FILM FORMING TECHNOLOGY

Wolfgang Hater, Andre de Bache and Ingo Königs, Kurita Europe, Germany, describe an innovative technology based on film forming amines for the treatment of boiler feed water.

A good treatment programme for boiler feed water is crucial to the smooth operation of steam generators. Faulty treatment can cause damage to the plant, with attendant high costs. Traditional treatment programmes have three components: oxygen scavengers, alkalising amines, and phosphate. In a treatment programme based on film forming amines (FFAs), the functions of both oxygen scavenger and phosphate are replaced by the FFAs. FFAs form a thin compact film on the metallic surfaces, preventing oxygen from coming into contact with the metal, and therefore preventing corrosion. In contrast to an oxygen scavenger, film forming amines are not consumed by reacting with oxygen. In addition, their volatility means that they protect the complete steam system, unlike some oxygen scavengers, e.g. sulfite. FFA based programmes are all organic and, therefore, make scarcely any contribution to the conductivity of the boiler water. In comparison to phosphate and sulfite, higher concentration cycles can be achieved, leading to lower amounts of blowdown water and, therefore, to a significant reduction in energy losses. New studies with FFAs have shown that the coefficients of heat transmission from the heating tubes into the water phase are significantly higher than when phosphate treatment is used. As a consequence, lower exhaust gas

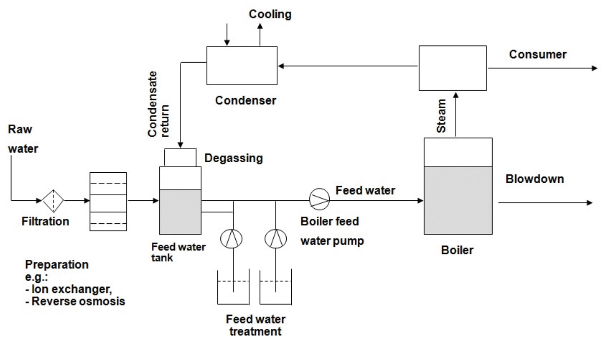

Figure 1. Simplified block diagram of a steam generator with feed water conditioning and dosing system for chemical additives.

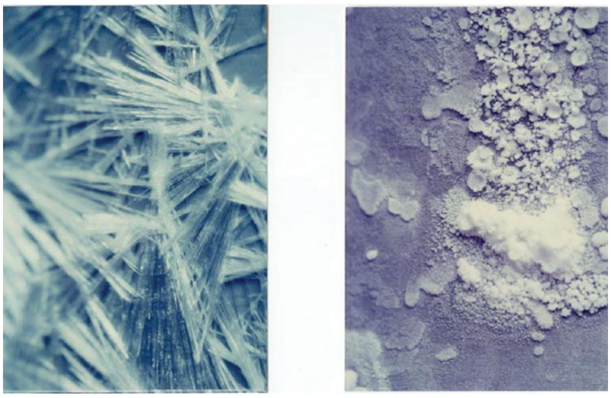

Figure 2. Structure of calcium carbonate crystals without (left) and with (right) added film forming amine.

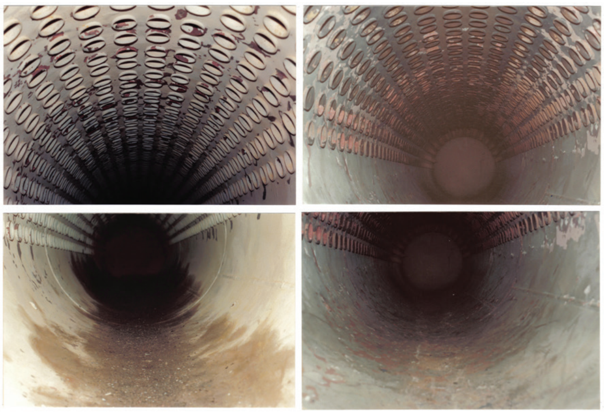

Figure 3. Gradual removal of existing calcium scale from a steam generator by film forming amines (left: before treatment; right: after one year of treatment).

temperatures and lower energy losses can be expected. FFAs have been successfully used in real applications for decades. Good results have sometimes been achieved even in cases where conventional treatment programmes failed to provide satisfying results.

Many industrial companies operate steam generators of different types and capacities to cover their process steam and energy requirements. The boiler feed water has to be treated in order to ensure reliable and economic operation of the boilers. To avoid damage to plant parts or degradation of plant efficiency through corrosion or scaling, the raw water is usually subjected to conditioning, and chemical additives are introduced into the resulting conditioned boiler feed water.

