



Film forming amines for closed cooling/heating water systems

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Summary

The corrosion inhibition of closed loop cooling water systems is quite a challenging task mainly due to very long holding times. As a consequence, any contamination entering the system will remain and accumulate over time in the water. Besides excellent corrosion inhibition, the inhibitor should not be harmful to humans nor the environment.

This paper presents a new corrosion inhibitor based on film forming amines (FFA). Corrosion protection is realized by the adsorption of the film forming amine on metal surfaces. The corrosion inhibition properties of FFA have been studied by means of electrochemical methods and in pilot plants simulating two different scenarios of practical application.

In accordance between lab and pilot plant studies, FFA based corrosion inhibitors provide a very high level of corrosion protection for carbon steel, yellow metals, and aluminum meeting at least the performance of standard corrosion inhibitors based on molybdate or nitrite.

Two field studies for a changeover of the treatment program from molybdate to film forming amines show a significant improvement of corrosion inhibition reflected in a significant reduction of the heavy metal content in the cooling water. As a consequence, partial or complete flushing of the systems could be sharply reduced thus leading to important water savings.

1 Introduction

The reduction of corrosion to a technical and economical level in water bearing systems is still a major challenge, although numerous studies have been carried out during the last few decades. In addition to an excellent technical performance, the corrosion inhibitors applied in cooling systems must comply with high environmental standards in order to avoid a deterioration of the aquatic community of life.

Closed circuit or closed loop water systems are a convenient way of heating or cooling building service applications and industrial processes. A system is considered to be “closed” if the cooling is not accomplished through evaporation of water and if it has low water losses. Thus, in theory, as the amount of make-up water is low and no concentration upgrading of the water occurs, it could be expected that closed systems should be only subject to minor scale and corrosion problems.

In reality, however, closed systems often suffer excessive water losses through leakage (e.g. ineffective sealing, losses inherent to the process, maintenance work, etc.), and are refilled with substantial amounts of softened or de-mineralized water. In addition, closed systems often contain various dissimilar materials such as copper, brass, aluminum or ferrous metals where water temperatures can vary from -20°C (chilled water systems) to 100°C or above (hot or pressurized hot water systems). In these conditions, circuits of this type can be subject to severe corrosion problems (e.g. by oxygen, galvanic corrosion, microbiologically induced corrosion, etc.), which leads not only to serious damage to installations but also causes significant environmental and economic consequences.

To reduce or eliminate these problems, the water in closed cooling and heating circuits is treated with formulations containing corrosion inhibitors. All corrosion products (e.g. metal oxides, dissolved metals) are removed from the system via water losses, which by intention should be as low as possible. Therefore, the demands on corrosion inhibition are very high. Corrosion rates measured according to ASTM D 2688 should be typically one order of magnitude lower in closed systems than in evaporative cooling systems.

State of the art protective treatments of carbon steels are often based on inorganic inhibitors (molybdate, nitrite). Formerly, chromate has been used for treatment programs. However, this substance is not accepted anymore due to its classification as CMR (carcinogenic, mutagenic, toxic for reproduction). In the European Community borate has been recently classified as CMR and put onto the SVHC list (Substances of Very High Concern).

Nitrite is toxic and has significant drawbacks such as the susceptibility to microbiological degradation, however, due to economic reasons it is still applied. Molybdate as a heavy metal, although non-toxic, is under general suspicion. Both such inhibitors need to be applied in high concentrations to obtain good inhibition.

Due to recent restrictive laws, new efficient and non-toxic formulations must be developed. For this purpose, this work is devoted to the corrosion inhibition of carbon steel with different types of inhibitive solutions having their compositions based on film forming amines (FFA). These film forming amines are able to form a protective film [1-3], which is adsorbed onto metal surfaces and thereafter constitutes a continuous protective barrier against corrosion.

FFAs, often referred to as polyamines or fatty amines, are defined as chemical substances, which belong to the oligoalkylamino fatty amine family. Typical representatives are oleylamine and oleyldiamine. Besides closed cooling/heating systems, FFAs are also applied in water-steam cycles [4, 5].

2 Experimental

For the corrosion inhibition studies, both lab methods and pilot plants have been used. Steady-state current-voltage and polarization curves were combined with electrochemical impedance measurements to characterize the inhibitive properties of multi-component inhibitors and to compare their anticorrosion efficiency with traditional treatment programs. Furthermore, tests were carried out in pilot simulation devices under more practical conditions.

Three different corrosion inhibitors were studied in the form of aqueous solutions for corrosion protection of industrial closed systems. The main inhibitor and application conditions are given in Table 1. Approximately 20 mg/l of a specific copper inhibitor (triazole) and an alkaline buffer were added to adjust the pH of the cooling water.

Table 1: Survey of tested corrosion inhibitors and test conditions

Inhibitor	Concentration	pH adjustment in cooling water for	
		Steel/Copper	Aluminum
Film forming amine	1-2 mg/l (ppm) as film forming amine	9.0 – 9.5	8.0 – 8.5
Molybdate	200 mg/l (ppm) as MoO ₄	9.0 – 9.5	8.0 – 8.5
Nitrite	600 mg/l (ppm) as NO ₂	9.0 – 9.5	Not studied

2.1 Electrochemical Measurements

Electrochemical measurements were carried out using an Autolab Metrohm frequency response analyser with an electrochemical interface. The impedance diagrams were plotted at the corrosion potential after 2 hours of immersion in a frequency range of 65 kHz to a few mHz with eight points per decade. The electrochemical results were obtained from a minimum of five experiments to ensure reproducibility.

The corrosive medium was a 200 mg/l NaCl solution in contact with air maintained at 25 °C (77 °F). The choice of this medium was based upon the following criteria [6]: (i) its low electrical conductivity is close to that encountered in industrial water circuit, (ii) its corrosivity is fairly high, and (iii) it is an easily reproducible baseline solution.

Depending on the concentration of the compounds, the pH of the inhibitive solutions varied between 8 and 10. In the inhibitor-free solution, the pH was adjusted to 9 by NaOH (for pH increasing) or HCl (for pH decreasing).

Three test materials were used for this study: carbon steel, copper and aluminum. For all the experiments, the sample materials were polished with SiC paper down to grade 2400, cleaned in ethanol and demineralized water and then dried in warm air.

For the three test samples, the working electrode was a rotating disc consisting of a rod of 1 cm² cross-sectional area to ensure a uniform thickness of the diffusion layer at the electrode surface, a heat-shrinkable sheath leaving only the tip of the cylinder in contact with the solution. All experiments were carried out at a rotation speed of 500 rpm. A saturated calomel electrode (SCE) was used as the reference and the counter-electrode was a platinum grid.

The carbon steel/solution interface was mathematically described in terms of an electric equivalent circuit consisting of a resistance electrolyte in series with a parallel constant phase element (CPE)/resistor combination. The semicircular shape of the impedance diagrams allowed for the modeling of an equivalent circuit with the following characteristic parameters: Rp, polarization resistance and C, double layer capacitance. The CPE is generally attributed to the roughness of the surface or to a non-uniform distribution of the current density on the electrode undergoing corrosion [7, 8].

2.2 Pilot cooling system studies

In addition to electrochemical studies, investigations under more practical conditions in a pilot plant (Figure 1) were carried out. The unit closely simulates the conditions in a closed cooling/heating system and is equipped with a heat exchanger (heated by thermostat controlled hot water), water cooled glass heat exchanger, water tank, recirculation pump, flow meters, standard coupon rack according to ASTM D 2688, and on-line corrosion measurement based on linear polarization resistance (Corrater[®]). The loop contains approximately 10 liters of water and could be operated in open (contact to air) or closed (no contact to air) mode.

