Technique to determine anti-scalants efficiency for industrial cooling water system

R S Chaudhary* & Harish Kumar
Department of Chemistry, Maharshi Dayanand University, Rohtak 124 001, India

Received 19 August 2003; revised received 17 June 2004; accepted 9 August 2004

Techniques, presently used for the measurement of the efficiency of anti-scalants for industrial cooling water do not provide reproducible results, are time consuming and difficult to perform. It is also not possible using these techniques to find the efficiency of anti-scalants in actual cooling water. A problem is faced by industries in finding the optimum concentration of the anti-scalants in a cooling water of particular composition as the efficiency of the anti-scalants depends on the quality of cooling water. Consequently, the dose of the anti-scalant required in the cooling water system, is not possible to ascertain. A technique based on theoretical considerations has been reported herein, which not only provides reproducible results but is also easy and quick to perform using actual cooling water.

IPC Code: CO2F 5/08

Keywords: Antiscalants, cooling water system, antiscalant efficiency

Cooling is the largest industrial use of the water. In general, scaling and corrosion are the two main problems encountered in open recirculating cooling water systems. Calcium carbonate scales are readily formed on flow surfaces in cooling water systems but scales of calcium sulphate, calcium phosphate, magnesium silicate, etc. are also found some times.

Chemical treatment of water in the cooling water system is required to avoid scaling problem and water parameters like pH, conductivity, alkalinity, total dissolved solids, total hardness, calcium hardness, chloride, sulphate, total phosphate, iron, residual chlorine etc. are controlled. Anti-scalants are available as branded products to control the scaling problem. Formulation and composition of these products are kept secret and the end user is required to pay a high price for the anti-scalants. Furthermore, the efficiency of the anti-scalant is measured usually by the manufacturer, using the techniques, which do not take into consideration the actual quality and composition of cooling water in industry.

A number of techniques are reported in the literature to determine anti-scalant’s efficiency. All these techniques are cumbersome, time consuming and do not provide reproducible results. Further, using these techniques it is not possible to measure the efficiency of an anti-scalant in actual cooling water of a particular composition. The required concentration of anti-scalant (dose of anti-scalant) in a cooling water system depends upon the composition of the cooling water. The composition of cooling water also changes during the operation of cooling water system and consequently the requirement of the anti-scalant will also change. The techniques being used at present to measure the efficiency of the anti-scalants do not provide an answer to this problem. It has often been observed in industries that anti-scalants are added to the cooling water systems without actually determining the required concentration of the anti-scalant for a particular composition of cooling water. It results in a poor monitoring and maintenance of the cooling water system.

Keeping in view the above problems and especially the idea that the anti-scalant efficiency must be known in the actual water composition of cooling water system, there is a need for a technique to measure anti-scalant efficiency which is easy, quick and provide reproducible results so that it may be possible to adjust the dose of the anti-scalant accordingly. A technique to measure the efficiency of the anti-scalants in actual cooling water, which is simple, easy to perform and based on theoretical considerations has been reported in the present work.

*For correspondence (E-mail: rschaudhary1@rediffmail.com)
Experimental Procedure

Preparation of synthetic cooling waters

Synthetic cooling water of six different compositions was prepared using A. R. grade chemicals and doubly distilled water. The purpose of taking six different compositions of cooling water was to cover the wide range of hardness available in cooling waters in industry depending upon the source of water. Consequently, six different compositions of cooling water varying from soft to hard water have been taken for carrying out the experiments. The compositions of all the six synthetic cooling waters have been recorded in Table 1. The pH, conductance, total dissolved solids (T.D.S.), P and M alkalinity, total hardness and calcium hardness were measured for each synthetic cooling water and are recorded in Table 2.

Measurement of anti-scalant efficiency

Six anti-scalants namely hydroxyethylene-1-diphosphonic acid (HEDP), sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP), trisodium phosphate (TSP), polyacrylate (PA) and R-II (A blend of carboxylate/sulphonate co-polymers) were used in the experiments. STPP, SHMP and TSP were procured from Loba Chemicals Pvt. Ltd., Bombay. BKC was procured from Ashok surfactant Pvt. Ltd., Mumbai. Polyacrylate (mol. wt. ~5000) was procured from Lalit Nitrochem., India and R-II polymer blend from Norsohaas, France. All the anti-scalants except polyacrylate and R-II polymer were of AR grade.

