaction between the decomposition and hydrolysis products of the bicarbonate ion of sea water with calcium and magnesium ions to produce CaCO₃ and Mg(OH)₂. A number of techniques – the controlled acidification of sea water [2], the use of anti-scale agents [3, 4] and the utilization of sponge – ball cleaning [5] are employed to control scaling. These techniques are employed singly or in combination, depending on the adopted working strategy of the plant. Inhibition of the decomposition of the bicarbonate ion was recently proposed as a possible means of stifling scale precipitation [6].

Many inhibitors have been used in cooling water systems in order to solve these problems [7]. Particularly chromates and many other heavy metals were the standard corrosion inhibitors of choice, because of a long history of successful commercial usage and their excellent effectiveness over a wide range of conditions. There is ample evidence in the literature [8, 9] that small amounts of metal ion impurities, notably Zn²⁺, Cu²⁺, Fe²⁺, Fe³⁺ and Mg²⁺, can affect the nucleation and crystallization rates of precipitating CaCO₃ and induce morphological changes of crystal habit. For example a scale suppression effect is obtained with 1 to 1.5 ppm Zn²⁺ ion, added to the water either by dosing a Zn²⁺ solution or by the release of Zn²⁺ ions through contact with a redox Zn-Cu alloy medium. However, the popularity of inhibitors containing heavy metals is diminishing, because of the concern over their toxic effects on aquatic and possibly animal life [10].

For the control of calcium carbonate scale in cooling water systems vinyl acetate-acrylic acid, vinyl acetate-methacrylic acid, were used, the former being the most effective [11]. Acrylic acid-acrylonitrile and methacrylic acid-acrylonitrile copolymers were used as antiscalants and they showed very good antiscaling performance at lower temperatures and pHs but at higher pH and temperatures they act as flocculents [12]. Polyacrylic acid and carboxylic acidsulphonic acid copolymer have a very good antiscaling, chelating and dispersing effect on several ions [13, 14]. Polymaleic acid reduces the formation of scale by acting on the nucleation and growth process namely at a concentration of 4 ppm [15].

The objective of this study was to develop new antiscale "polyacrylamide" that would inhibit both scale and corrosion in cooling water systems. A preliminary series of laboratory experiments were carried out in synthetic cooling water containing different doses of polymer antiscale at 70°C.
The work is also extended to study the inhibitive effect of
the studied polymer to the corrosion of both C-steel and copper
in the synthetic sea water through Tafel and Linear polarization measurements. Analysis of calcium carbonate de-
positions on both C-steel and Cu surfaces were studied by optical microscopy.

2. EXPERIMENTAL

2.1. Antiscale Polymer Structure and Properties

Polyacrylamide (CH₂ = CHCO NH₂)x, where X is about
5,000,000, i.e. high molecular weight type [16]. Analair
(USA made), very pure samples will be used. Polymerization
conditions must be carefully controlled to obtain a polymer with the particular molecular weight distribution desired. The functional groups present on the polymer "backbone" play a key role in establishing the polymer’s properties and utility. The chemical nature of these groups determines the functionality of the polymer. Our polymer serves as non-ionic type. The solution can be made by dissolving 1g of a polymer in (1L) of triple distilled water and heat, the resulting stock solution containing 1000 ppm Polymer concentration.

2.2. Synthetic Cooling Water Composition (Table 1)

Table 1. Composition of Anion and Cation Brine

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Concentration</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium bicarbonate NaHCO₃</td>
<td>7.36 g/L</td>
<td>7360</td>
</tr>
<tr>
<td>Sodium sulphate Na₂SO₄</td>
<td>0.0294 g/L</td>
<td>29.4</td>
</tr>
<tr>
<td>Sodium chloride NaCl</td>
<td>33 g/L</td>
<td>33000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Concentration</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium chloride CaCl₂·2H₂O</td>
<td>12.15 g/L</td>
<td>12150</td>
</tr>
<tr>
<td>Magnesium chloride MgCl₂·6H₂O</td>
<td>3.68 g/L</td>
<td>3680</td>
</tr>
<tr>
<td>Sodium chloride NaCl</td>
<td>33 g/L</td>
<td>33000</td>
</tr>
</tbody>
</table>

All stock solutions were prepared from analytical reagents (Merck Co.) and triply distilled water without further purification.