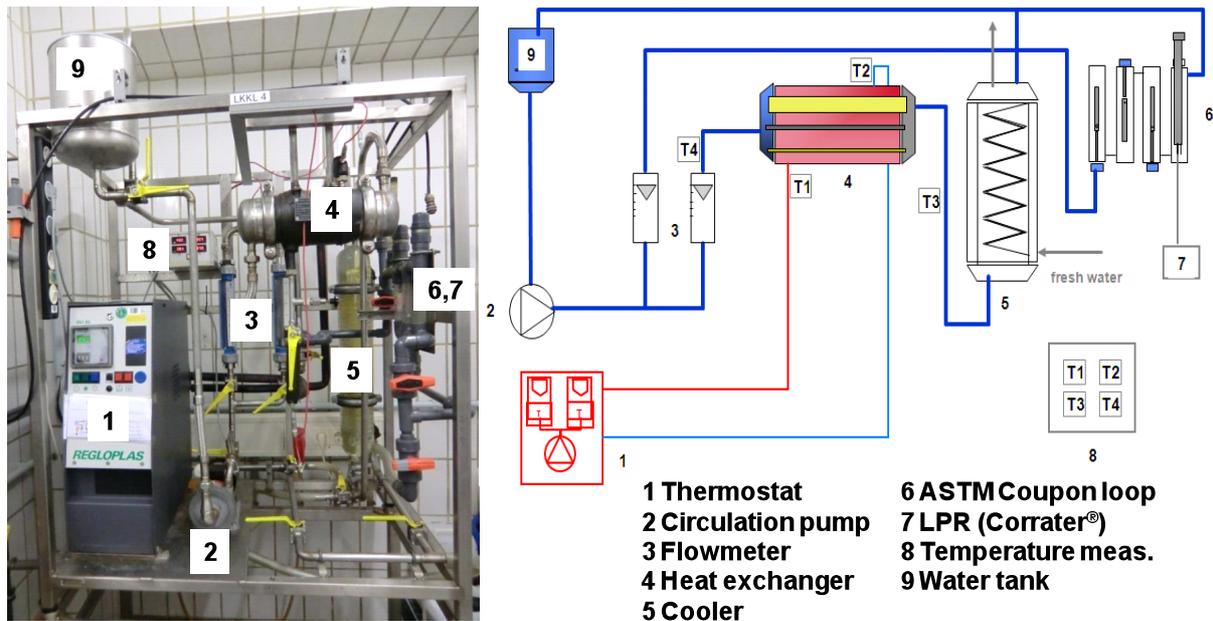


Figure 1: Illustration (left) and schematic representation (right) of the pilot closed cooling system

For the trials, the cleaned and rinsed water loop was filled with demineralised water (conductivity < 1 $\mu\text{S}/\text{cm}$). A different water quality could be investigated, (e.g. softened water) by preparing synthetic water with the addition of salts to the demineralised water. The quantity of corrosion inhibitor is added at the beginning of the experiment. In the case of FFA based treatment, the amount of free FFA is measured after one day. If the FFA concentration is below the targeted concentration of 1 mg/l (ppm), then the corrosion inhibitor is replenished accordingly. Thereby, it is ensured that the surfaces of the test loop are properly filmed. Throughout the test duration (typically two to four weeks), there is no water exchange or further addition of corrosion inhibitor.

During the tests the water was continuously circulated in the loop with a water velocity of 1.0 m/s (3.3 ft/s) in the coupon rack. Water temperature was monitored and water samples were taken regularly to determine water composition, concentration of the corrosion inhibitor and heavy metals according to the material of coupons installed. At the end of the test run, the coupons were removed from the plant and evaluated visually and by weight loss measurement.

Determination of the FFA concentration was carried out photometrical as a complex with a specific dye. The method is described elsewhere in detail in the literature [9].

3 Results and discussion

These series of experiments have been carried out to evaluate and to compare the corrosion inhibition efficiency of the film forming amine compounds (FFA) with the traditional anodic inhibitors (molybdate and nitrite) for the protection of carbon steel, copper and aluminum.

3.1. Electrochemical impedance spectroscopy

Electrochemical impedance is usually measured by applying a potential to an electrochemical cell and then measuring the current response. EIS experiment involves the application of a sinusoidal electrochemical perturbation (potential) in a wide range of frequencies (from high frequency to low frequency domain). If a sinusoidal potential excitation is applied, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase. This current signal can be analyzed as a sum of sinusoidal functions (Fourier series). The EIS instrument records the real (resistance) and imaginary (capacitance) components of the impedance response of the system.

The excitation signal, expressed as a function of time, has the form $E_t = E_0 \sin(\omega t)$ where E_t is the potential at time t , E_0 is the amplitude of the signal, and ω is the radial frequency.

The response signal, I_t , is shifted in phase (\emptyset) and has a different amplitude, I_0 . $I_t = I_0 \sin(\omega t + \emptyset)$. An expression analogous to Ohm's Law allows us to calculate the impedance of the system as : $Z = E_t/I_t = E_0 \sin(\omega t) / I_0 \sin(\omega t + \emptyset) = Z_0 \sin(\omega t) / \sin(\omega t + \emptyset)$ with $Z_0 = E_0 / I_0$. The impedance is therefore expressed in terms of a magnitude, Z_0 , and a phase shift, \emptyset . The impedance is then represented as a complex number : $Z = E/I = Z_0 \exp(j\emptyset) = Z_0 (\cos \emptyset + j \sin \emptyset)$.

The expression for $Z(\omega)$ is composed of a real $\text{Re}(Z)$ and an imaginary part $\text{Im}(Z)$. If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we obtain a "Nyquist diagram" (see Figure 2). Notice that in this plot the Y-axis is negative and that each point on the Nyquist Plot is the impedance at one frequency.

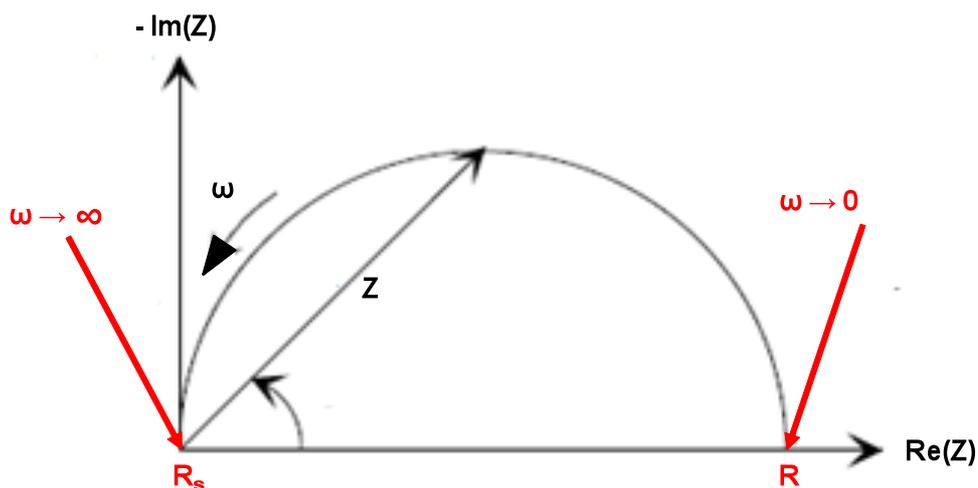


Figure 2: Illustration of the evaluation of an electrochemical impedance spectrum (EIS). The polarization resistance R_p is given by the difference between R (real part of the impedance $\text{Re}(Z)$ for low frequency) and R_s (real part of the impedance $\text{Re}(z)$ at high frequency).

The Nyquist Plot for a simplified cell theoretically is a semicircle (loop). The solution resistance R_s can be found by reading the real axis value at the high frequency intercept (in Figure 2 $R_s = 0$), the real axis value at the other (low frequency) intercept is the sum R of the polarization resistance and the solution. The diameter of the semicircle (loop) is therefore equal to the polarization resistance R_p ($R_p = R - R_s$), which is a measure for the corrosion inhibition.

For each experiment, the impedance diagrams were recorded separately after 2 hours of immersion at the corrosion potential for the different corrosion inhibitors and compared with the inhibitor-free solution.

a) Comparison of corrosion inhibitors on steel

Figure 3 shows the impedance diagrams obtained for different inhibitive mixtures in presence of carbon steel. They are characterized by a single capacitive loop. Previous studies showed some impedance diagrams with 2 loops in the presence of a film forming inhibitor [6], however, it is important to note that an immersion time of 2 hours would not be sufficient to show the occurrence of a clear loop in the high-frequency range.

