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Film-Forming Amines in Steam/Water Cycles – structure, properties, and influence on corrosion and deposition processes

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Summary

Corrosion products in the secondary side of pressurized water reactors, as well as in the steam-water cycle of fossil plants and process industries primarily deposit on the steam generator tubes. These deposits can inhibit heat transfer, lead to thermal-hydraulic instabilities through blockage of tube supports, and create occluded regions where corrosive species can concentrate along tubes and in tube-to-tube support plate crevices. The performance of the SGs can be compromised not only through formation of an insulating scale, but also through the removal of tubes from service due to corrosion. The goal of the present task is to report a literature study on the use of film-forming amines in nuclear reactor secondary side and in conventional power plants with regard to their composition, structure, thermal stability, and interaction with deposits during their formation and consolidation. The mechanisms of interaction of film forming amines with structural materials and deposits, their chemical stability and degradation, as well as the efficiency of their action during laboratory and in-plant tests are reviewed in detail. The review of the use of filming amines presented below consists of the following parts. First, the composition and structure of film-forming amines, their physical and chemical properties, surface activity and interaction with structural materials are described. Second, their role as corrosion inhibitors in combination with other chemicals to form suitable compositions is discussed. Third, the effect of film-forming amines on fouling mitigation is considered. Finally, in a short outlook chapter, the mechanism of action of such amines is discussed and further areas of research in the field are outlined. On the basis of the literature data, conclusions on the prospective application of film-forming amines in existing and newly commissioned plants are drawn.

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Preface

This literature survey was compiled as part of the project “Water chemistry and plant operating reliability” (WAPA 2014) within the SAFIR 2014 –research programme.

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Contents

1 Introduction

Major components related to materials in cooling systems of pressurized water reactors (PWRs) are shown in Figure 1 [1]. Defects of steam generator tubing often interrupt PWR plant operation but they have never caused a serious accident. In each system, uniformly controlled cooling water is in contact with different materials, which complicates corrosion problems. Corrosion behavior is much affected by water quality and differs according to the values of water quality and the materials themselves.

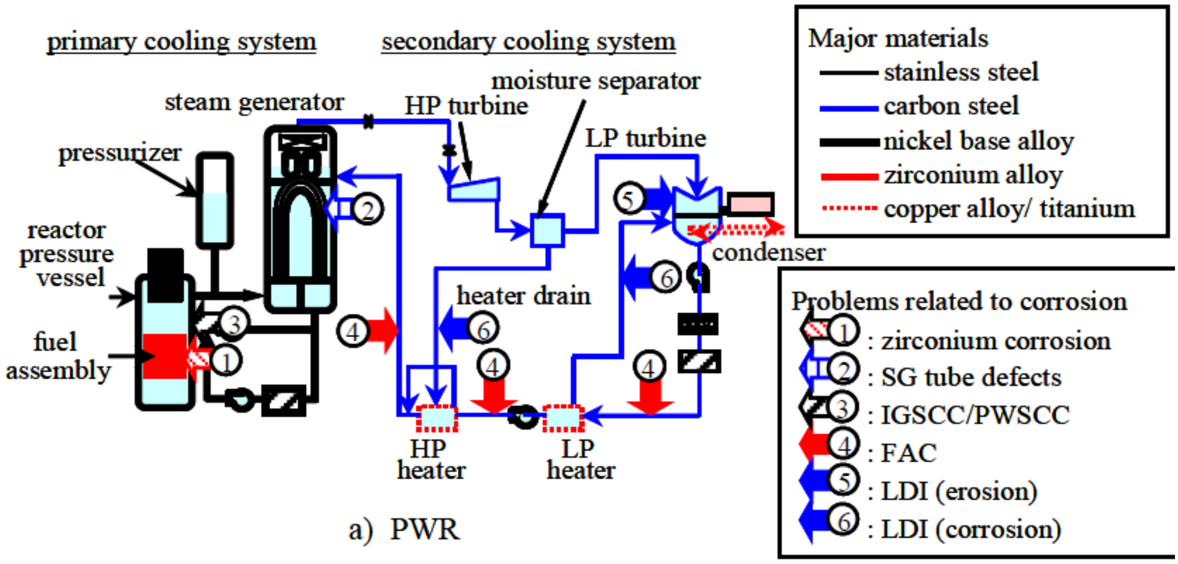

Figure 1 Major components related to materials in cooling systems of nuclear power plants.

In addition to corrosion, the associated fouling remains a potentially serious issue that can lead to degradation of the safety and performance of steam generators (SGs) [2]. It has been demonstrated that the majority of the corrosion product transported with the feed water to the SGs accumulates in the SG on the tube-bundle. By increasing the risk of tube failure and acting as a barrier to heat transfer, deposit on the tube bundle has the potential to impair the ability of the SG to provide a barrier to the release of radioactivity from the primary coolant and removal of heat from it during power operation and under certain post-accident scenarios.

Especially in US, where the majority of problems were reported on the secondary side of SG tubes (Figure 2), the industry made a lot of efforts to improve the design and materials of the SGs and the secondary side water chemistry to minimize the SG degradation problems. Although significant progress has been made in controlling the SG degradation problems, minimizing its impact on plant operation will remain a continuing challenge. Another SG problem caused by corrosion products is the primary to secondary heat transfer degradation, the so-called SG tube fouling. Majority of the corrosion products transported by FW into SGs are absorbed on the heat transfer surfaces of the tubes, building oxide scales.