This article describes an innovative technology, based on FFAs for the treatment of boiler feed water. It gives an overview of the properties and practical advantages of this technology, and describes the opportunities it presents for reducing the resource consumption and emissions of steam generators.

Principles of boiler water treatment

Boiler water treatment should prevent problems from arising due to reactions between substances in the water and the surfaces of the plant, and in particular it should prevent corrosion and scaling.

Scaling can occur in steam generators when substances separate out of the water at the plant surfaces. It can also occur as a secondary effect of corrosion, when corrosion products are transported by the circulating water and are deposited on plant surfaces. The main components of scale in steam generators are calcium carbonate, calcium phosphate, silicates, iron oxide and iron hydroxide.

Scale is a poor conductor of heat, and therefore hinders heat transmission. This can result in local overheating, which may damage the thermally stressed parts, and reduced plant efficiency, with considerable associated costs.

There are basically two corrosion mechanisms in steam boilers. One is corrosion by oxygen, which enters the system with the feed water or through leaks in the condensate zone. The other is corrosion by carbonic acid, which is formed from the CO_2 in the water. The CO_2 itself is formed primarily by the thermal decomposition of carbonates in the boiler.

Corrosion should not be confused with the desirable formation of a passivation layer (magnetite layer formation). The formation of an excessively thick magnetite layer is, however, undesirable, in view of the associated reduced heat transmission.

The risk of scaling and corrosion is minimised by treating the raw water (complete demineralisation and degassing) and adding chemicals to the resulting feed water. Figure 1 shows a simplified block diagram of a steam generator with feed water treatment and an additives dosing system. The composition of the additives depends on the quality of the feed water, the operating conditions and the configuration of the plant.

Scale inhibitors

If the ingress of water hardness ions cannot be ruled out, the addition of a scale inhibitor is advisable. Phosphate binds water hardness ions as non-scaling calcium phosphate sludge, which is periodically blown down from the boiler. Polycarboxylates interfere with the process of crystal growth, and therefore delay the formation of calcium carbonate from a supersaturated solution. Their dispersing action prevents the sedimentation of insoluble solids and keeps the surfaces free.

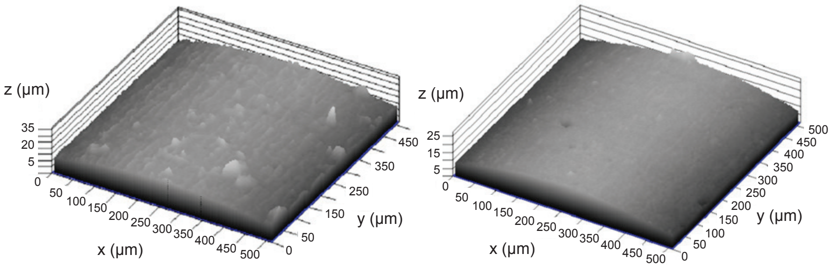

Figure 4. Confocal laser scanning microscopy (CLSM) of tubes from a test steam generator treated with sodium phosphate (left) and film forming amine (right).

Corrosion inhibitors

A basic distinction is made between two groups of corrosion inhibitors. Oxygen scavengers such as sulfite, diethylhydroxylamine and hydrazine, remove oxygen from water by reacting with it, so that only a low level of corrosion of the metallic surface can take place.

Film forming inhibitors create a thin impermeable layer on the surfaces, so that corrosive substances cannot come into contact with them. As a result, a corrosive reaction can no longer occur. Film forming inhibitors are not consumed by entering into chemical reactions. It is therefore only necessary to add them in the quantities needed to maintain the protective film.

Alongside oxygen corrosion, corrosion caused by the carbon dioxide in steam and condensate systems is also significant. Steam volatile alkalising amines prevent corrosion by raising the pH of the condensate. The material, length and complexity of the condensate system are all factors that influence the choice of amine to be used. Alkalising amines differ in terms of their volatility, basicity and thermal stability. Examples include ammonia, cyclohexylamine, morpholine and aminomethylpropanol.

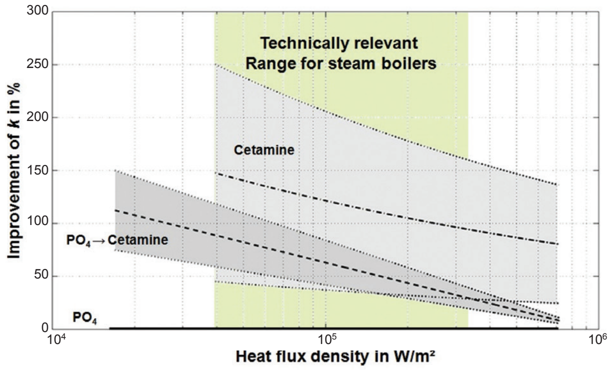

Figure 5. Relative improvement in the heat transmission coefficient k after treatment with film forming amines as a function of the heat flux density.