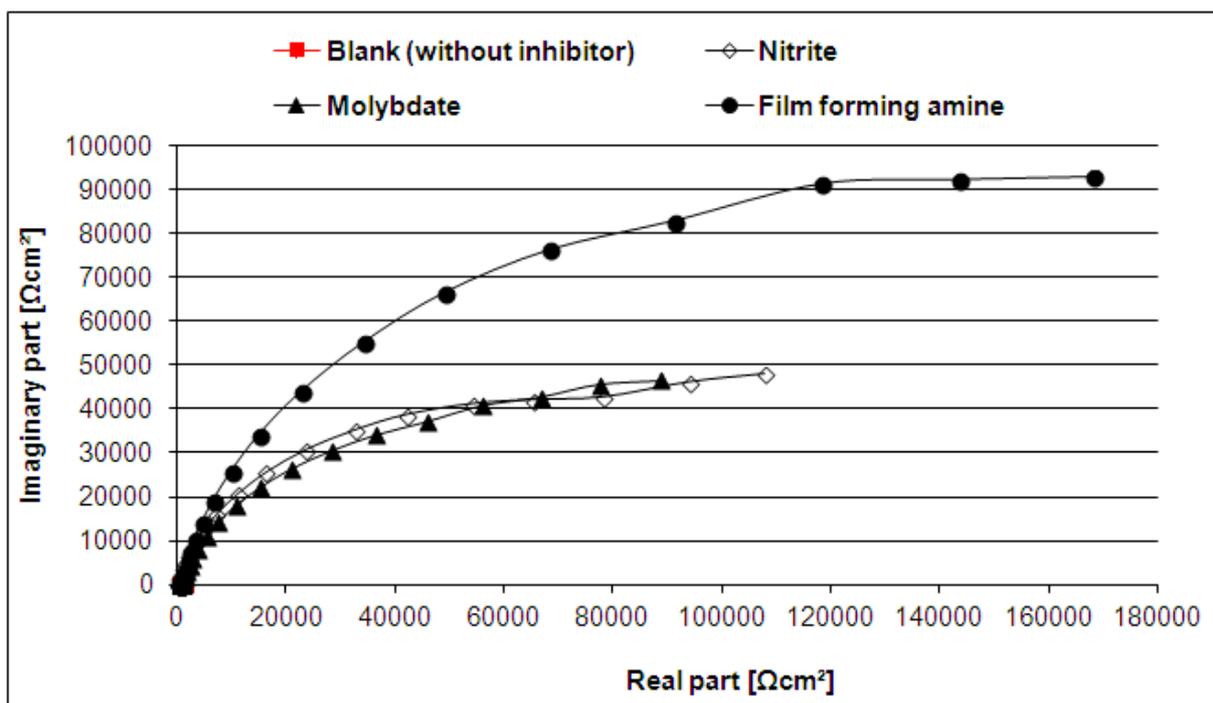


Figure 3: Electrochemical impedance diagrams obtained after 2 hours of immersion at E_{corr} for the tested corrosion inhibitors solution in presence of carbon steel

The polarization resistance values (R_p) obtained from the diagrams can be related to the charge transfer resistance of iron dissolution in the pores of the inhibitive layer [6, 10]. Assuming that electrochemical processes are taking place only at the pores, the change of the polarization resistance value gives direct information on the quality of the protective layer [11, 12], such that the higher the R_p value, the better the anticorrosion efficiency. The R_p values for each tested corrosion inhibitor are reported in Table 2.

Table 2: Polarization resistance deduced from the impedance diagrams presented in Figure 3 for carbon steel immersed in NaCl solution containing different corrosion inhibitors

Corrosion inhibitor	R_p [$\Omega \cdot \text{cm}^2$]
FFA	168000
Nitrite	108000
Molybdate	88300
Blank (solution without inhibitor)	1080

The polarization resistance values of all tested inhibitors are much higher than that obtained for the blank solution without inhibitor. Indeed, from the diagram, the lowest R_p value obtained in presence of inhibitor is more than 35 times higher than the R_p value measured without inhibitor. It clearly shows that each inhibitor provides a protective effect on the carbon steel against corrosion.

The best inhibitive effect was observed with the film forming amine which showed significantly higher anticorrosion efficiency than the two anodic inhibitors. Indeed, the carbon steel protection (polarization resistance) obtained with nitrite and molybdate was observed to be lower, 40 % and 50 % less than FFA, respectively.

b) Comparison of corrosion inhibitors on copper

This second series of electrochemical experiments was performed to compare the corrosion efficiency of the tested inhibitors on copper. Figure 4 reports the impedance diagrams obtained with the three corrosion inhibitors mixtures and a solution without inhibitor (blank).

As observed previously with carbon steel, the impedance diagrams are characterised by a single time constant (single loop). These diagrams show a significant anticorrosion protection of the copper, with the measured R_p values higher with the inhibitor than without the inhibitor (Table 3).

Table 3: Polarization resistance deduced from the impedance diagrams presented in Figure 4 for copper immersed in NaCl solution containing different corrosion inhibitors

Corrosion inhibitor	R_p [$\Omega \cdot \text{cm}^2$]
FFA	116000
Nitrite	78900
Molybdate	16000
Blank (solution without inhibitor)	1540

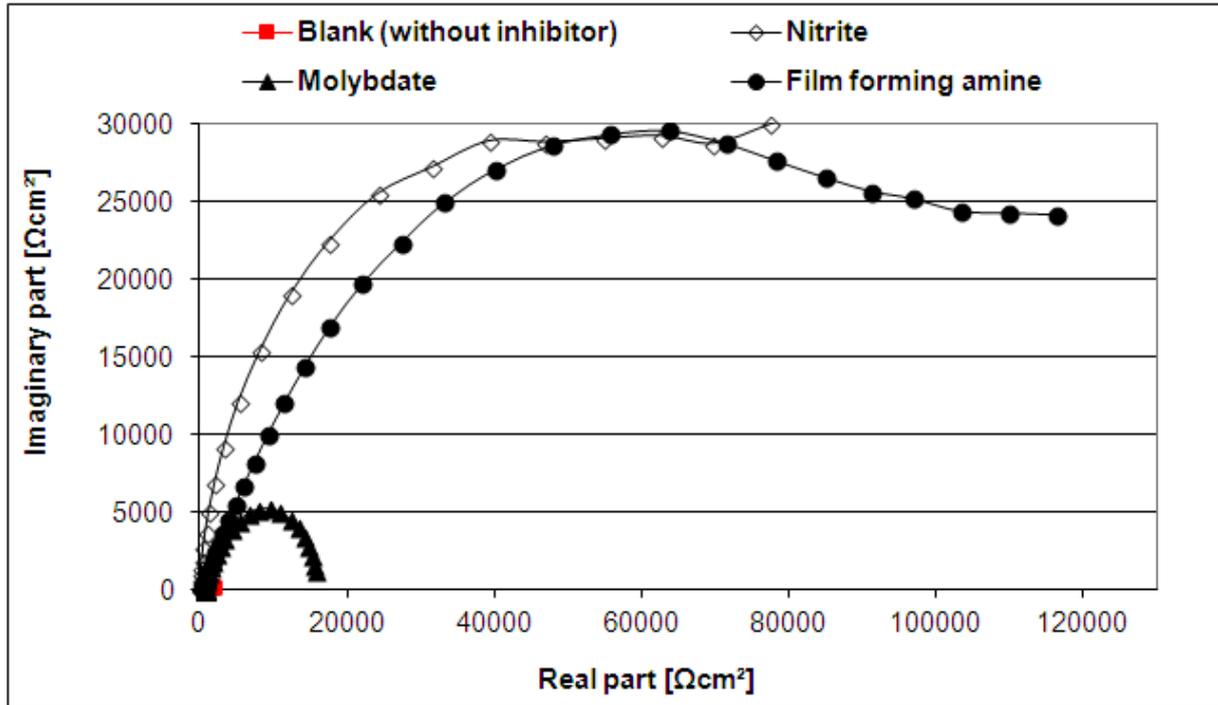


Figure 4: Electrochemical impedance diagrams obtained after 2 hours of immersion at E_{corr} for three corrosion inhibitor solution with copper.

The three inhibitors contain triazole, which contributes to the observed R_p values. However, the best anticorrosion protection (highest polarisation resistance: $R_p > 100000 \Omega\text{cm}^2$) of copper was obtained with the film forming amine containing inhibitor.

Nitrite provides a significant anticorrosion protection of the copper, although the measured values remain below the R_p values obtained with the film forming amine.

Finally, it appears that molybdate shows a significant inhibitive effect (10 times more than blank) but was observed to be less than the film forming amine and nitrite.

Further experiments would be necessary to confirm our hypothesis about the involved mechanisms, but the high polarization resistance could mean that the synergetic effect between film forming amine and triazole is higher than with the traditional anodic inhibitors molybdate and nitrite.

The protective chemisorbed film formed on copper with triazole (copper-azole complex) could be reinforced by the adsorption of the film forming amine which, by its hydrophobic nature, would lead to the formation of a thicker, more compact, and less porous protective film on the metal surface. Previous studies [1, 13] showed a relationship between inhibition efficiency and the hydrophobic properties.

c) Comparison of corrosion inhibitors on aluminum

The impedance diagrams obtained at the corrosion potential of aluminum for the different corrosion inhibitors tested separately are presented in Figure 5. As observed previously with the other materials, the R_p values of each inhibitor (film forming amine or molybdate) were significantly higher than those obtained for the blank solution without inhibitor. It was observed that the inhibitor induced a protective

effect on the aluminium against corrosion mechanisms, especially in our experimental conditions which were highly corrosive for aluminium (high content of chlorides).

The R_p values taken from Figure 5 are reported in Table 4. It can be noted, that the protection of aluminium was higher with film forming amine compared to molybdates. The R_p value with FFA was twice as high than the R_p value with molybdate.