Experiments were performed at room temperature in the range of 34-38°C and using 2, 5, 10, 15 and 20 ppm of concentration of the anti-scalants for all the six investigated synthetic cooling waters.

Initial experiments were conducted by using the technique reported by Boffardi. Equal volume of a 500 mg/L calcium solution (as the ion) and a solution of 1200 mg/L total alkalinity made from 80/20 ratio of bicarbonate/carbonate solutions were mixed. The solution was then kept at 55°C for 24 h and then filtered through a 0.22 micron filter paper and the Ca²⁺ concentration in the filtrate was determined by EDTA titration. The procedure was repeated in presence of anti-scalant and the efficiency was calculated.

The same experiments were also carried out using the technique followed by oil and gas industry to measure the anti-scalant efficiency. In this technique, the solutions of the following four combinations were prepared using distilled water and making the volume 1L in each case.

1) 14.67g CaCl₂·2H₂O + 50g NaCl;
2) 1.864g NaHCO₃ + 50g NaCl;
3) 50g NaCl;
4) 1g antiscalant.

The above prepared solutions were taken in three stoppered conical flasks as given below.

1) 50mL of solution (i) + 50mL solution (ii) + 1 mL distilled water.
2) 50 mL of solution (i) + 50mL solution (iii) + 1 mL distilled water.
3) 50mL of solution (i) + 50mL solution (ii) + 1 mL solution (iv).

These three flasks were kept at 65°C for 18 h and then contents were filtered using 0.22 micron filter paper. 10mL sample of each filtrate was titrated against standard EDTA solution and anti-scalant efficiency was calculated.

The results of percentage efficiency obtained from Boffardi technique (Technique 1), oil and gas Industry technique (Technique 2) are recorded in the table given below.

<table>
<thead>
<tr>
<th>Anti-scalant (20ppm)</th>
<th>Percentage efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Technique 1</td>
</tr>
<tr>
<td>HEDP</td>
<td>69.1, 57.5, 62.4</td>
</tr>
<tr>
<td>STPP</td>
<td>58.2, 70.3, 64.2</td>
</tr>
<tr>
<td>SHMP</td>
<td>52.6, 55.2, 59.6</td>
</tr>
<tr>
<td>TSP</td>
<td>43.8, 48.7, 53.8</td>
</tr>
<tr>
<td>PA</td>
<td>65.3, 75.3, 77.4</td>
</tr>
<tr>
<td>R-II</td>
<td>74.5, 80.7, 82.5</td>
</tr>
</tbody>
</table>

Considering the problems in the measurement of anti-scalant efficiency by using the above mentioned techniques, the following method was adopted using synthetic cooling water. 100 mL of synthetic cooling water was taken in a conical flask and its pH was adjusted to 7.0 by adding acetic acid solution or sodium hydroxide solution as per requirement. 0.2 N sodium carbonate solution was slowly added to the conical flask containing 100 mL cooling water of 7.0 pH with constant stirring using a teflon coated magnetic rotor until turbidity just appears. The same experiment was repeated in presence of anti-scalant (in ppm) also in 100 mL of cooling water of pH 7.0. The percentage anti-scalant efficiency was calculated by:
Duplicate, in some case triplicate, experiments were performed to check the reproducibility of the data. Appearance of turbidity at the end point was noted by naked eye as well as by turbidity meter. It was observed that the results with turbidity meter were exactly the same as with naked eye. However, in case of synthetic cooling water VI having total hardness of 750 as CaCO₃, some difficulty was observed with naked eye in exactly determining the end point but this problem was overcome with experience and watching the stirred solution carefully.