Film forming amines

Conventional boiler water treatment programmes generally have three components: oxygen scavengers, phosphate and alkalising amines. In contrast, a treatment programme based on FFAs is based on a combination of a film forming component with alkalising amines. Both treatment concepts can be widened to include a polycarboxylate.

FFAs, often referred to as polyamines or fatty amines, are defined chemical substances that belong to the oligoalkylamino fatty amine family. The general chemical formula is $R1-[NH-(R2)-]n-NH_2$, where n is a whole number between 0 and 7, R1 is an unbranched alkyl chain with 12 to 18 carbon atoms (fatty alkyl chain) and R2 is a short chain alkyl group. The simplest representative is octadecylamine (n = 0, R1 = $C_{18}H_{37}$), which has been the subject of numerous studies. The main disadvantages of octadecylamine are its poor formulatability, which makes the addition of acetic acid necessary, and its marked overdosage sensitivity.

Modern treatment programmes often contain oleyl amine (n=1, R1 = $C_{18}H_{35}$) or oleyl propylene diamine (n=1, R1 = $C_{18}H_{35}$, R2 = C_3H_6). The FFAs are always used in combination with alkalising amines in order to adjust the pH of the boiler water and the condensate and at the same time to ensure the necessary storage stability of the formulations.

Properties of film forming amines

When FFA based treatment programmes are used, knowledge of the specific properties of these substances and the practical consequences of these properties is essential. A number of important properties are described in the following.

Surface affinity

FFAs are not pronounced anti scalants, such as polycarboxylates. However, they are adsorbed by the microcrystallites that form at the start of the crystallisation process and interfere with their growth. Amorphous, low scaling structures are formed (Figure 2).

FFAs have a very strong affinity to metal surfaces. The process of film formation was studied in detail, especially with the help of electrochemical impedance spectroscopy and photelectron spectroscopy. The polarisation resistance values derived from the impedance spectra are a measure of the charge transfer resistance when iron dissolves in the pores of the covering layer. For oleyl propylene diamine and oleyl amine, the polarisation resistance, and therefore the stability of the film, reached a maximum.

The film acts as a barrier against corrosive substances such as oxygen and CO_2, or carbonic acid. Once formed, a

Figure 6. Inhibition of corrosion of steel strips from a condensate system of a steam generator treated with programmes based on sulfite, phosphate and alkalising amine (left) and film forming amine and alkalising amine (right).

protective film remains intact even after the dosage has been adjusted, so that if the dosage falls below the required level or is interrupted for a short period, no direct harm occurs. Due to their strong surface affinity, FFAs can gradually remove attached substances such as calcium scale or loosely adhering magnetite from the surface (Figure 3).

Improved magnetite protective layer

Compact, thin and smooth magnetite layers are desirable in steam generators. An uneven, rough and porous covering layer tends to lose particles or larger fragments to the liquid or steam phase, especially when load changes occur, with the associated thermal stresses.

As part of a research project at the University of Rostock,[1] magnetite layers were formed on tubes under defined conditions in test steam generators and subjected to surface analysis. Tubes treated with FFA (Cetamine® V 211) had a much smoother and homogeneous surface than tubes examined after a conventional sodium phosphate based treatment programme. Figure 4 shows the images obtained from the tubes with the help of confocal laser scanning spectroscopy (CLSM). The measured microroughness was 1.45 µm after FFA based treatment and 2.25 µm after the phosphate programme.

The main aim of the project was to determine the influence of FFA on the thermal behaviour of steam generator tubes subjected to different treatments. The very thin film on the magnetite layer has a significant positive influence on heat transmission. The boiling curves of the tubes treated with FFA were above those obtained after the phosphate treatment over the total spectrum of industrially relevant heat fluxes. Consistently higher heat transmission coefficients were measured after FFA treatment.

Figure 5 shows the net improvement relative to tubes analysed after phosphate treatment. When the tests with FFA (V 211) were carried out using tubes with bare metal surfaces, there was a relative improvement of between 90 and 150% in the heat transmission coefficient. When the tubes had first been treated with phosphate and the treatment was then changed to FFA (PO_4 --> V 211), the improvement was still 40 - 90%.

When feed water is treated with FFA, the temperature of the exhaust gas can be expected to be lower. This increases the efficiency of the steam generator and therefore cuts the CO_2 emissions. For reasons of complexity, the expected effect cannot be calculated quantitatively.