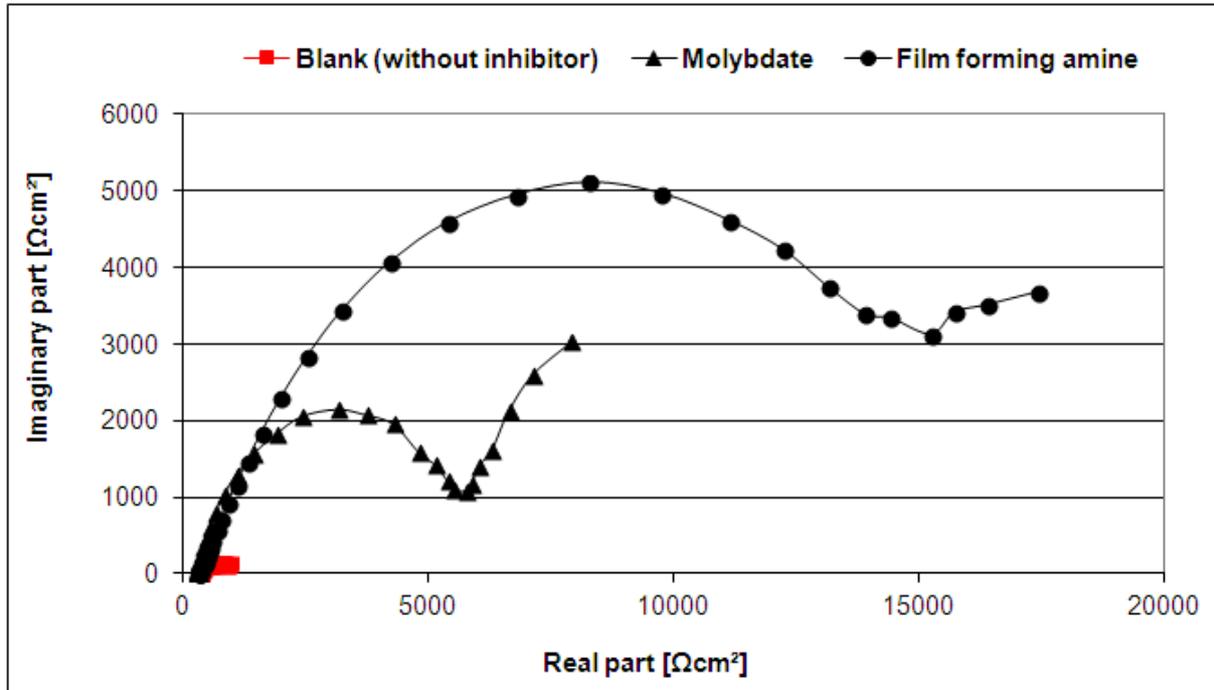


Figure 5: Electrochemical impedance diagrams obtained after 2 hours of immersion at E_{corr} for the tested corrosion inhibitor solution with aluminium.

Table 4: Polarization resistance deduced from the impedance diagrams presented in Figure 5 for aluminium immersed in NaCl solution containing the tested inhibitors.

Corrosion inhibitor	R_p [$\Omega.cm^2$]
FFA	17102
Molybdate	7700
Blank (solution without inhibitor)	750

From the curves of the impedance spectra (double loop), it can be derived that a protective film adsorbed on the surface was formed, but some further experiments would be necessary to identify and better understand the nature of interaction mechanisms involved with the surface (e.g. chemisorption, complexation, etc.).

3.2 Pilot plant studies

Two different test series are presented in this paper. The first study was carried out at 40°C (104 °F) applying nitrite, molybdate and FFA as corrosion inhibitors for steel and yellow metals. The second study focuses on the comparison of molybdate with FFA on a multi-metal system in addition to aluminum at an elevated temperature of 75°C (167 °F). For each series a blank was determined using non-treated water. The tests were carried out with DI-water, respectively medium soft water (Table 5) for the trials with aluminum. The pH of the DI-water was stabilized with 60 mg/l bicarbonate (TAC: 50 ppm CaCO₃). Test duration was 2 weeks in all cases. For all tests, the water had contact to air.

Table 5: Water composition for trials with aluminum.

pH	7.6			
Total Hardness	2.2	Mol/m³	220	ppm CaCO₃
Calcium	1.8	Mol/m³	180	ppm CaCO₃
Total Alkalinity	3.5	Mol/m³	175	ppm CaCO₃
Chloride	80	mg/l	80	ppm
Phosphate	< 0.1	mg/l	< 0.1	ppm

a) Studies at medium water temperature (40°C, 104 °F)

The first test conditions simulate a standard system containing carbon steel and copper using DI-water. The water temperature is critical since it strongly favors microbiological growth. Therefore, the water was treated at the beginning of the trial with a biocide based on isothiazolinon. The plant was operated with an open water tank. Therefore, the water was oxygen containing.

Table 6 shows the water composition for the three different corrosion inhibitors (nitrite, molybdate, film forming amine) as well as for the water without corrosion inhibitor (blank).

Table 6: Comparison of water composition for trials without aluminum at 40 °C (104 °F) for three different corrosion inhibitors.

Parameter	Unit	Corrosion inhibitor			
		None (Blank)	Nitrite	Molybdate	Film forming Amine (FFA)
Conductivity	µS/cm	130	3100	1200	240
pH		7.6	10.8	9.7	8.7
Iron	mg/l (ppm)	7.6	0.61	1.4	0.3
Nitrite (NO₂)	mg/l (ppm)	-	695	-	-
Molybdate (MoO₄)	mg/l (ppm)	-	-	202	-
FFA	mg/l (ppm)	-	-	-	1.5

All three corrosion inhibitors had shown a significant reduction of the corrosion rates for both carbon steel and copper (Figure 6). With all inhibitors, excellent corrosion inhibition could be achieved. The corrosion rates are very low for both carbon steel (< 0.2 mpy; < 0.005 mm/y) and copper (< 0.08 mpy; < 0.002 mm/y), in accordance within the error of the experiment. Figure 7 shows the coupons before etching.

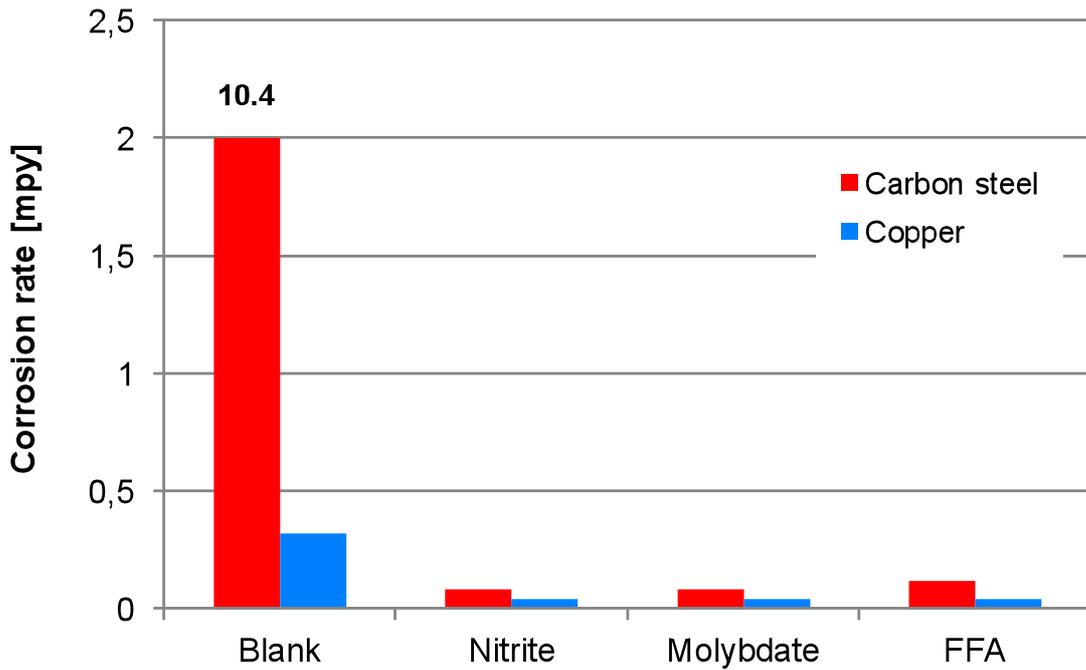


Figure 6: Corrosion rates according to ASTM D2688 for different corrosion inhibitors at 40 °C (104 °F).