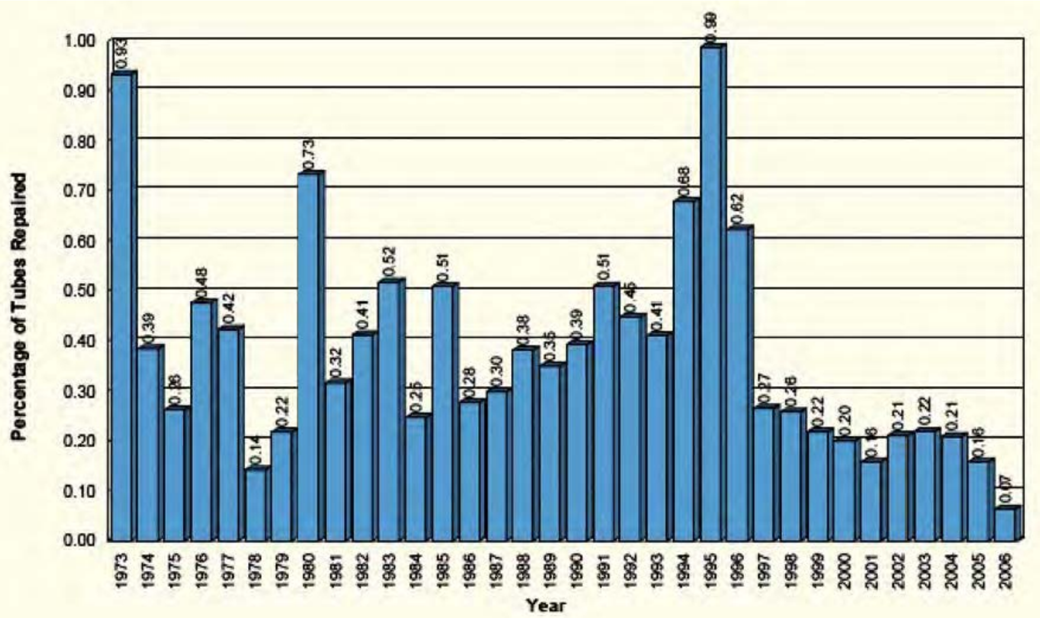

Figure 2 Worldwide percentage of SG tubes plugged.

Utilities employ a variety of deposit control strategies, including sludge lancing, chemical cleaning, and advanced scale conditioning agent soaks, deposit minimization treatment, upper bundle flushing, and on-line injection of chemical additives. It is important to understand the benefits and limitations of each of these strategies, especially as each relates to specific objectives such as quantity of deposit removed, location of deposit removal, and effect on SG heat transfer capability (e.g., steam pressure).

Understanding and quantifying the benefits and limitations of each strategy is the first step in determining which strategy or combination of strategies would address the technical needs of the particular plant. In a previous literature study, one such strategy, namely the use of dispersants for secondary side deposit control and minimization, was described in some detail [3]. In the present report, another possible mitigation treatment – the use of film-forming, or so-called filming amines, is discussed in relation to both the minimisation of corrosion rates and deposit formation.

2 Goal

The goal of the present task is to report a literature study on the use of film-forming amines in nuclear reactor secondary side and in conventional power plants with regard to their composition, structure, thermal stability, and interaction with deposits during their formation and consolidation. The mechanisms of interaction of film forming amines with structural materials and deposits, their chemical stability and degradation products, as well as the efficiency of their action during laboratory and in-plant tests are reviewed in detail. On the basis of the literature data, conclusions on the prospective application of film-forming amines in future plants are drawn.

3 Description

Practically all steam generators in power plants use some type of neutralizing amines or a blend of neutralizing and filming amines to prevent corrosion in the secondary water system [4]. Neutralizing amines such as cyclohexylamine, methoxypropylamine, ethylamine, ethanolamine, morpholine, and dimethylaminoethanol, work by controlling pH (normally in the range $9.2 < pH_{RT} < 10$) and thus minimizing the source term of corrosion release. Film forming amines, on the other hand, form a continuous layer between the metal and the coolant, thus preventing the attack of corrosive agents. When they attach to the corroded metal surface, they modify it, reducing the apparent corrosion rate. It has been observed that corrosion inhibitors adsorb better on iron-based materials in the active state than in the passive state. The adsorption behavior on iron oxides is not very sensitive to the chemical structure of the adsorbing molecule, but is due to the nature of the surface and chemical effects of the oxidized surface [5]. At high temperatures the decomposition of organic amines can induce the formation of amine compounds and or nitrile functional derivatives [6].The mechanism or mechanisms by which amines inhibit fouling is still under debate [7].

The ultimate driving force when selecting an amine is minimization of the SG fouling rate, accounting for factors such as cost, toxicity, volatility, etc. In general, the following aspects need to be accounted for when selecting a treatment agent:
- Transport of corrosion byproducts to the steam generator
- Impact on condensate polisher or demineralizers when they exist
- Low toxicity when released to the environment
- Thermal stability at operational temperature
- Decomposition product(s)
- Concentration required to reach the desired pH
- Commercial availability and cost.

No systematic assessment has been published in the open literature on the effect of various alternative amines used for pH-control in the secondary systems on the rate of different types of corrosion and/or SG fouling [2]. There are numerous papers on the effect of alternative amines on the rate of iron transport to the SGs, and while this must be of prime concern to power plant operators these reports tend not to include sufficient information to deduce an amine-specific effect on the rate of corrosion and/or SG fouling.

As noted in a recent review on steam generator fouling [2], there is increasing interest in the use of filming amines to mitigate corrosion in the steam cycle and fouling in SGs. Filming amines have been used since the 1960s to mitigate corrosion in steam condensate systems in numerous industrial applications [8-16], where their effectiveness is proposed to be related to the establishment of a non-wettable film on metal surfaces [8]. The film is proposed to be monolayer in thickness, and so its effectiveness does not increase with continued treatment beyond that required to maintain the monolayer coverage of the system surfaces.

The review of the use of filming amines presented below consists of the following parts. First, the composition and structure of film-forming amines, their physical and chemical properties, surface activity and interaction with structural materials are described. Second, their role as corrosion inhibitors in combination with other chemicals to form suitable compositions is discussed. Third, the effect of film-forming amines on fouling mitigation is considered. Finally, in a short outlook chapter, the mechanism of action of such amines is discussed and further areas of research in the field are outlined.

4 Limitations

The main limitations to the present literature study come from the fact that in the last 6-7 years, the results of one of the important research and development programs in the field – that funded by US DOE and EPRI – have remained confidential and proprietary to the funding group of US utilities and regulators [17-19]. Thus the description of the progress of this program is based mainly on conference presentations and is not as detailed as the authors would have liked it to be. In addition, the exact composition and chemical state of some of the commercial formulations is not described in sufficient detail due to the lack of appropriate data in the open literature. In addition, in several places commercial names for specific film-forming inhibitor formulations are used due to the fact that the exact composition of the employed mixtures is part of the proprietary information for the specific product.

5 Composition and Structure of Film-Forming Amines

The most effective filming amines are aliphatic (known also as fatty) amines with 10 to 18 carbon atoms in the chain. They are defined chemical substances that belong to the oligo-alkyl-amino fatty amine family. The general chemical formula is $R1\text{-}[NH\text{-}(R2)\text{-}]_n\text{-}NH_2$, where n is an integer between 0 and 7, R1 is an unbranched alkyl chain with 12 to 18 carbon atoms and R2 is a short chain alkyl group that usually contains 1 to 4 carbon atoms.