2.3. Scale Tests

Before carrying out any scale tests, standardization for stock solutions was made by titrations with 0.01M EDTA solution using Murexide as indicator. The polymer was added in flasks to which calcium and M-alkalinity, Mg(OH)₂ were present. Solutions of synthetic cooling water can be made by mixing 50ml of anion brine to 50ml of cation brine solutions. Adopted method involves addition of known vol-
umes of cation brine solutions followed by careful addition of the appropriate amount of the stock solution of the antis-
cale polymer used each time, the appropriate amount of an-
ion brine stock solution was accurately added next in stopper
flasks. The pH of the working, supersaturated solutions was
next adjusted at 8.0 by the addition of standard potassium hydroxide solution (Merck, Titrisol). Test conditions were the following: without polymer (Blank, hot), with polymer doses (0.5, 1, 3, 5, 10 and 15 ppm) respectively. The flasks were incubated for (1, 3, 7, 10) days in a thermostat at 70°C. After the incubation period, the flasks were removed from the heat source and an aliquot was filtered through a 0.45 μm membrane. The filtrate was titrated for calcium using 0.01M EDTA and murexide indicator, the percent calcium carbonate inhibition was calculated from the following equation:

\[
\text{% Inhibition} = \frac{C_{a_i} - C_{a_b}}{C_{a_i} - C_{a_b}} \times 100
\]

Cₐᵢ = Calcium ion concentration with the inhibitor.
Cₐᵦ = Calcium ion concentration in the blank.
Cₐᵢ = Calcium ion concentration before the test.

2.4. Electrochemical Tests

Carbon steel containing C = 0.7%, P = 0.03%, Mn = 0.3-
0.6%, S = 0.035%, Si= 0.5-0.75% and iron is the remainder, and copper of 99.994% purity were used for the electrochemical corrosion tests in synthetic cooling water environments. A sheet cut of the same composition of both C-steel and copper embedded in araldite with an exposed area of 2.0 cm² were used for both Tafel and Linear polarization studies. The electrode was polished using different grades of emery papers and degreased by acetone, and washed by triply dis-
tilled water. All tests were performed in synthetic cooling water environment and 5 ppm polymer antiscale addition at 25°C. An electrochemical corrosion cell, containing the working electrode, a glass capillary probe connected to a reference electrode (SCE), and platinum electrode as a counter electrode was used. Tafel current – voltage characteristics were recorded using potentiostat model 273/81 at 5 mV/s scan rate. For linear polarization studies, the scan rate was 1.66 × 10⁻⁴ mV/s and the polarization resistance (Rₚ) values were measured in the absence and presence of polyacrylamide dose.

2.5. Surface Morphology Investigation

Examination of the surface of both C-steel and copper samples after exposure to the synthetic cooling water solutions for 24 hours at 70°C with and without addition of optimum dose (5 ppm, polymer) was carried out using optical polarizing microscope (Nikon, Japan) attached with control box and camera AFX IIA.

3. RESULTS AND DISCUSSION

3.1. Scale Tests

The ability of the polyacrylamide to inhibit calcium carbonate scale was compared with the blank in flask tests. These results are shown in Fig. (1, curves a-d). In case of no polymer application, percent calcium carbonate inhibition was (18%), whereas, in the presence of doses of polyacryla-
mide, percent calcium carbonate inhibition was observed to achieve 90% at some polymer concentrations.

Series of runs were made with synthetic sea water and 46
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treatment concentrations ranging from 0.5-15 ppm of polyacrylamide having the molecular weight > 5,000,000, (classified as high molecular weight polymer). Except for this variation in the treatment concentration of the synthetic wa-
ter, all other experimental conditions were maintained iden-
tactical to those adopted for runs made without any treatment. At a treatment concentration of 0.5 ppm polyacrylamide, 36% scale reduction was obtained. Increase in treatment concentration to 5 ppm increase the percent scale reduction to ≈ 80%. However, at 10 and 15 ppm concentration, scale reduction was 66% and 76% respectively, as indicated by Fig. (1, curve a) which is a plot of percent scale reduction versus polymer concentration in ppm, for 1 day incubation at 70°C.