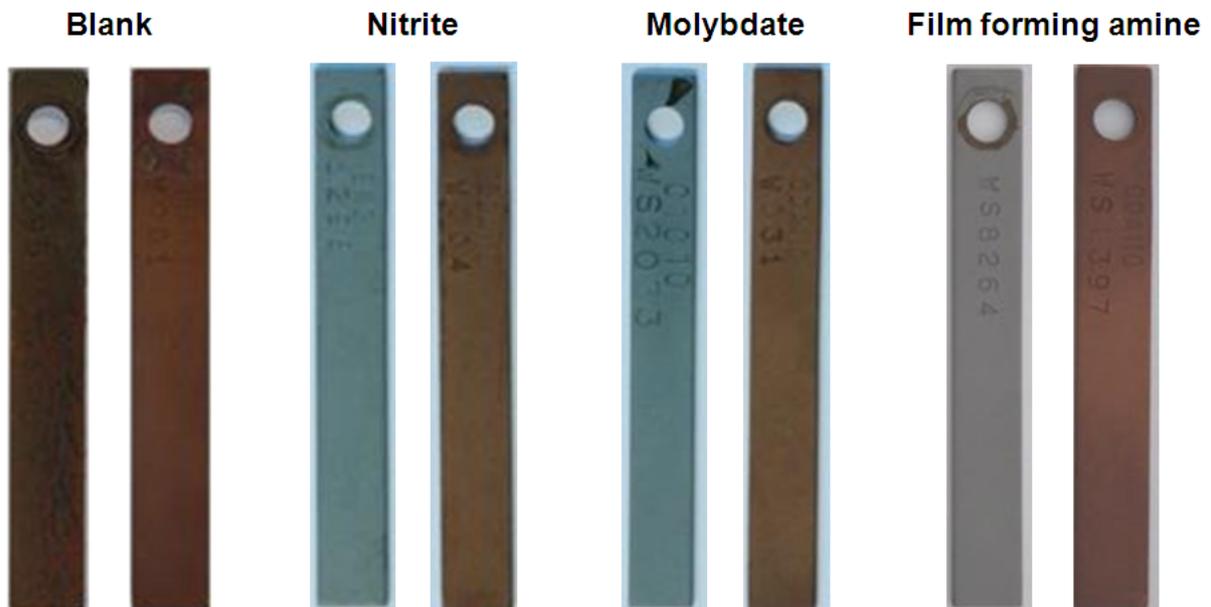


Figure 7: Coupons before pickling treated with different corrosion inhibitors in a pilot closed cooling system at 40 °C (104 °F). Left coupon: carbon steel, right coupon: copper

The corrosion inhibition is also reflected in both the average iron concentration in the cooling water and the development of the iron concentration during the experiment (Figure 8). The untreated water is characterised by a continuous increase of the iron concentration, whereas it was essentially stable for all three inhibitors throughout the length of the experiment. For the film forming amine, the average iron value was observed to be the lowest (0.32 mg/l).

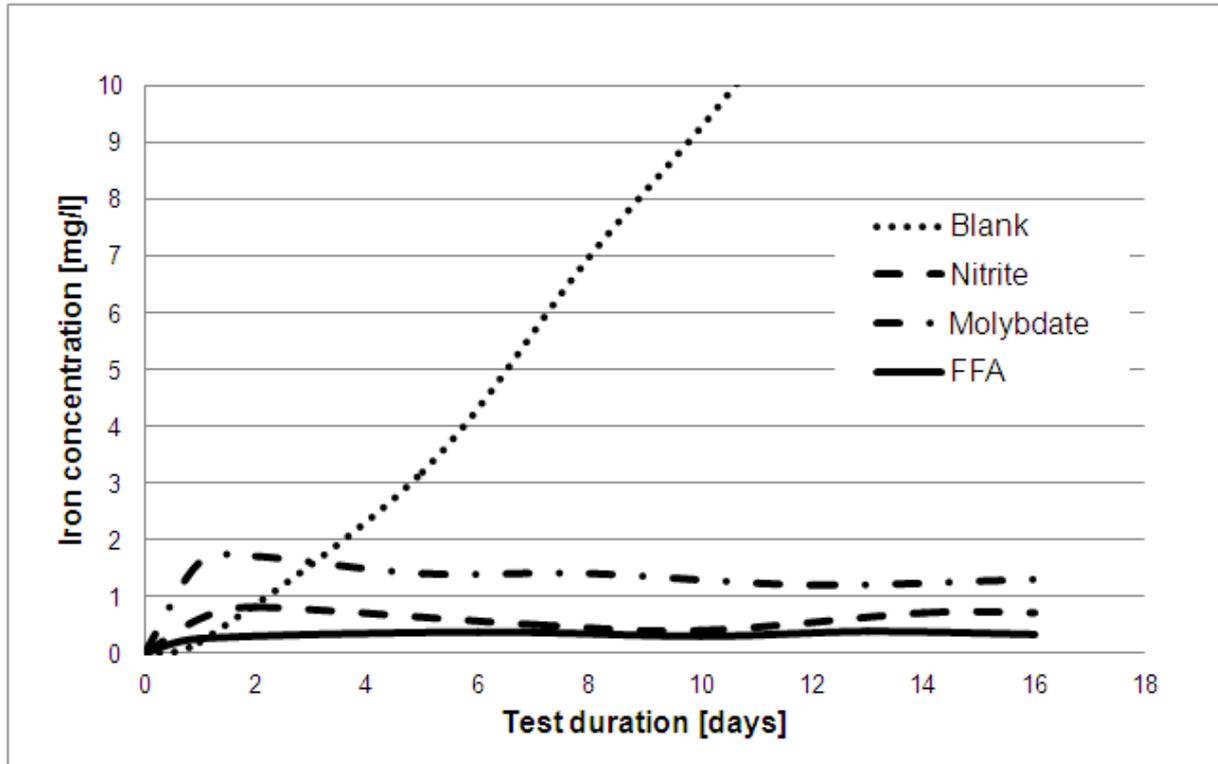


Figure 8: Development of iron concentration in cooling water of a pilot closed cooling systems treated with different corrosion inhibitors at 40°C (104 °F).

b) Studies at high water temperature (75°C, 167 °F)

This test layout represents realistic worst case conditions: a multi-metal system containing carbon steel, brass (admiralty) and aluminum operated with poor water quality at high temperature. At the same time the water has contact to air and as a consequence contains dissolved oxygen.

Table 7 shows the average values of the water analysis for all three test runs. It should be noted that the pH was adjusted to a range suitable for aluminum. As expected in all systems, a loss of calcium, typically from 1.8 to 0.9 mol/m³ (180 to 90 ppm CaCO₃) and total alkalinity was observed due to the precipitation of calcium carbonate. The soluble heavy metal content was in all cases low and in the same concentration range, although the corrosion rate on coupons showed obvious differences (Figure 9). It can be assumed that iron and zinc were precipitated as oxides.

Table 7: Water composition for trials in closed cooling pilot system with carbon steel and aluminum at 75 °C (167 °F).

Parameter	Unit	Corrosion inhibitor		
		None (Blanc)	Molybdate	Film forming Amine
Conductivity	µS/cm	500	980	780
Iron	mg/l (ppm)	0.2	0.3	0.2
Copper	mg/l (ppm)	0.3	0.2	0.3
Zinc	mg/l (ppm)	< 0.1	175	< 0.1
Aluminum	mg/l (ppm)	0.5	80	< 0.5

From the comparison between the blanks of both the first (Table 6) and second (Table 7) series, the conditions during the second series were much more severe. The corrosion rate at 75 °C (167 °F) was 38 mpy (0.95 mm/y), whereas it was 10.4 mpy (0.26 mm/y) at the lower temperature. The corrosion rates were reduced with both corrosion inhibitors (Figure 9). With the film forming amine the corrosion rate on aluminum is significantly lower compared to that of molybdate (4mpy [0.10 mm/y] for molybdate respectively 2.4 mpy [0.06 mm/y] for FFA). Figure 10 shows the coupons before etching.