The simplest representative is the known octadecylamine ($n = 0$, $R1 = C_{18}H_{37}$). Octadecylamine (ODA) is a commonly used filming amine for the protection of industrial condensate systems [10]. The main disadvantages of octadecylamine are its poor ability to enter more complex formulations, which makes the addition of acetic acid necessary to introduce it in ionic form, and its marked overdose sensitivity. Modern treatment programs therefore contain film-forming amines in which two or more amino functionalities are present, e.g. oleyl propylene diamine ($n=1$, $R1 = C_{18}H_{35}$, $R2 = C_3H_6$) or stearyl dipropylene triamine ($n = 2$, $R1 = C_{18}H_{37}$, $R2 = C_3H_6$). Other prospective members of the family include oleylamine ($n=1$, $R1 = C_{18}H_{35}$) and talgamine ($R1 = C_{16/18}H_{33/37}$). In general, the film-forming amines are not added as individual substances but rather in combination with pH controlling amines such as cyclohexylamine, in order to adjust the pH of the boiler water and the condensate to the necessary value. At the same time they serve to provide the necessary storage stability of the formulations. As a result, there is often no need for additives whose sole function is to stabilize the formulations.

6 Properties of Film-Forming Amines and their influence on coolants and structural materials

Power plants are designed to run with pure water and steam. For simple cycles (no export steam) no other products should be necessary. In the chemical process industry, the steam cycle is of secondary importance: the chemical process comes first. High heat flux designs and - generally unavoidable – water quality problems make industrial boilers susceptible to corrosion. The selected steam cycle treatment has to be tolerant towards organic contaminants. Conventional programs are not always suitable to meet the specific challenges of individual plant steam cycles. If organic additives are used, the possible side effects have to be carefully addressed. Possible side effects include corrosive degradation products, interference with monitoring cation conductivity, influence on boiling and on condensation, and fouling. Organic amines produce volatile acidic degradation products, but the amine provides cations for pH counterbalance. In contrast, organic oxygen scavengers, dispersants, chelants as well as organic impurities generally produce volatile acidic degradation products, but with no cation for counterbalance. For this reason, such products must be considered as potentially corrosive. From a power plant manufacturer’s point of view, any organic matter in the steam/water cycle brings the risk of detrimental side effects. The general use of organic additives should thus be avoided and restricted to specific needs and situations, as for example in certain process steam systems. A polyamine program can be a worthwhile alternative. The process plant experience with polyamines so far has been very positive and has provided confidence to consider these products for up to 12.5 MPa steam systems [11-13].

6.1 Surface activity/adsorption

Film-forming amines have a strong affinity to metal surfaces, thanks to the free electron pair of the amine nitrogen (Figure 3) [14, 14]. Monoamines can form a bond with metal surfaces. The carbon chain in this case projects outwards, hair-brush style. Due to the existence of a large number of amino groups in polyamines, the bonding to the metal surface takes place at several points and it is therefore quite strong. The carbon chains are directed mostly horizontally or on the metal surface and offer therefore a better cohesive protection. The protective film formed is more stable than the one formed by mono-amines (Figure 4). The process of film formation has been the subject of a variety of studies, especially with the help of electrochemical impedance spectroscopy [20-22] and X-ray photoelectron spectroscopy [21-22].

The film that forms on the metal surface acts as a barrier against corrosive substances such as oxygen, carbon dioxide and carbonic acid. The hydrophobic alkyl group makes the metal surface un-wettable with water [15]. Once formed, a protective film remains intact even after the dosage has been stopped, so that if the dosage falls below the required level or is interrupted for a short period, no immediate harm occurs. The strong surface affinity can result in gradual removal of attached substances such as loosely adhering magnetite [14]. A sketch of the possible way of interaction of a film-forming amine with hydroxylated iron oxide involving surface complex formation is presented in Figure 5.

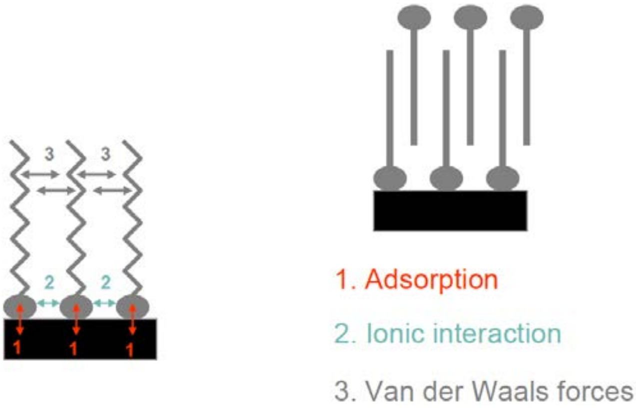

Figure 3 Adsorption of amines on a structural material surface in high-temperature water.

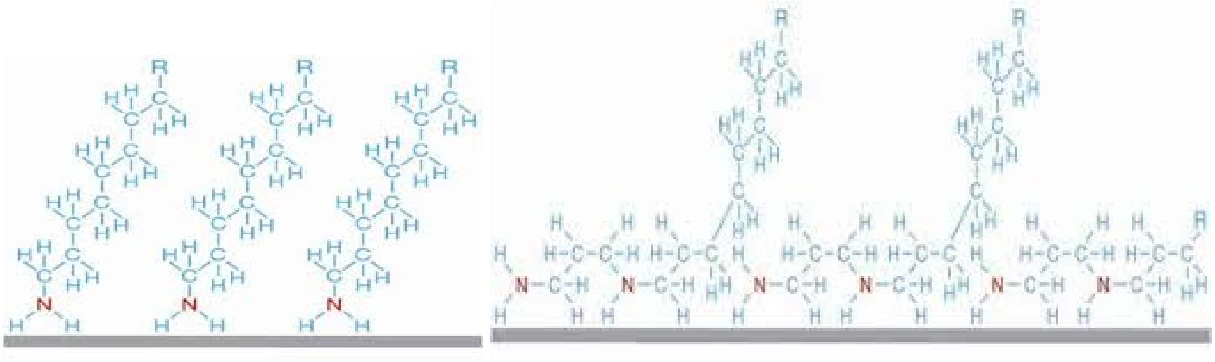

Figure 4 Film formation with mono- (left) and polyamines (right).

