Corrosion is a major threat facing closed cooling water systems, and it can drastically reduce the system’s lifetime and performance. As the retention time in closed systems is very long and water exchange is minimal, contaminations that can lead to severe problems will accumulate in the system. Hence, a good corrosion inhibition programme is essential.

Typically, corrosion protection is achieved by high concentrations of molybdate and nitrite, both being anodic inhibitors with well-known advantages but also certain disadvantages. Kurita Europe has developed a corrosion inhibition programme based on the application of film forming amines (FFAs) to overcome the drawbacks of these inhibitors.

FFA technology has successfully been applied in hot water and boiler systems for decades. Besides excellent test results in R&D facilities, FFAs have already proven their strong corrosion inhibition properties in various industrial closed cooling circuit applications.

Troubles in closed cooling water systems
Closed cooling water systems are designed to add or remove heat from industrial processes. The temperature in such systems is reduced by secondary coolers without evaporation. Hence, the concentration of ions remains low so it could be expected that scaling and corrosion are
minor problems. On the other hand, such systems often suffer from certain water losses, which have to be compensated. Furthermore, closed systems contain various materials (such as copper, brass, aluminium or ferrous metals) and temperatures vary from -20°C up to 100°C or more. Under these conditions, different kinds of corrosion are a threat; equipment could be seriously damaged and there could be significant environmental and economic consequences.

Corrosion products, such as iron oxides, accumulate in closed systems due to the low water exchange. This increases the importance of having an effective corrosion inhibition programme. Therefore, the corrosion rates in closed systems should typically be one order of magnitude lower than in evaporative cooling systems.

State-of-the-art protective treatments consist of inorganic inhibitors based on molybdate and nitrite applied at high concentrations. Nitrite is a toxic substance that can easily be decomposed by microorganisms. While this makes it ineffective, it is still applied for economic reasons. Molybdate is a heavy metal and, even though non-toxic, it is under general suspicion. Furthermore, the price of molybdate is high in comparison to other corrosion inhibitors.

Due to the mentioned drawbacks and laws becoming more restrictive, new efficient and non-toxic formulations have to be developed. For this purpose, Kurita Europe implemented the Cetamine® technology, based on FFA and efficiently applied in boiler systems for decades, to closed cooling water systems.

R&D studies on corrosion inhibitors

Before applying FFA-based corrosion inhibitors in industrial closed cooling circuits, a lot of research was conducted in the company’s European R&D centre. Both laboratory methods and pilot plants were used for the corrosion inhibition studies.

Steady-state current-voltage and polarisation curves were combined with electrochemical impedance measurements to characterise the inhibitive properties of multi-component inhibitors and to compare their anti-corrosion efficiency with traditional treatment programmes. While the results are not discussed in this article, these tests have already shown that FFAs are an efficient alternative to common corrosion inhibitors.

In addition to electrochemical studies, investigations under more practical conditions in a pilot plant were carried out. The unit simulates the conditions in a closed cooling/heating system. It is equipped with two heat exchangers simulating the primary and secondary heat exchanger in an industrial system. Corrosion rates are measured by a standard coupon rack according to ASTM D 2688 and by a linear polarisation resistance probe. Details of the pilot plant can be seen in Figure 1.

Two test series will be presented in this article. The first was conducted at a temperature of 40°C using demineralised water with a conductivity of less than 1 µS/cm. The pH was stabilised by 60 mg/l of bicarbonate. Nitrite, molybdate and FFAs were added to the system, and corrosion rates were investigated on carbon steel and yellow metals. Microbiological growth was inhibited by the addition of a non-oxidising biocide (isothiazolinone).

Throughout the two week test duration, there was no water exchange or further addition of corrosion inhibitor. A constant circulation with a velocity of 1 m/sec. was kept and the water was analysed to observe unwanted fluctuations and follow the increase of iron as indicator for corrosion processes. The analysis results of the three corrosion inhibitors, as well as for a blank test, are shown in Table 1.

Table 1. Comparison of the analysis results of the three inhibitor solutions and the blank

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Corrosion inhibitor</th>
<th>None (blank)</th>
<th>Nitrite</th>
<th>Molybdate</th>
<th>Film forming amine (FFA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (µS/cm)</td>
<td>130</td>
<td>3100</td>
<td>1200</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.6</td>
<td>10.8</td>
<td>97</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>Iron (mg/l)</td>
<td>7.6</td>
<td>0.61</td>
<td>1.4</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Nitrite (mg/l)</td>
<td>-</td>
<td>695</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Molybdate (mg/l)</td>
<td>-</td>
<td>-</td>
<td>202</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>FFA (mg/l)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Illustration (left) and schematic representation (right) of the pilot closed cooling system.
For the FFA, the average iron value was observed to be the lowest with 0.32 mg/l.