**Table 1**—Composition of various ions in various synthetic cooling waters

<table>
<thead>
<tr>
<th>Composition</th>
<th>C. W. I</th>
<th>C. W. II</th>
<th>C. W. III</th>
<th>C. W. IV</th>
<th>C. W. V</th>
<th>C. W. VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>75</td>
<td>115</td>
<td>150</td>
<td>200</td>
<td>225</td>
<td>300</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>305</td>
<td>305</td>
<td>305</td>
<td>305</td>
<td>305</td>
<td>305</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>262</td>
<td>320</td>
<td>430</td>
<td>509</td>
<td>530</td>
<td>692</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Na⁺</td>
<td>253</td>
<td>196</td>
<td>253</td>
<td>251</td>
<td>203</td>
<td>253</td>
</tr>
</tbody>
</table>

**Results and Discussion**

Scaling tendency of each cooling water was measured by using the following equations

Langelier Saturation Index

(L. S. I.)12 = pH – pHs … (1)

where pH is actual pH measured value in water and pHs is the pH of saturation calculated from the following expression.

\[
\text{pHs} = 10.49 - 8.15 \log \left[ \text{HCO}_3^- \right] - \log \gamma \left[ \text{HCO}_3^- \right] - \log \gamma \left[ \text{Ca}^{2+} \right]
\]

ΔG values were calculated12 for the equilibrium,

\[
\text{CaCO}_3 + [\text{H}^+] \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-
\]

using the expression,

\[
\Delta G = \Delta G^0 - RT \ln Q
\]

Here Q is ratio of concentration of product species to the reactant species.

Positive value of ΔG signifies that equilibrium will shift in backward direction and scaling would occur.

Saturation index (SI) value13 for all the investigated waters was calculated using the following equation,

\[
\text{SI} = \text{pH} - \text{pHs}
\]

where pHs = \(pk_2 - pk_4 + p\left[\text{Ca}^{2+}\right] + p\left[\text{HCO}_3^-\right] + 5pf_m\)

Here \(f_m\) is the activity coefficient for monovalent species at water temperature and is given by

\[
pf_m = \left( \frac{A \sqrt{I}}{1 + \sqrt{I}} \times 0.31 \right)
\]

\[
I = \frac{1}{2} \sum [X_i] Z_i^2
\]

LSI from activity coefficient, ΔG values and saturation index (SI) values have been calculated and recorded in Table 2.

After a series of experiments the following observations were made,

(i) both Boffardi and ONGC techniques do not provide reproducible results.

(ii) the techniques are cumbersome and do not allow the measurement of anti-scalant efficiency in the cooling water of a particular composition.

(iii) using these techniques it is not possible to conduct experiments and find out the exact concentration of a particular anti-scalant to achieve maximum efficiency in the cooling water of specific composition.

(iv) the techniques are highly time consuming and it is just not possible to quickly monitor the dose of anti-scalant in the cooling water system using these techniques.

Percentage anti-scaling efficiency values determined by the technique used in the present work, for all the investigated anti-scalants at various concentrations and for all the synthetic cooling waters are given in Table 3. Plots of percentage anti-scaling efficiency...
efficiency versus concentration of all the anti-scalants and cooling waters are shown in Fig. 1(a-f).

It is observed that TSP provides minimum anti-scaling efficiency in all the cooling waters. HEDP and STPP are good anti-scalants especially when total hardness in cooling water is more than 500 ppm. Polyacrylate provides reasonably good efficiency till 300 ppm of calcium hardness. Its efficiency sharply