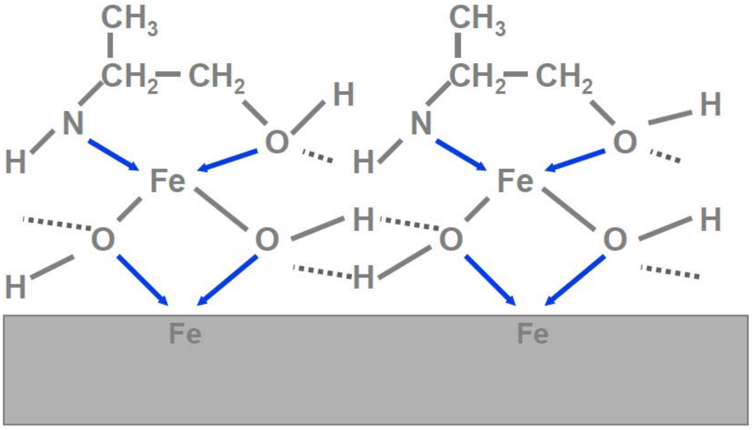

Figure 5 Surface complex formation between an amine and a (hydr)oxidized iron surface.

A research project at the University of Rostock aimed to determine the influence of film-forming amines (FFA) on the thermal behavior of steam generator tubes subjected to different treatments [16]. The study included formation of magnetite layers on tubes under defined conditions in test steam generators and subjected to surface analysis. Tubes treated with FFA (Cetamine V211, commercial formulation by Henkel) had a much smoother and more homogeneous surface than tubes examined after a conventional sodium-phosphate based treatment program. The FFA is adsorbed on almost all surfaces, also in the sample container. The results show that FFA is determined either as cationic surfactant or as a complex by means of a specific dye. It is also found that the cleanliness of critical plant parts, especially those of the turbine, is improved by film-forming amines.

6.2 Film formation analysis

The intrinsic nature of film formation is such that the analytical monitoring of film-forming amines, as the central component of a steam generator treatment concept, is subject to special rules, which must be strictly observed in order to obtain reliable information as a basis for control decisions. The first consideration is that the free film-forming amine (also denoted as micelle) in the boiler water and condensate samples can be analytically determined, but not the amine bonded to the metal surface (Figure 6)[14].

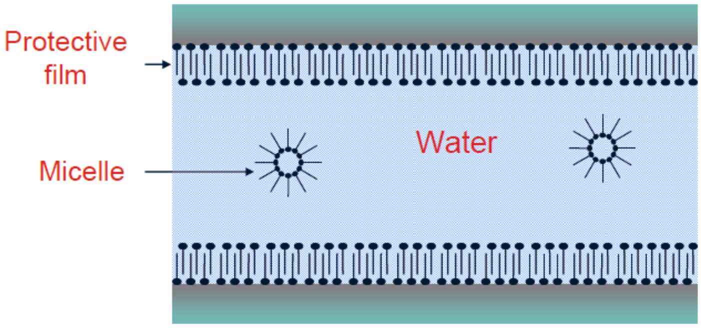

Figure 6 Soluble and attached form of filming amines.

The adsorption of the film-forming amine depends on the area of the metal surface, the temperature and the excess amine in the water phase, so that in general it is impossible to arrive at any correlation between the dosage and the amount of free amine detected in the water. The dosing of a product based on film-forming amines usually is adjusted in a manner, so that a small amount of amine can be detected in the condensate, feed water and boiler water. In most cases, the presence of the smallest reliably detectable amount of amine suffices. The amine can usually be detected quantitatively at concentrations as low as 0.5 ppm. The film-forming amine is determined either as cationic surfactant (possible interference due to use of dishwashing detergents) or as a complex by means of a specific dye.

6.3 Distribution ratio

Due to the steam volatility of film-forming amines, film formation also occurs on the steam and condensate system. Steam volatility can easily be demonstrated qualitatively by analyzing the free film-forming amine in the condensate. However, relatively few data are available on the distribution ratio between steam and water [14]. To determine the distribution ratio quantitatively, tests were carried out using OPDA in a pilot steam generator. The determination of the distribution ratio is made more difficult by the fact that the equilibrium between adsorbed and free amine must be taken into consideration. In the tests, therefore, the distribution ratio was determined as a function of the elapsed test time. The test was continued until a constant value was established. Further systematic studies in a pilot steam generator were carried out in order to determine the distribution ratio at an operational pressure range from 20 to 100 bar depending on the initial concentration and the chemical structure of the film forming amine

[15]. The distribution ratio was calculated as the ratio of the concentration of the film forming amine in the boiler water and in the condensate. Additionally, the average surface coverage was estimated by a mass balance. As an example, Figure 7 shows distribution ratio of OPDA as a function of time at a dosage of 100 ppm and a pressure of 20 bar.

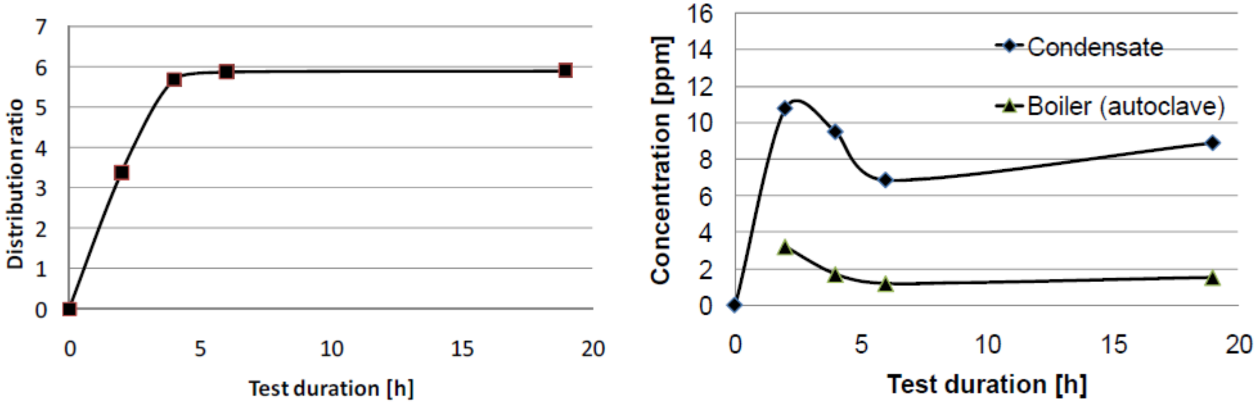

Figure 7 Distribution ratio for oleyl propyl diamine (left) and the measured concentrations in condensate and boiler (autoclave) (right) at a pressure of 20 bar as a function of the test duration. Initial concentration, 100 ppm.