Steam volatility

The steam volatility of FFAs in the condensate of a steam generator can be demonstrated by qualitative analysis. Steam volatility is described quantitatively by the distribution equilibrium, which was determined for various representatives of this class of substances.[2]

Through its steam volatility, FFA protects the plant completely against corrosion, as film formation takes place throughout the steam generator. Figure 6 shows the improvement in corrosion protection using strips that were built into the condensate system of a boiler plant. Oxygen corrosion can be seen clearly on the strip from the boiler with a conventional treatment programme of sulfite, phosphate and alkalising amine, while the strip from the boiler treated with FFA shows only slight flash rust.

Dosing film forming amines

As is the case with conventional treatment programmes, an FFA based product can best be added to the feed water by means of a dosing pump that is controlled on the basis of the volume of make up water. Commercial products are supplied as solutions that are ready for dosing. When an FFA based product is used, there is no longer any need to go through the error susceptible process of preparing solutions from powders and adjusting the quantities of different components to the treatment result.

The dosing system must not have any parts made of Viton, as the film forming components attack this material. Ethylene propylene diene monomer rubber (EPDM) is recommended as the sealing material and Teflon is recommended as the membrane material.

Product dosing systems based on the measurement of FFA are usually designed to deliver the product at a rate that ensures that only a small amount of FFA can be detected in the condensate, feed water and boiler water. Detection of just the presence of FFA suffices. Sustained overdosage can cause agglutination in system parts, e.g., filters.

The treatment should be monitored by regularly determining the dosing rate by balancing the product consumption with the quantities of make up water. In addition, the iron content of the boiler water and the condensate should be analysed, as well as the pH and the concentration of the FFA in the feed water, boiler water and condensate.

Analysis

When FFA is determined as the central component of the treatment concept, special rules must be observed in order to obtain meaningful results.

FFA can only be determined analytically in its free state in the water phase. The FFA bonded to the metallic surfaces cannot be determined. The adsorption of the FFA depends on the area of the metallic surface, the temperature and the excess FFA in the water phase. There is therefore no correlation between the added quantity and the amount of free FFA determined in the water.

The FFA is adsorbed on almost all surfaces, also in the sample container. Only plastic sample containers that have been thoroughly cleaned should be employed, and the FFA should be determined onsite immediately after sampling. The FFA is determined either as cationic surfactant (possible interference due to use of dishwashing detergents) or as a complex by means of a specific dye (bengal rose). The detection limit of the bengal rose method is approximately 0.1 ppm.

Conclusion

In comparison with conventional treatment programmes, FFAs have a number of advantages:

- They protect the total plant against corrosion. As FFAs are steam volatile, protective film formation occurs on the surfaces of all parts of the plant. In contrast to programmes that use oxygen scavengers, the film forming component is not consumed by entering into chemical reactions.
- The treatment programme with FFA is based solely on organic substances, which contribute very little to the conductivity. High cycles of concentration can be achieved, associated with savings through lower consumption of water and energy (blowdown).
- The substances used exhibit only slight human toxicity. There is therefore no need for extensive occupational health and safety measures such as those associated with hydrazine.
- Very smooth and homogeneous magnetite layers are formed in the plant. The improved heat transmission coefficients can increase the efficiency of a steam generator and cut its energy consumption relative to conventional phosphate based treatment methods.
- The cleanliness of critical plant parts, especially those of the turbine, is often improved by film forming amines.

FFAs have been used successfully for boiler water treatment for a number of decades in industrial power stations and steam boilers also in refineries and petrochemical plants, and sometimes even in cases where conventional treatment programmes failed to yield satisfactory results.[3-5]

References

1. *TOPP, H., STEINBRECHT, D., HATER, W., and DE BACHE, A., The Influence of Film-Forming Amines on Heat Transfer during Saturated Pool Boiling; PowerPlant Chemistry 2010, 12 (7), pp. 388 - 395.*
2. *VOGES, N., and HATER, W., Distribution Ratio and Average Surface Coverage of Film-Forming Amines; PPlantChem 2010, 12 (3), p. 132.*
3. *HATER, W., RUDSCHUETZKY, N., and OLIVET, D., The Chemistry and Properties of Organic Feed Water Additives Based on Film-forming Amines and Their Use in Steam Generators; PPChem 2009, 11(2), pp. 90 - 96.*
4. *JANSSEN, P., and SAVELKOUL, J., In Search of an Alternative High-Pressure Boiler Water Treatment Program. PPChem 14, 7 (2012), p. 440.*
5. *VAN LIER, R., GERARDS, M., and SAVELKOUL, J., VGB PowerTech 8 (2013), p. 84.*