### Table 2—Various parameters of six different synthetic cooling waters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>C.W.I</th>
<th>C.W.II</th>
<th>C.W.III</th>
<th>C.W.IV</th>
<th>C.W.V</th>
<th>C.W.VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.26</td>
<td>8.53</td>
<td>8.26</td>
<td>8.08</td>
<td>8.30</td>
<td>8.08</td>
</tr>
<tr>
<td>Conductance</td>
<td>1.54</td>
<td>2.02</td>
<td>2.16</td>
<td>2.30</td>
<td>2.50</td>
<td>2.70</td>
</tr>
<tr>
<td>T.D.S.</td>
<td>1027</td>
<td>1347</td>
<td>1440</td>
<td>1534</td>
<td>1667</td>
<td>1800</td>
</tr>
<tr>
<td>p-alkalinity</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M-alkalinity</td>
<td>285</td>
<td>290</td>
<td>300</td>
<td>305</td>
<td>310</td>
<td>320</td>
</tr>
<tr>
<td>Ca-hardness</td>
<td>119</td>
<td>182</td>
<td>238</td>
<td>317</td>
<td>357</td>
<td>480</td>
</tr>
<tr>
<td>Total hardness</td>
<td>187</td>
<td>287</td>
<td>374</td>
<td>498</td>
<td>560</td>
<td>750</td>
</tr>
<tr>
<td>L.S.I. from Activity coeff.</td>
<td>1.04</td>
<td>1.14</td>
<td>1.25</td>
<td>1.30</td>
<td>1.35</td>
<td>1.47</td>
</tr>
<tr>
<td>ΔG Value</td>
<td>1.09</td>
<td>1.10</td>
<td>1.26</td>
<td>1.38</td>
<td>1.48</td>
<td>1.63</td>
</tr>
<tr>
<td>S.I. Value</td>
<td>0.43</td>
<td>0.54</td>
<td>0.69</td>
<td>0.75</td>
<td>0.83</td>
<td>0.98</td>
</tr>
<tr>
<td>Water type</td>
<td>Composition of C. W. (mg/L)</td>
<td>Conc. of A. S. (ppm)</td>
<td>% efficiency</td>
<td>HEDP</td>
<td>STPP</td>
<td>SHMP</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------</td>
<td>----------------------</td>
<td>--------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>CW I</td>
<td>Ca^{2+} 75, Mg^{2+} 24, CO_3^{2-} 30, HCO_3^- 305, Na^+ 253, Cl^- 262, SO_4^{2-} 120</td>
<td>2, 5, 10, 15, 20</td>
<td>33.3, 88.5, 97.2, 98.5, 99.0</td>
<td>63.6, 82.3, 88.8, 90.9, 92.5</td>
<td>80.9, 84.9, 86.1, 88.3, 90.5</td>
<td>60.7, 73.6, 71.2, 82.2, 82.6</td>
</tr>
<tr>
<td>CW II</td>
<td>Ca^{2+} 115, Mg^{2+} 24, CO_3^{2-} 30, HCO_3^- 305, Na^+ 196, Cl^- 320, SO_4^{2-} 120</td>
<td>2, 5, 10, 15, 20</td>
<td>68.7, 73.6, 78.2, 78.2, 81.1</td>
<td>60.0, 62.9, 66.6, 66.6, 75.0</td>
<td>50.0, 54.5, 61.0, 61.0, 61.9</td>
<td>45.4, 50.0, 60.0, 60.0, 61.5</td>
</tr>
<tr>
<td>CW III</td>
<td>Ca^{2+} 150, Mg^{2+} 24, CO_3^{2-} 30, HCO_3^- 305, Na^+ 253, Cl^- 430, SO_4^{2-} 120</td>
<td>2, 5, 10, 15, 20</td>
<td>61.2, 66.6, 67.0, 67.3, 68.5</td>
<td>55.0, 58.6, 60.9, 62.3, 67.4</td>
<td>44.4, 52.3, 54.6, 56.2, 56.2</td>
<td>40.6, 44.7, 50.4, 50.9, 51.9</td>
</tr>
<tr>
<td>CW IV</td>
<td>Ca^{2+} 200, Mg^{2+} 24, CO_3^{2-} 30, HCO_3^- 305, Na^+ 251, Cl^- 509, SO_4^{2-} 120</td>
<td>2, 5, 10, 15, 20</td>
<td>51.3, 52.2, 67.0, 67.3, 57.8</td>
<td>49.2, 55.3, 60.9, 62.3, 61.7</td>
<td>30.6, 33.9, 54.6, 56.2, 39.6</td>
<td>20.2, 25.9, 50.4, 50.9, 33.5</td>
</tr>
<tr>
<td>CW V</td>
<td>Ca^{2+} 225, Mg^{2+} 24, CO_3^{2-} 30, HCO_3^- 305, Na^+ 203, Cl^- 530, SO_4^{2-} 120</td>
<td>2, 5, 10, 15, 20</td>
<td>45.9, 50.7, 53.5, 53.5, 56.0</td>
<td>38.8, 45.4, 59.2, 49.2, 49.2</td>
<td>25.0, 30.9, 38.6, 37.0, 37.8</td>
<td>10.2, 23.9, 32.2, 31.6, 34.6</td>
</tr>
<tr>
<td>CW VI</td>
<td>Ca^{2+} 300, Mg^{2+} 24, CO_3^{2-} 30, HCO_3^- 305, Na^+ 253, Cl^- 692, SO_4^{2-} 120</td>
<td>2, 5, 10, 15, 20</td>
<td>20.0, 30.3, 33.3, 38.3, 43.3</td>
<td>27.2, 33.3, 38.4, 38.4, 38.4</td>
<td>20.0, 27.2, 33.3, 33.5, 33.9</td>
<td>01.0, 11.1, 18.0, 18.1, 18.7</td>
</tr>
</tbody>
</table>
decreases in cooling water of more than 560 ppm total hardness. R-II polymer blend provides good anti-scalant efficiency in all the cooling waters. This anti-scalant has a potential for its application in industries for cooling water treatment where the total hardness is approximately 750 ppm. In almost all the cases it seems that the efficiency initially increases with increase in concentration of anti-scalant and becomes almost constant after a certain optimum concentration.