The dissociation constants K_d (left) and distribution coefficients (right) and of different amines and FFAs are shown as a function of temperature in Figure 8 [24]. Considering the K_d values of the FFA, it has to be taken into account that at lower temperatures the values show a higher uncertainty caused by changes of the physical properties of the solution due to the beginning aggregate formation and the solid state of the FFAs.

The solubility of the FFA is an important characteristic, which mainly determines the feasibility of its application, i.e. dosing strategy and distribution in the liquid phase of the working medium. The solubility of FFAs in water rises with increasing temperature, whereas the solubility at room temperature normally is very low (see Figure 9). For optimal working conditions the temperature and concentration dependency has to be taken into account whereby the presence of additional ions can also have an influence. The best conditions are in the range of the solubility curve (turbidity points). The interception point of the saturation concentration of the turbidity point gives the KRAFFT point of the colloidal solution. The critical concentration of the micelle formation (CMC) is the concentration at the KRAFFT point where the physical properties of the solution are changing due to the beginning aggregate formation.

When assessing these results, it must be considered that the tests were carried out with a very large excess of amine so that the amine could be measured with sufficient analytical accuracy for the distribution ratio to be determined. Further work on determining the distribution ratio and the surface coverage as a function of pressure and initial concentration has already been reported [15,23-25].

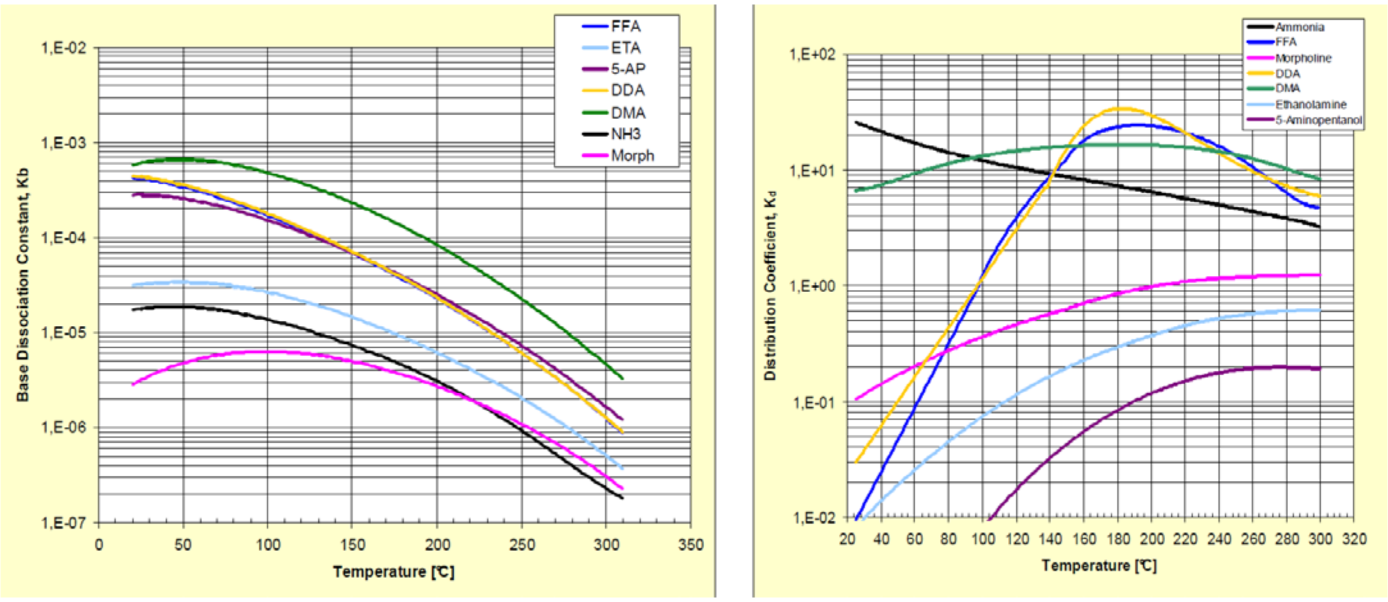

Figure 8 Dissociation constants (left) and distribution coefficients (right) of different amines as a function of temperature [24].

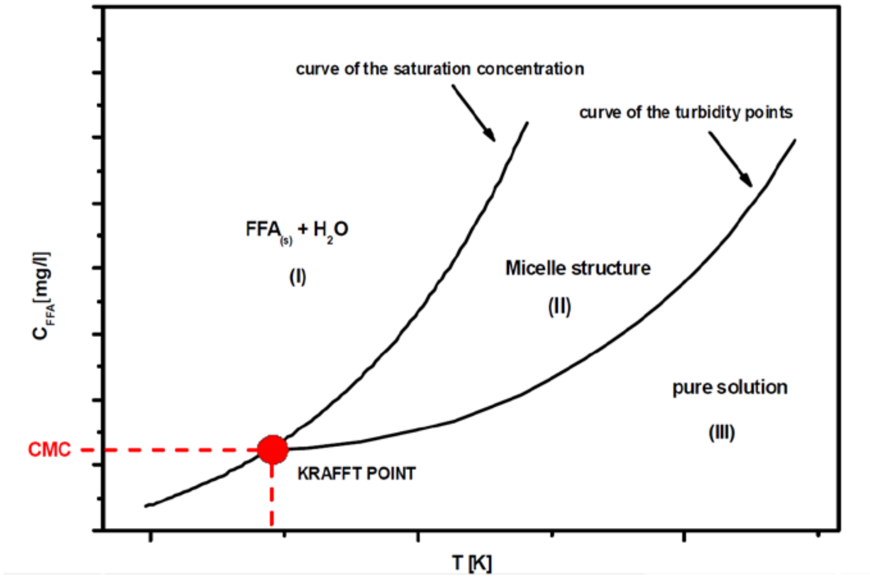

Figure 9 Schematic phase diagram of the system film forming amine / water [24]

6.4 Interaction with solid surfaces

The mechanism through which protective films of amines are generated on the surface of pipelines and equipment is still not quite clear. According to the concept currently adopted in documents and papers, the positively charged hydrophilic “tail” of a molecule of amine tends to the negatively charged metal surface and loosens the previously formed deposits as it approaches this surface. Unfortunately, this concept does not explain many factors; e.g., why the protective amine films generated at different temperatures have different compositions and adhesive properties [26]. According to these authors, the action of a film-forming amine (e.g. ODA) can be understood in the following way.