![Fig. (1). Effect of polymer dosage on scale reduction at 70°C after: (a) 1 day incubation; (b) 3 days incubation; (c) 7 days incubation; (d) 10 days incubation.](image1)

As in the first series, for 3 days incubation at 70°C, polyacrylamide of lower dose 0.5 ppm in synthetic sea water showed an increase in percent scale reduction 73%. An increase in polymer concentration, showed a marked effect in preventing scale deposition. At 15 ppm concentration, the percent scale reduction was maximum 90% (Fig. 1, curve b). As indicated by the curve of Fig. (1, curve c) percent scale reduction was observed to be increasing with increasing concentration of polymeric material, after 7 days incubation at 70°C. It is observed that, after 10 days incubation of 6 flasks at 70°C the effect of polymer doses, in reducing sea water calcium carbonate scaling, was moderate (Fig. 1, curve d).

Effect of time used as a criterion for measuring the performance of the polyacrylamide using 5 ppm concentration as an optimum dose is shown in Fig. (2). It is observed that, at 5 ppm polymer concentration in synthetic sea water, the percent scale reduction was 80% on average over a period of 168 hours, then decreases after that.

The calcium carbonate scale reduction by polymer can be explained in terms of adsorption on foulant surfaces – imparting a like charge to them and thereby causing the particles to remain in suspension, because of charge repulsion. In addition, the polymer can distort scale crystals by disrupting their lattice structure and normal growth patterns. The inclusion of relatively large irregularly shaped polymer in the scale lattice tends to prevent the deposition of a dense uniformly structured crystalline mass on the metal surface [17].

In conclusion, it appears to be the opinion of the majority that the function of this polymer is to inhibit the crystal growth of the scale – forming material (CaCO₃).

### 3.2. Electrochemical Tests

The work is also extended to study the corrosion inhibition effect of polyacrylamide on both C-steel and copper electrodes in synthetic sea water environment using 5 ppm, optimum polymer concentration. Fig. (3) shows Tafel polarization curves of C-steel in synthetic cooling water in the absence and in the presence of polyacrylamide corrosion inhibitor. The polarization curve indicates a shift in the corrosion potential towards more positive value of potential (-565 mV compared with the control sample without inhibitor -600 mV). The anodic polarization curve obtained in the presence of 5 ppm polyacrylamide indicates a greater tendency towards passivity than without the inhibitor.

![Fig. (2). Effect of time on the performance of 5 ppm polymer on calcium carbonate scale inhibition.](image2)

![Fig. (3). Tafel polarization curves of C-steel (a) with and (b) without inhibitor.](image3)
However, according to the corrosion potential, the inhibitor tended towards anodic inhibition. Referring to Table 2, anodic Tafel slopes obtained are 188.6 × 10^{-3} V/d (blank) 94.25 × 10^{-3} V/d (5 ppm polyacrylamide) and this indicates that the polymer inhibits the anodic reaction more strongly. Form the polarization curves, the corrosion current density \( I_{\text{corr}} \) was determined by the Tafel extrapolation method. Corrosion rates were then calculated from \( I_{\text{corr}} \) values. The corrosion current density in the synthetic cooling water decreased considerably in the presence of the inhibitor, Table 2. The value of the corrosion rate of C-steel in the presence of the inhibitor was much smaller than that in the absence of inhibitor. The inhibition efficiency of the inhibitor for the corrosion of C-steel was calculated using \( I_{\text{corr}} \) [18] as follows:

\[
\text{IE} (%) = \frac{[I_{\text{corr}} - I_{\text{corr}}(\text{inh})]}{I_{\text{corr}}} \times 100 = 68.2\%
\]

where \( I_{\text{corr}}(\text{inh}) \) and \( I_{\text{corr}} \) are the corrosion current density values with and without the inhibitor, respectively.