In the present technique pH of cooling water was brought to 7.0 by adding solution of either glacial acetic acid or sodium hydroxide. At pH 7.0 buffering action of carbonic acid takes place,

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]
\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]
\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

It was necessary to do so in order to mark a reference point so that the comparison of efficiency is possible for different anti-scalants and in various cooling waters.

Between pH 7.0 to 8.2, HCO\textsubscript{3} ions are present and above pH 8.2, HCO\textsubscript{3} ions dissociate to CO\textsubscript{3}\textsuperscript{2-} ion.

Below pH 7.0, Ca(HCO\textsubscript{3})\textsubscript{2} will decompose to give CO\textsubscript{2}

\[ \text{Ca(HCO}_3)_2 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + 2\text{CO}_2 + 2\text{H}_2\text{O} \]

The balance between calcium ion, bicarbonate ion, carbonate ion and CO\textsubscript{2} is delicate and this balance slowly shifts to right hand side to achieve the precipitation of CaCO\textsubscript{3}.

\[ \text{Ca(HCO}_3)_2 \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

This shift in equilibrium can be brought about either by heating or precipitation or increase of pH. In the present work, this equilibrium has been shifted to right hand side by increase of pH by adding 0.1 N Na\textsubscript{2}CO\textsubscript{3} solution. As the reference point of pH has already been fixed at 7.0, the turbidity observed on adding 0.1 N Na\textsubscript{2}CO\textsubscript{3} solution is only due to the precipitation of CaCO\textsubscript{3} which will occur at pH > 8.2.

This technique is simple, easy to carry out and is based on actual theoretical considerations in the precipitation of CaCO\textsubscript{3}. The technique provides highly reproducible results and any change either in quality of the water or the concentration of anti-scalant becomes evident in the results of anti-scalant efficiency as is clear from the data recorded in Table 3. The technique can be helpful in determining the efficiency of branded anti-scalants and finding their optimum concentration in actual cooling water.

**Nomenclature**

\[ A = 1.82 \times 10^6 (ET)^{-1.5} \]
\[ [\text{Ca}^{2+}] = \text{concentration of Ca}^{2+} \text{ion (gmol/L)} \]
\[ [\text{HCO}_3^-] = \text{concentration of HCO}_3^- \text{ion (gmol/L)} \]
\[ E = \text{dielectric constant} \]
\[ I = \text{ionic strength} \]
\[ K_s = \text{solubility product for CaCO}_3 \text{ at the water temperature} \]
\[ p_{K_2} = -\log \text{of second dissociation constant for carbonic acid at the water temperature} \]
\[ T = \text{absolute temperature} \]
\[ V_a = \text{volume of 0.2 N sodium carbonate used for water containing anti-scalant} \]
\[ V_b = \text{volume of 0.2 N sodium carbonate solution used for water without any anti-scalants} \]
\[ [X_i] = \text{concentration of different components in cooling water} \]
\[ Z_i = \text{the valency of the different components in cooling water} \]

**References**

10. NACE Std No. TMO 374-2001 (Houston, TX:NACE, 2001).
11. NACE Std No. RPO300-2000 (Houston, TX:NACE, 2000).