At low temperatures (40–80°C), the process can be represented in the following way. Free valences, or dangling bonds, denoted as V, are always available on the surface of structural materials and are related to point defects. Upon addition of a neutral molecule such as ODA the following reaction is proposed to occur

$$V + C_{18}H_{37}NH_2 \rightarrow V \equiv C_{18}H_{37}NH + H \bullet$$

This reaction produces the radical H• that will give its electron either to the surface or to the surface complex of amine. The result will be a second bond of N on the surface, and another radical H will be generated, the electron of which will transfer to the surface and the cycle of surface deposition of ODA will be repeated. As the surface is gradually covered with amine, it will replace the surface complexes formed by impurities such as Cl^- and SO_4^{2-} and alter the electric and electrochemical properties of that surface.

At temperatures above 100°C and in the presence of a large number of OH• radicals, the first stage of the ODA molecule oxidation process is proposed to be

$$C_{18}H_{37}NH_2 + OH\bullet \rightarrow C_{18}H_{37}NH \bullet + H_2O$$

The adsorption of a free radical $C_{18}H_{37}NH\bullet$ on a metal surface can be regarded as the reaction of a radical with a neutral molecule, which proceeds with the activation energy equal to around 16–32 kJ/mol [26]. This process generates a new molecule, which is the $VC_{18}H_{37}NH$ chemisorbed by the surface, and a new radical, i.e., the free valence V at the neighboring point of that surface. Either way, efficient formation of an amine film acting as a barrier to corrosion is considered as a chain reaction analogous to surface polymerization.

6.5 Interaction with the coolant

In order to understand the reasons for the increased acid conductivity in the steam of a refuse-derived fuel heating and power plant treated with film-forming amines, laboratory and in-plant studies were carried out concerning the direct conductivity, acid conductivity and degassed acid conductivity [27]. Furthermore, the LC-OCD method was applied in order to analyze organic traces in water and steam samples taken from various points in the water/steam system. According to the results, the increased acidic conductivity is caused by carbon dioxide, decomposition of organic compounds, and by the amines applied. Boiler and turbine inspections showed that the plant was in excellent condition. The treatment of the water-steam cycle was judged to be very satisfactory.

As mentioned above, amines used to maintain the optimized pH for the prevention of corrosion in the secondary side of a PWR are differently dissociated as a function of temperature which is not same in each location of the water-steam cycle. The pH at the operational temperature depends on temperature of fluid and equilibrium constants of water and amines. Thus, every amine provides a different pH in the entire secondary side so that pH alone is not a sufficient parameter in corrosion control. The secondary parameter, i.e., buffer capacity, is the ability to maintain a stable pH when H^+ are added or removed due to the ingress of impurities or the corrosion reaction of structural materials. The buffer capacities of DMA and 3-methoxypropylamine (MPA) were reviewed over the entire operational temperature of PWRs [28]. A sufficient buffer capacity is provided for the inhibition of corrosion by ammonia in low temperature (25-100 °C) and by DMA in high temperature (150-250 °C). In terms of buffer capacity, i) the best pH agent is an amine with pKa(T) which is pH(T)- 1 ≤ pKa(T) ≤ pH(T) + 0.5 and ii) the amine solution should have minimum buffer intensity, β, and iii) FAC rate may be maximum at the temperature, where β_B/β ratio is lowest.

In turn, the study presented in [29] focused on the polyamine/amine regime in cycles with drum boilers, although one case study is presented which reports on application of this treatment in units with once-through steam generators. The major hindrance with the use of this treatment in utilities is the fact that the cation conductivity of steam increases slightly when this treatment is applied. Operational experience in industrial power and steam generation and in utilities demonstrates that a slight cation conductivity increase in the steam does not cause any turbine-related problems, assuming that the pH is correctly set by low-molecular volatile amines being a part of the polyamine/amine formulation. Steam cation conductivity-related studies for establishing the actual interaction of slightly contaminated steam and turbine materials in the presence of an adequate alkalizing agent, i.e., when the early condensate is adequately alkaline, were suggested. Industry experience proved that even at increased cation conductivity, failure- and damage-free operation of the cycle in the presence of organic alkalizing agents is possible due to the favorable distribution ratios of low-molecular volatile amines. Thus in the phase transition zone of a low-pressure turbine amines are capable of coping not only with their own decomposition products (e.g. acetates and formates), but also with certain levels of inorganic contaminants. The place of amine/polyamine treatment in the mitigation of operational problems due to impurities, according to Bursik [29], is presented in Figure 10.

In addition, results obtained from six-year observations of the state of the steam–water path of a combined- cycle plant-based power unit operating with Helamin (includes a FFA) water chemistry were presented. The conductivity and pH of coolant over the power unit process path, which serve as the main indicators of its water chemistry, were analyzed [30]. The authors concluded that the use of type 906H Helamin made it possible to ensure protection of surfaces of heat-recovery boilers. It was also concluded that improper selection of reagents resulted in the following:
(i) It became impossible to obtain the required quality of coolant by the indicators of electrical conductivity in the path
(ii) An increased content of sodium in high-pressure boiler water was observed
(iii) It led to excessive consumption of reagents and increased content of salts, and hence higher conductivity) in boiler water, due to which the flow rate of continuous blow-down could not be reduced.

In that relation, controlled laboratory tests were performed to ascertain the impact of three different brands of film-forming amines on system parameters and online measurement instrumentation [31]. Specific conductivity, pH drift, cation resin retention, pH stability, sodium step response, sodium calibration, oxygen sensor response and ORP probe response were considered. Differences in some results depending on the FFA used were noted. While with some measurements no negative influence could be observed, with other equipment there was a loss of sensitivity and speed of response time due to coating effects. No negative influence was observed on pH, ion-selective sodium measurement and Clark-type oxygen probes. On the other hand, loss of sensitivity and speed of response due to coating effects were observed during measurement of oxygen reduction potential.

In addition coating effects on conductivity probe resulted in a drift of specific conductivity as well as the calculated pH.