The polarization resistance method was used to identify the action of the inhibitor after 24h. The polarization resistance of C-steel in the inhibited solution was much higher than that for the inhibitor – free solution, Table 2. The inhibition efficiency of the corrosion of C-steel is calculated from the following equation by using the average polarization resistance:

\[
\text{IE} (%) = \frac{[R_p - R_p(\text{inh})]}{R_p} \times 100 = 66.6\%
\]

where \( R_p(\text{inh}) \) and \( R_p \) are the average polarization resistances with and without the inhibitor, respectively.

In aqueous synthetic sea water environment, polyacrylamide exists as neutral species. Thus, the adsorption of the polymer molecules on C-steel surface can occur directly via donor – acceptor interactions between the \( \pi \)-electrons of the oxygen atom of the polymer and the vacant d orbitals of iron surface atoms, involving the displacement of water molecules from the metal surface and the sharing of electrons between the oxygen atoms and the metal surface [19].

Fig. (4) shows typical anodic and cathodic polarization curves recorded on copper in synthetic cooling water solution alone and containing 5 ppm concentration of polyacrylamide at 25°C. The extrapolation of the anodic Tafel straight line to the corrosion potential allows the calculation of the corrosion current density \( I_{\text{corr}} \). The values of \( I_{\text{corr}} \), the corrosion potential \( E_{\text{corr}} \), anodic Tafel slope \( \beta_a \), cathodic Tafel slope \( \beta_c \), corrosion rate \( CR \), and inhibition efficiency \( IE\% \) are given in Table 2. The results reveal an inhibiting effect of polyacrylamide for corrosion of copper in synthetic sea water media. At 5 ppm polymer concentration, the inhibition efficiency \( IE\% \) was 72.15, and the polymer may be classified as a mixed type inhibitor. Since, \( E_{\text{corr}} \) value do not show resultant variation, and the polymer acts roughly in the same way both at cathodic as well as anodic sites.

![Fig. (4). Tafel polarization curves of copper (a) with and (b) without inhibitor.](image)

<p>| Table 2. Variation of Polarization Parameters for Both C-Steel and Copper Electrodes in Synthetic Sea Water Environment at 25°C in Absence and Presence of 5 ppm Polyacrylamide Addition |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Inh.dose</th>
<th>( E_{\text{corr}} )</th>
<th>( \beta_a \times 10^{-4} \text{v/d} )</th>
<th>( \beta_c \times 10^{-4} \text{v/d} )</th>
<th>( I_{\text{corr}} \mu\text{A/cm}^2 )</th>
<th>( R_p \Omega )</th>
<th>( CR \text{ mpy} )</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Steel</td>
<td>Blank</td>
<td>-660</td>
<td>188.6</td>
<td>48.91</td>
<td>111.1</td>
<td>35</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 ppm</td>
<td>-565</td>
<td>94.25</td>
<td>45.56</td>
<td>35.3</td>
<td>104.9</td>
<td>17.5</td>
<td>68.2</td>
</tr>
<tr>
<td>Copper</td>
<td>Blank</td>
<td>-440</td>
<td>108.5</td>
<td>641.4</td>
<td>108.2</td>
<td>120.6</td>
<td>98.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 ppm</td>
<td>-443</td>
<td>107.8</td>
<td>680.2</td>
<td>30.13</td>
<td>378</td>
<td>27.22</td>
<td>72.15</td>
</tr>
</tbody>
</table>
group of polyacrylamide molecule is not dissociated in the solution of synthetic cooling water, and the copper surface is positively charged. The inhibitive action results from physical adsorption that will be favored by electrostatic interaction between the inhibitor dipole moment (carbonyl group C = O) and electric field owing to metal charge. Moreover, the increase in the inhibition efficiency at the inhibitor concentration of 5 ppm at 25°C, suggests electron transfer from the –NH₂CO group to the orbitals of copper [21].