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

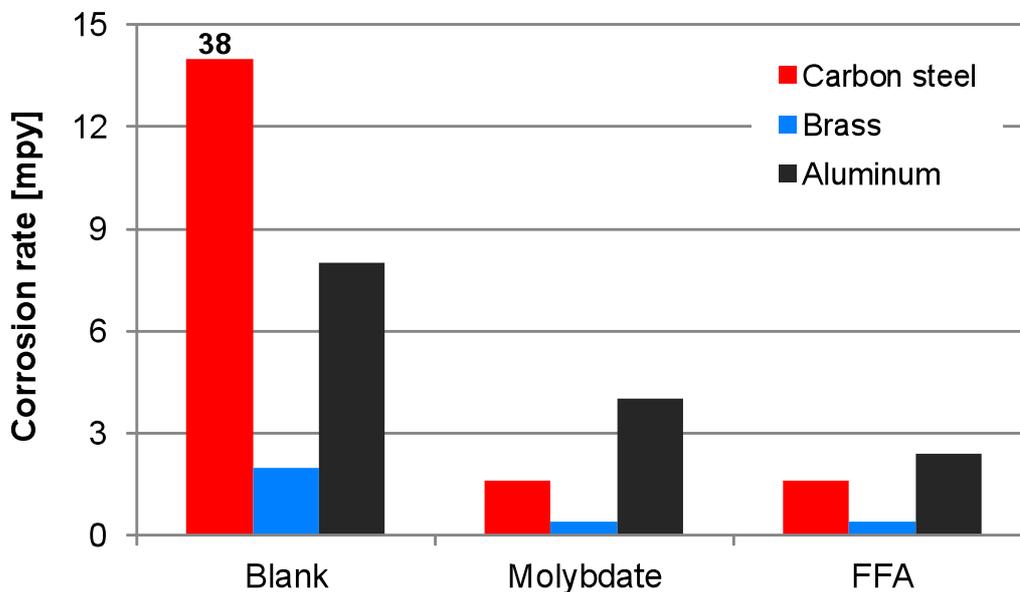


Figure 9: Corrosion rates according to ASTM D2688 for different corrosion inhibitors at 75 °C (167 °F).

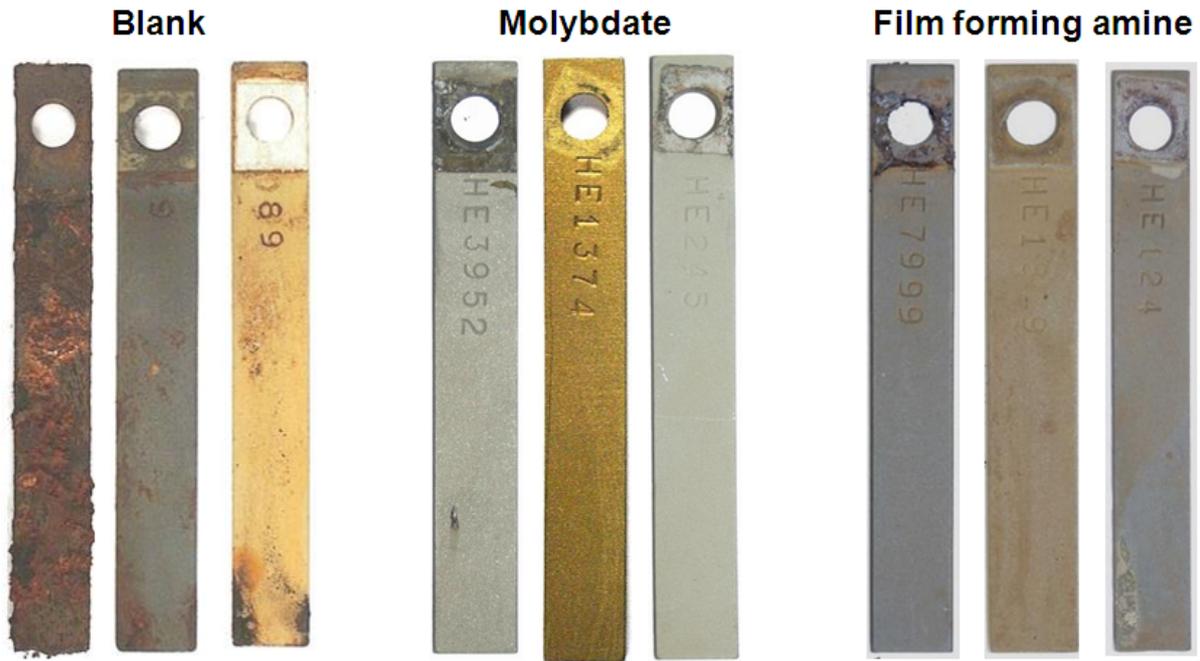


Figure 10: Coupons before etching treated with different corrosion inhibitors in a pilot closed cooling system at 75 °C (167 °F). The coupon material was (from left to right): carbon steel, brass, aluminum.

4 Field results

Both electrochemical and pilot plant studies demonstrate that film forming amines provide a very good corrosion inhibition under the conditions of closed cooling systems. Before discussing the two case studies from the field, some general comments are given to explain the specific features of a treatment program based on film forming amine.

The mechanism of corrosion protection depends on the adsorption of the FFA on the metal surfaces in the system. Therefore, there is no straightforward correlation between the amount of FFA dosed to a system and the concentration of free FFA in the water. Since the adsorption is principally reversible, it has to be assured that the necessary amount of free FFA (> 1 mg/l) can be found in the system. Desorption is a slow process, therefore, a few days of underfeeding of FFA can be bridged.

Besides film forming amines, a commercial product can contain further components: alkalizing agents, e.g. organic amines such as monoethanolamine or caustic, adjust the pH of the cooling water to the desired range depending on the metals used in the system. Triazole supports corrosion protection of yellow metals and dispersants help to keep the surfaces free from debris.

The film forming amine itself has an emulsifying effect as well as acting as a dispersant. This leads to a certain remobilization of suspended matter in dirty systems, which can be measured by an increase of suspended matter or turbidity as well as an increase of particulate metal oxide. This is a normal effect of on-line cleaning and should not be confused with active corrosion. However, this effect has to be taken into consideration, when a treatment program based of FFA is started-up, especially in the case of an old and poorly managed system. In this case the total amount of product for the first fill should be added to the system in portions to limit the effect mentioned above.

The quantity needed to achieve a concentration of free FFA can be estimated from the system volume. However, it cannot be exactly calculated due to the intended adsorption of the FFA on the surfaces. During start-up the concentration of FFA should be monitored regularly, as the FFA will be consumed by adsorption on the surfaces, and product added to the system until 1 mg/l of FFA can be found.

An increase of suspended matter can be counter-acted by a temporary side stream filtration, increased blow-down of water or a cleaning of the system before start-up of changeover of treatment. During normal operation the water remains normally very clear and the product has to be added as normal in order to compensate water losses only.

Film forming amines are compatible with all major materials typically used in closed systems, with the exception being Viton. This material is not compatible with film forming amines and will be destroyed. Therefore, the dosing unit and the system should not contain any Viton.

4.1 Closed cooling systems containing carbon steel and aluminum

This first example describes a case of a closed cooling circuit containing aluminum for which a changeover of anticorrosion program from molybdate to film forming amine based inhibitor improved strongly the protection of steel and aluminum against corrosion and bio-corrosion phenomena.

Cooling system description

District cooling systems are comprised of collective equipment to produce chilled water which is mainly used for air-conditioning and cooling in buildings, but also for dehumidification. Refrigeration facilities are composed of refrigerating units, pumps, electric and electronic equipments. Amongst the different cooling water circuits involved in the chilled water production plant, there are very small closed systems with a very important role.

For example, the case presented in this paper concerns several closed circuits with a small capacity (total volume does not exceed 1 m³ (35 cft)), which are used for the cooling of electronic equipment on engine driven pumps via plate exchangers.

The water temperature in the closed system can oscillate between 25 and 45 °C (77 and 113 °F). The material of the plate heat exchanger is aluminum, and 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 (ppm)
Aluminum:	< 0.5 mg/l (ppm)

Corrosion treatment programs

Historically these systems were operated with molybdate under alkaline conditions which led to more or less elevated levels of aluminium content in spite of the corrosion inhibition. At this period, the water was regularly exchanged in order to maintain the metal concentration, especially aluminum, below the specified limits.

After a curative cleaning phase in order to remove the corrosion by-products, the corrosion treatment program was finally changed to a film forming amine compound. The system was flushed, refilled with softened water with the addition of 5000 mg/l of commercial product.

Within a short time period, the system became stable again and was then operated completely inside the specified limits of aluminum and iron. The system was replenished only in order to compensate water losses. The measured concentration of FFA was generally between 0.5 and 1.5 mg/l (ppm).

The iron and aluminum levels in the water during these two corrosion treatment programs are presented in Figure 11. It was observed that the aluminium content was not stable during the phase with the molybdate based program, moreover some very high values (> 3 ppm) were measured with a peak concentration up to 10 mg/l (ppm). The iron concentration during this same phase was not as high but occasionally reached the limit value of 1 mg/l (ppm).

It is interesting to note that the average concentration of aluminium was strongly reduced and maintained to a stable level below 0.5 mg/l (ppm) after the changeover from molybdate to film forming amine program. Indeed, during the period of treatment with film forming amines, the limits of aluminum and iron concentrations in the water were continuously maintained without any sudden increase, confirming a strong improvement of the anticorrosion protection. Furthermore, improved control of the pH could be maintained with the FFA. The pH was maintained close to 8.5, which is important to avoid corrosion phenomena of aluminum containing materials.