The corrosion coupons before pickling are shown in Figure 2. With all inhibitors, excellent corrosion inhibition could be achieved. The corrosion rates were very low for both carbon steel (<0.005 mm/yr) and copper (<0.002 mm/yr), the same good protection within the error of the experiment. For comparison, the blank test resulted in a corrosion rate of 0.26 mm/yr on carbon steel and approximately 0.008 mm/yr on copper.

In the second test series, a critical closed cooling water system with poor water quality operated at a high temperature of 75°C was simulated. Table 2 shows the average values of the water analysis for all three test runs. The pH was adjusted to a range that was suitable for aluminium. As expected, a loss of calcium in all systems (typically from 1.8 to 0.9 mol/m³) and total alkalinity was observed due to the precipitation of calcium carbonate. In all cases, the soluble heavy metal content was low and in the same concentration range, although the corrosion rate on coupons showed obvious differences (Figure 3). It can be assumed that iron and zinc were precipitated as oxides/hydroxides.

When comparing the corrosion rates of the two-test series it becomes obvious that the conditions in the second test series were much more severe. Corrosion rates of the blank test were approximately four times higher (0.26 – 0.96 mm/yr). Even though the conditions were critical, both inhibitor programmes showed good results on carbon steel and brass. Inhibitors could also reduce the corrosion rates on aluminium, but with the FFAs the corrosion rate is significantly lower compared to that of molybdate.

These results show that the FFAs provide excellent corrosion inhibition under aggressive conditions. An important advantage of FFA technology is the much lower contribution to the conductivity of the cooling water.

**Case study of FFA application – closed cooling systems containing carbon steel and aluminium**

In this case study, several closed circuits used for the cooling of electronic equipment on engine driven pumps via plate heat exchangers are described. The water temperature in these systems fluctuates between 25°C and 45°C. The material of the plate heat exchanger is aluminium, while the main pipelines are made of carbon steel. The closed cooling system is fed with softened water. According to the internal specifications, the following limits have to be maintained in the water:
- Iron: <1 mg/l.
- Aluminium: <0.5 mg/l.

In the past, these systems were treated with molybdate-based corrosion inhibitors under alkaline conditions, which lead to elevated levels of aluminium. A regular water exchange became necessary to reduce the metal (especially aluminium) concentrations below the design specification.

To overcome this situation, curative cleaning was conducted and the treatment was changed to a FFA compound. Within a short period of time, the system became stable again and was operated completely inside the specified limits of aluminium and iron. The system was only replenished to compensate for water losses. The measured concentration of FFAs was generally 0.5 – 1.5 mg/l.

The iron and aluminium levels in the water during the molybdate treatment and after the cleaning during the FFA treatment are shown in Figure 4. It is clear that with the molybdate treatment the metal concentrations were highly fluctuating with aluminium levels sometimes exceeding 10 mg/l. The iron concentration was not as high, but exceeded the
limit of 1 mg/l. Both cases lead to complete water exchanges.

With the FFA treatment, the concentration of metals was stabilised without any sudden increase, indicating a strong corrosion protection. The aluminum concentration in the cooling water never increased above 0.5 mg/l and the iron level never exceeded its limit of 1 mg/l. Furthermore, improved control of the pH could be maintained with the FFA. The pH was stable and close to 8.5, which is important to avoid corrosion phenomena of aluminium containing materials.

Interestingly, the sulfate reducing bacteria (SRB) content in the water phase was reduced between two

and four orders of magnitude after the cleaning phase and the implementation of the FFA-based treatment. The SRB activity most probably decreased due to reduced deposit amounts of corrosion byproducts. It suggests that the FFA treatment allows maintaining the cleanliness of the metal surface and thus indirectly helps to reduce microbiological growth.

Conclusion
Through intensive R&D studies, Kurita proved that FFA-based technologies are a good alternative and could outperform state-of-the-art inhibitors in closed cooling water systems. All typically applied materials can be well protected from corrosion with low active concentrations of inhibitor and, subsequently, with a minimum impact on the environment.

The performance of FFA has been confirmed by industrial case studies. Corrosion rates and metal concentrations in the treated systems were stabilised and reduced to a minimum. The overall performance of the systems was greatly improved and the water consumption could be drastically reduced, resulting in high cost savings. These findings have been confirmed by numerous successful applications in various closed cooling systems.