3.3. Morphological Investigation

Alkaline scale formation in thermal desalination plants addresses the separation of CaCO₃ and related compounds from sea water. The necessary CO₂⁻ evolves from the thermal decomposition of HCO₃⁻. Two theories are found in the literature to account for this reaction. According to the classical work of Langelier et al. [22], heating sea water above 45°C causes the breakdown of HCO₃⁻ as:

$$2\text{HCO}_3^- = \text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \quad (1)$$

This leads to the precipitation of CaCO₃

$$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3(s) \quad (2)$$

Once its solubility limit is reached (K = 4.7 – 6.9 × 10⁻⁹). At still higher temperatures (≥ 80°C), CO₂⁻ hydrolyzes to OH⁻ according to:

$$\text{CO}_3^{2-} + \text{H}_2\text{O} = 2\text{OH}^- + \text{CO}_2 \quad (3)$$

The correctness of reactions (1) and (3) was confirmed by studying the behavior of pure NaHCO₃ and Na₂CO₃ solution upon heating [23]. Careful analysis of brines in equilibrium with alkaline scales always revealed the presence of measurable quantity of free CO₃²⁻ [24]. Apparently, other processes, eg., super – saturation, ion – pair formation and/or complexation play a role.

Photomicrographs of both C-steel and copper coupons in synthetic sea water, in absence and presence of optimum 5 ppm dose of polyacrylamide concentration were illustrated in Figs. (5-8). Generally, the polymer molecules minimize the deposition of large amounts of calcium carbonate, because they have a "crystal distortion effect"[25]. It can be seen that the control solution produces mainly aggregates of very fine calcite crystals (Fig. 5), while the treated solution precipitates very few amount of calcite crystals (Fig. 6). This effect is similar to those of chemical inhibitors reported by Yang et al. [26]. Some photomicrograph images were obtained for copper specimens, untreated solutions precipitate CaCO₃ consisted predominantly of aggregates of rhombohedral calcite crystals with some of euhedral Rhomb crystals (Fig. 7). However, it is interesting to note that these crystals are nearly always present in the treated water but in much reduced quantities (Fig. 8). It is probable that the major factor affecting the quantity of scale forming is the availability of nucleation sites at metal surface imperfections. This behavior may be interpreted as the nucleation and growth of CaCO₃ particles. At the beginning the former particles remain suspended in the solution due to their small size and help by the solution agitation, while other nuclei are formed and grow. Once the formed particles have reached certain critical size their precipitation takes place to form the above mentioned scale.

4. CONCLUSIONS

1. Percent scale reduction using polyacrylamide, molecular weight > 5,000,000, at 5 ppm concentration was found to be 86.7% after 7 days incubation at 70°C.
The corrosion rate of C-steel in synthetic cooling water containing a newly developed inhibitor was reduced by more than 68.2%, and acted to inhibit the anodic reaction.

3. Polyacrylamide was found to be effective in inhibiting copper corrosion in synthetic cooling water at 25°C; the results obtained from polarization curves indicate that the mechanism of inhibition is mixed for anodic and cathodic reactions.

4. Due to the crystal modification effect, the inhibitor exhibited a good inhibition efficiency of 90% for calcium carbonate scale.

5. No reference to the use of such scale and corrosion inhibitor has been found in the literature; it is thus believed to represent potentially new safe polymer suitable for treating cooling water systems.

6. Photomicrographs of both C-steel and copper in synthetic cooling water containing the optimum dose 5 ppm of polyacrylamide indicate reduction in the precipitation of calcite (CaCO₃) crystals.

**LIST OF SYMBOLS**

- \( E_{cor}(mV) \) = Corrosion potential
- \( I_{cor}(\mu A/cm^2) \) = Corrosion current density
- \( \beta_a (v/d) \) = Anodic Tafel polarization constant
- \( \beta_c (v/d) \) = Cathodic Tafel polarization constant
- \( R_p (\Omega) \) = Polarization resistance
- \( CR (mpy) \) = Corrosion rate
- \( IE \% \) = Inhibition efficiency

**REFERENCES**