Furthermore, the level of sulphate reducing bacteria (SRB) was regularly determined in the cooling water (Figure 12). The SBR content in the water phase has been reduced by at least 2 orders of magnitude and up to 4 orders after the cleaning phase and the implementation of the film forming amine based treatment. These results seemed to confirm the previous data: corrosion phenomena are prevented. It is assumed that the SBR activity was decreased due to reduced deposit amounts of corrosion by-products. It suggests that the FFA treatment allows maintaining the cleanliness of the metal surface and thus helps indirectly to reduce microbiological growth.

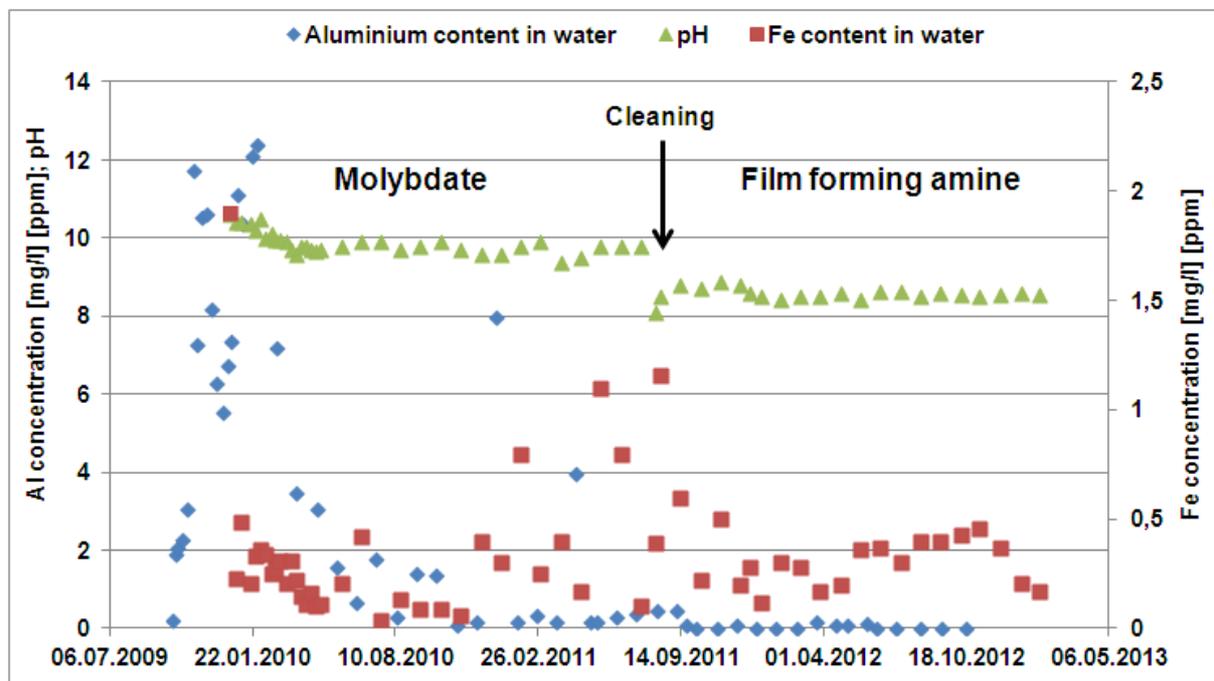


Figure 11: Metal concentrations (Fe and Al) in water and pH in the presence of two different corrosion treatment programs: molybdate based product and film forming amine based product.

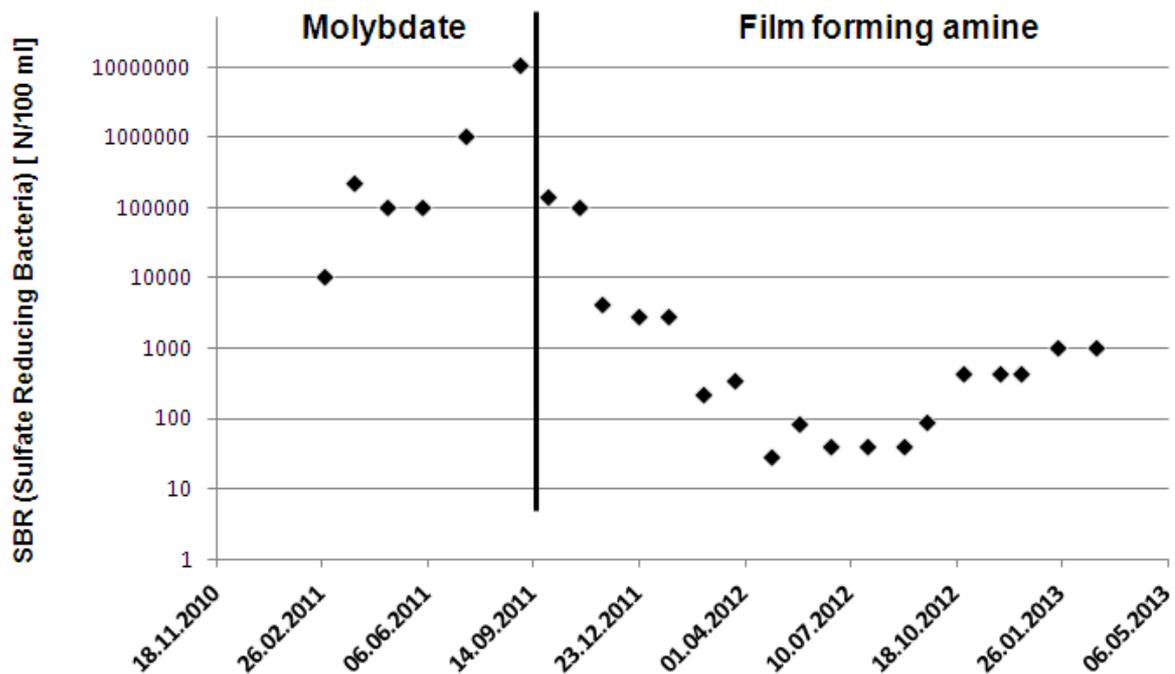


Figure 12: Sulphate reducing bacteria determined in cooling water during two different corrosion programs (until 14.09.2011 molybdate, afterwards film forming amine)

4.2 Closed cooling systems of a combined heat and power plant

The second case study reports the very successful change-over of the treatment of two closed cooling systems from a molybdate program to film forming amine based program.

Plant and cooling system description

A combined heat and power plant in South Europe operates two units, each one equipped with a closed cooling system (CCW11 and CCW21) for the cooling of the auxiliary systems. The plant is located in a port at the sea, thus the secondary closed cooling systems are connected via plate heat exchangers to the primary once-through cooling system using sea water. Amongst others the following installations are cooled by the closed cooling circuit:

- Oil coolers
- Hydraulic power unit
- Air compressor
- Hydrogen drying
- Hydrogen generator
- Sampling unit of the water/steam cycle
- Blow-down of steam generators.

The two systems are identical and have a total volume of approximately 35 m³ (1240 cft) each.

The two closed cooling systems are fed with DI-water. According to the internal specifications the following limits have to be kept in the water:

Iron:	< 700 µg/l (ppb)
Copper:	< 1000 µg/l (ppb)

Materials in the cooling system

The main pipelines of the two circuits from the compensation tank to the sea water cooled plate heat exchangers and to the various coolers of the equipment are made of carbon steel. The compensation tank itself is also made from carbon steel. The material of the hydrogen generator cooler is copper and the plate heat exchanger material is stainless steel.

System particularities

The mode of operation in the system is varying depending on the cooling needs. The water flow is adjusted according to the heat load. Furthermore, the primary cooling system is operated only, if the water temperature in the closed system exceeds 40 °C (104 °F) and is stopped again, if the water temperature drops below 30 °C (86 °F). As a consequence the water temperature in the closed system is oscillating between these two limits.

Corrosion treatment programs

The systems were put into operation without prior passivation and operated without corrosion protection for more than six months. Due to the ever increasing iron and copper levels, finally a molybdate based corrosion inhibition was implemented. In spite of the corrosion inhibition addition, the iron and copper levels in the system were continuing to increase, so that regularly cooling water was replenished by DI-water in order to maintain the heavy metal concentration (especially iron, near the specified limits).

Tables 8a,b show a comparison of the water data for the molybdate based program and the corrosion inhibitor based on film forming amine for both circuits. The average concentration of iron could be reduced from 740 to 240 µg/l (ppb) iron in system CCW 11. At the same time the copper concentration decreased from 380 to 220 µg/l (ppb). In CCW 21 the iron concentration decreased from 870 to 140 µg/l (ppb) and the copper concentration was reduced from 110 to below 20 ppm. During the period of treatment with film forming amines the limits of iron and copper in the water were well maintained.