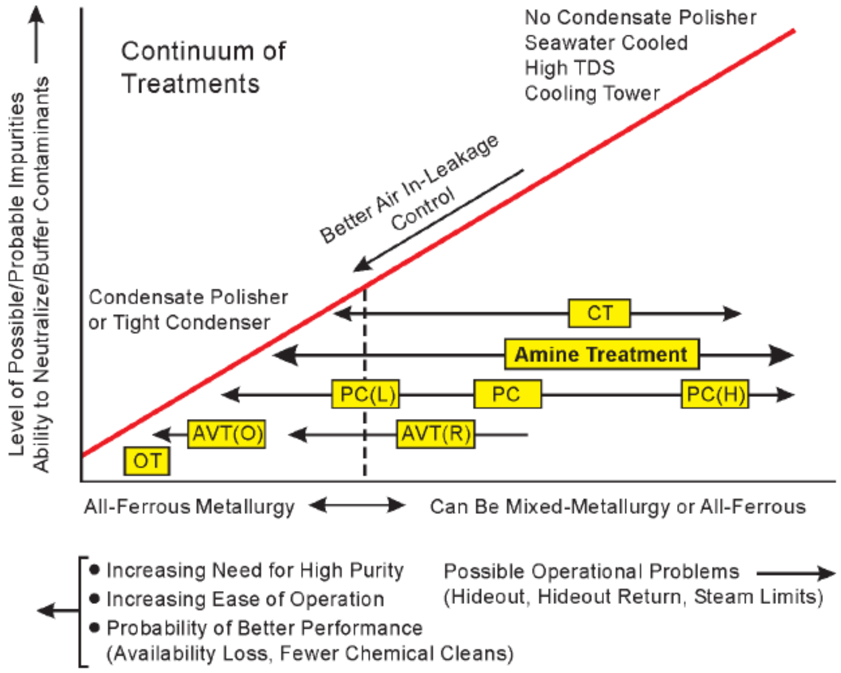

Figure 10 Amine/polyamine treatment in the continuum of treatments for the mitigation of operational problems due to impurities.

Some nuclear plants using ETA and associated amines also report fouling of the anion resin resulting in reduced service life [32]. The authors discuss the impact of fouling mechanisms on ion exchange resin performance by investigating alternative amines to ETA. Efforts were made to qualitatively correlate plant data obtained from previous surveys and studies with a possible diffusion/reaction mechanism defined by this project. Derivatives of ETA methylated at the alcohol terminus or singly methylated at the amine nitrogen were more deleterious to anion resin kinetics in column experiments than was ETA. However, the dimethyl-amino derivative of ETA had minimal impact on anion resin, suggesting that the amine end of ethanolamine is the culprit in resin degradation reactions, possibly due to steric effects that block nucleophilic displacement reactions. The superiority of the dimethylated ethanolamine versus the monomethyl derivative strongly suggested that displacement of trimethyl amino functionality by the amine group of the pH control agents is an important resin degradation pathway. However, the project team could not discount the influence of redox reactions on resin degradation. Batch reactions showed a synergistic effect between cation and anion resin on oxygen consumption. In particular, redox potential measurements demonstrated that the interaction of pH control agents with cation exchange resin released strongly oxidizing species that attacked anion exchange resin. SEM micrography demonstrated the synergism between cation and anion resins in the physical deterioration of the anion resin and in the transfer of cation resin fragments to the anion resin. A novel fluorescent tagging method was used that also confirmed the fouling of anion resin beads with cation resin fragments [32].

In a field test with the Cetamine V211 formulation (includes a FFA), it was stressed that the reasons for the increased conductivity in the condensate when film forming amines are used for treatment, and the significance of this phenomenon, are not fully understood [25]. The iron content of the feed water and the condensate was never higher than 0.02 ppm. The temporary increase in the iron content that frequently occurs when treatment with film forming amines is started was not observed. The conductivity downstream of the acid ion exchanger was 0.2 µS/cm, whereas it reached 0.5 µS/cm in the feed water, saturated steam and condensate, being within the operator's internal specification (Figure 11). However, the requirements of VGB R 450 L guideline concerning the conductivity in condensate downstream of acid ion exchangers were not satisfied.

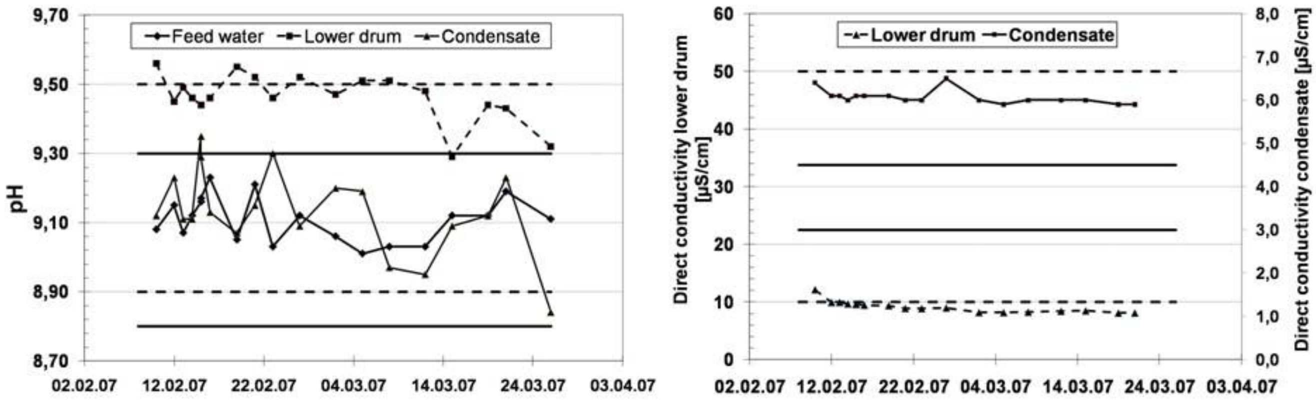

Figure 11 Variation of pH (left) and the direct conductivity (right) during the field test with Cetamine V 211. The limits of the operator's internal specification are marked by lines.

6.6 Effects on thermal efficiency

Since the heat transfer coefficients during boiling at steel heating surfaces typically degrade in time, the interaction of the heating surface with boiling water can lead to a drop in efficiency as well as boiler malfunctions or breakdowns, which inevitably entail expensive and time-consuming measures.

The influence of the responsible physicochemical processes on the steel under saturated pool boiling conditions was studied in detail via thermo-technical measurements in a special apparatus using chemically conditioned water [33]. For this purpose, an oxide layer, whose surface structure, composition and thickness vary with the respective kind of treatment, was generated on single horizontal carbon steel tube heating surfaces under specified conditions. The impact of a corresponding treatment program, comprising inorganic and organic feed water agents, on the heating surface was examined thermo-technically and further characterized by means of analytical methods. In a long-term test, significantly higher heat transmission coefficients (*k*) have been observed for the film-forming amine treated tubes as compared to the classic sodium phosphate conditioning (Figure 12). Thus the film-forming amine apparently caused an earlier steam bubble nucleation. The overall difference between the heat transmission coefficients under film -forming amine and phosphate treatment is less significant at 2 bar than at 15 bar. Such behavior was unexpected, as the influence on the surface tension becomes less dominant with increasing system pressure.