Figures 13a,b show the development over a one year period of the heavy metal concentration in both circuits during molybdate treatment, and during and after the transition from molybdate to film forming amine. The changeover from the molybdate treatment to film forming amines was evaluated by plant personnel, and seen as completely successful. Water consumption and maintenance time could be substantially reduced leading to considerable savings.

Table 8a: Comparison of measured data of cooling system CCW11 of a Combined Heat and Power Plant treated with molybdate (02.04.2012-02.11.2012) and film forming amine (FFA) (02.01.2013-02.04.2013)

CCW11		Iron	Copper	pH	Conduc-tivity	Molybdate	FFA
		µg/l	µg/l	-	µS/cm	mg/l	mg/l
Molybdate	Max	2500	700	10.0	880	280	-
	Min	214	113	7.7	260	< 5	-
	Avg.	740	380	8.6	560	171	-
FFA	Max	600	990	10.1	230	-	0.9
	Min	140	130	7.1	31	-	0.5
	Avg.	240	220	7.9	230	-	0.7

Table 8b: Comparison of measured data of cooling system CCW21 of a Combined Heat and Power Plant treated with molybdate (02.04.2012-02.11.2012) and film forming amine (FFA) (02.01.2013-02.04.2013)

CCW21		Iron	Copper	pH	Conduc-tivity	Molybdate	FFA
		µg/l	µg/l	-	µS/cm	mg/l	mg/l
Molybdate	Max	2250	290	9.4	1090	310	-
	Min	180	10	7.0	405	115	-
	Avg.	870	110	8.6	710	210	-
FFA	Max	260	34	7.4	440	-	0.9
	Min	84	4	6.9	170	-	0.5
	Avg.	140	15	7.2	360	-	0.7

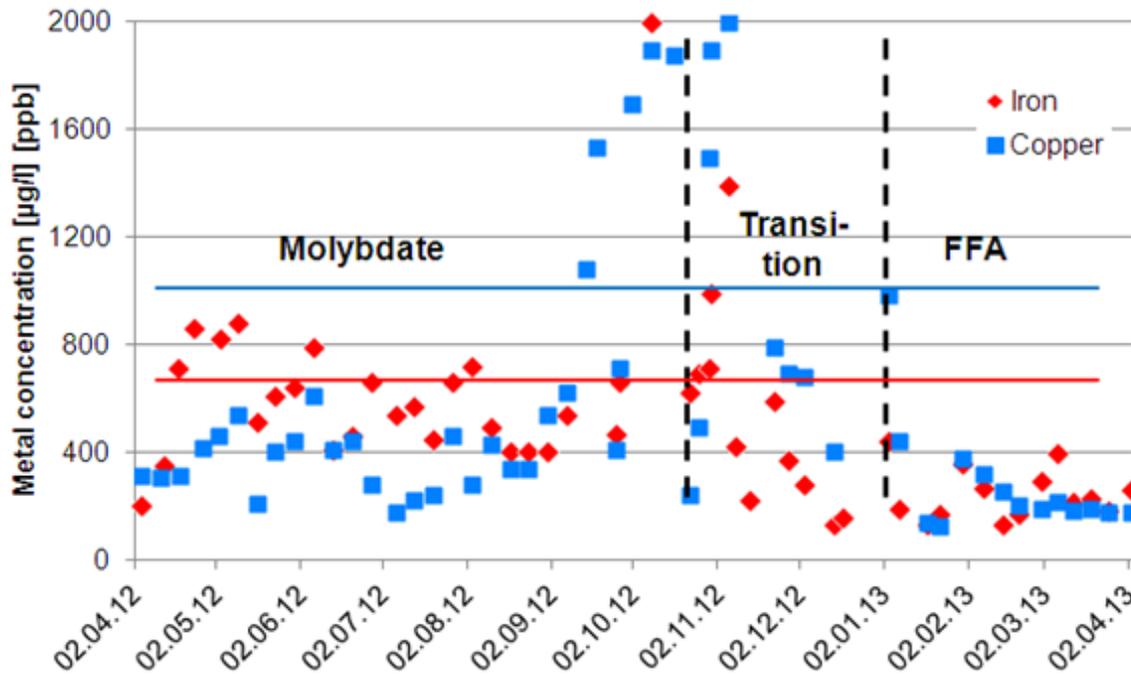


Figure 13a: Iron and copper concentration in cooling water of closed system CCW11 of a Combined Heat and Power Plant.

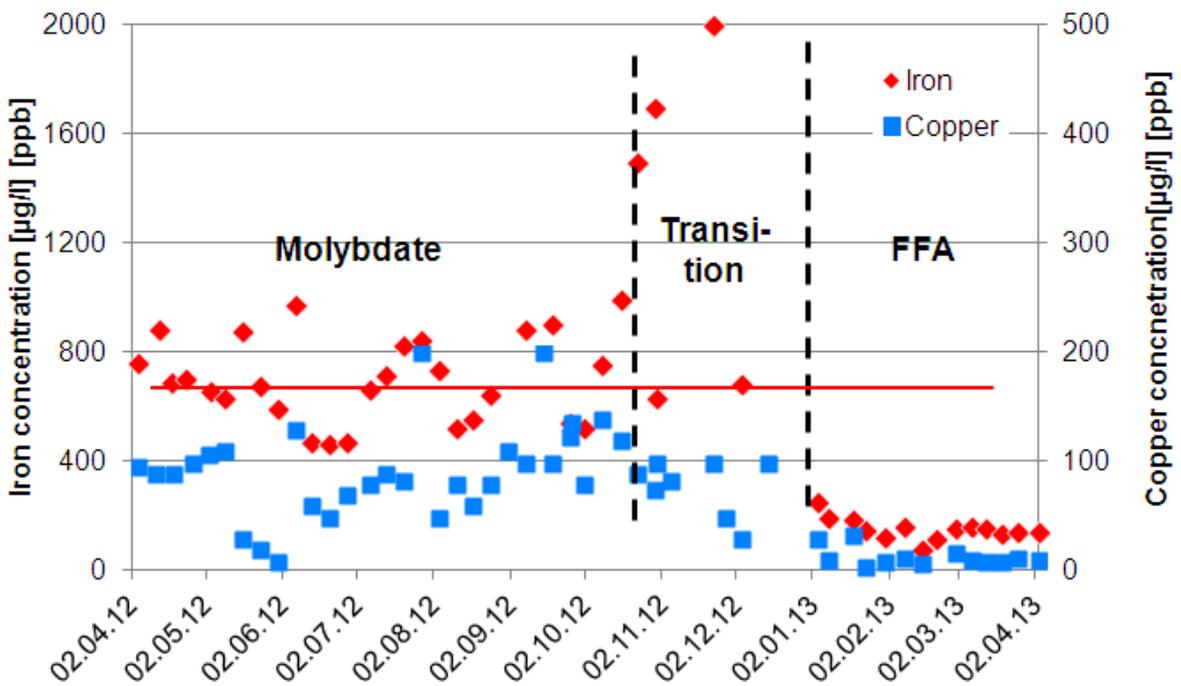


Figure 13b: Iron and copper concentration in cooling water of closed system CCW21 of a Combined Heat and Power Plant.

5 Conclusions and outlook

Film forming amines have been investigated at the lab scale by electrochemical methods (Electrochemical Impedance Spectroscopy) as well as in pilot plant trials closely simulating practice-like conditions. According to these results, corrosion protection could at a minimum be maintained, while in some cases corrosion protection was enhanced as compared to well established corrosion inhibitors based on molybdate or nitrite. The mechanism of corrosion inhibition is believed to be the formation of a protective film on the surfaces which prevents the contact of corrosive agents with the surface.

Control of the corrosion inhibitor is accomplished by colorimetric determination of the free film forming amine concentration in the cooling water. A concentration above 1 mg/l (ppm) is generally recommended. Due to the intended adsorption of the film forming amine on the surfaces, there is no direct correlation of the FFA added to the system and the resulting concentration in the water.

Two field studies show that film forming amines can provide excellent corrosion inhibition even in cases where traditional corrosion inhibitors are not capable in delivering satisfying treatment results. Water consumption and effort for maintenance could be reduced through such treatments, and thus considerable savings could be realized. FFA based programs are suitable for various metals, such as carbon steel, yellow metals and aluminium. In the case of aluminum containing systems, the pH must be less alkaline similar to other corrosion inhibitors.

With FFAs, much lower conductivities in the cooling water could be achieved as compared to corrosion inhibition programs based on inorganic inhibitors (nitrite, molybdate). This is especially important for special application in systems in which the conductivity is limited by the process such as with electromagnetic stirring units in the steel casting process.

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