The influence of a chemical pre-treatment of the sample on the reproducibility of the initial boiling behavior and the time response of the heat transmission coefficients during operation was also characterized. The type of preparation indicates an effect regarding the departure from nucleate boiling. Surface morphology showed a comparably smoother roughness profile for the Cetamine treated tube samples. Although the surface was more homogeneous when using filming amine than after phosphate conditioning, the surface activity of the amine was demonstrated to cause more intense nucleation. As predicted from the thermo-technical experiment and verified by microscopic investigations, the oxide layer morphology was comparable for steady state samples under the mentioned conditioning.

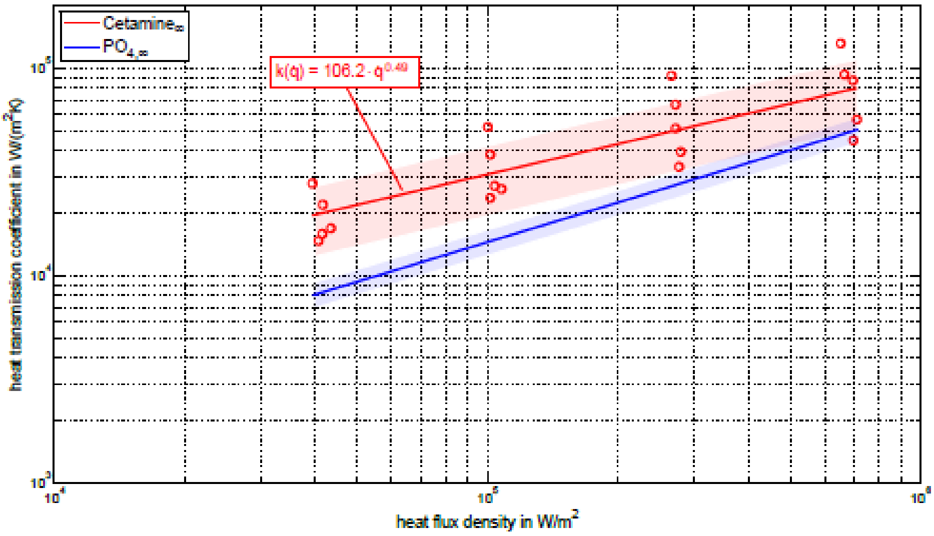

Figure 12 Steady state boiling curves for Cetamine1 and $PO_{4,\infty}$ *conditioning at* $p_s = 15$ *bar.*

The oxide layer of Cetamine treated samples featured a smaller thickness than after phosphate conditioning, as evidenced from a comparably smaller decline in the convective heat transport. As there was an oxide layer on the organically treated tube samples, the term 'corrosion inhibitor' must be reconsidered. On the one hand, there was an oxide layer on the surface after treatment, so oxidation was not totally prevented [33]. Further, as the observed layers are compact and firmly adhering passivating layers, the film-forming amine actually apparently does have an inhibitory effect regarding further metal dissolution. The inhibition of corrosion achieved by the application of film-forming amine treatment is discussed at length in the following section.

7 Film-Forming Amines as Corrosion Inhibitors

7.1 General considerations

Organic amines have been widely used to treat high-purity boiler feed-water since at least the 1940s. Although notable benefits have been derived, some consider the use of these amines to be risky. In addition, the use of organic chemicals for boiler feed-water treatment often causes steam and condensate cation conductivity levels to exceed current power industry guidelines. The benefits that can be derived and questions concerning the use of both neutralizing and filming amines are presented to help plant operators assess the potential value to be gained from using these amines in their systems [34-41].

The progress until the mid-80s concerning research efforts in preventing PWR steam generator corrosion is adequately summarized in a comprehensive review of the technology [40]. Methods described center on reduction of sludge deposition through control of secondary cycle water chemistry. The basics of the theory and experiences with use of organic amines as alternate pH control agents in all – volatile treatment (AVT) are described. An approach to selecting an integrated water chemistry program for PWR Secondary Coolant was outlined.

Within that integrated program, filming amines are usually recommended for protecting condensate piping from both oxygen and carbonic acid corrosion. Performance is accomplished by laying down a very thin non-wettable film on the surface. The film acts as a barrier between the metal surface and the corrosive condensate. In order for film-forming amines (or filming amines) to work, the condensate pH must be high enough for the film to form [8]. Octadecylamine is a commonly used filming amine. It requires that the condensate pH be controlled within a range of 8.0 to 8.5. If the pH is outside this range, the film strips off and can cause deposits in the steam traps and condensate lines. Octadecylamine is not volatile and therefore must be fed to the steam header. The total surface area to be covered is the prime consideration in determining dosage. Typical filming amine programs are monitored based upon product residual in the condensate. In addition to octadecylamine, several proprietary filming amines are available. These may include tallow or soya based amines. These formulations are stable over a wider pH range of 8.5 to 9.5.

Plant experience suggested that filming amines must be injected into the steam header. Typical filming amines are not totally volatile and in fact in most cases are considered non-volatile. Injection into the steam header also assures distribution throughout the entire system. Feed to the boiler or boiler feed-water will result in loss of the filming amine in the boiler blow-down. Under all treatment programs, the inhibitors must be fed continuously to prevent corrosion of the condensate system. For optimum application and distribution throughout the condensate system, all condensate corrosion inhibitors should be fed neat (undiluted) to the system. Neat feed of chemical allows for accurate measurement of the exact amount of chemical being fed. Dilution water can introduce impurities to the steam system which can result in other system problems. These may include turbine deposition, steam hammer, erosion and line failure. Depending upon the source of dilution water, if the dilution water temperature is higher than 32°C the high vapor/liquid ratio amines will flash from the dilution tank, causing release of amine vapors and disproportionate amine feed. Satellite feed is always a viable alternative when dealing with any of these programs, especially in light of the fact that condensate systems typically are extensive. Satellite feed consists of injecting the chemical just before areas of condensation, for instance, prior to a heat exchanger. Due to multiple condensation points along the pipe, amine could be lost to the condensate at the exchanger. The steam continuing to the outlying areas of the condensate network may not have enough amine [34].

Extensive operating data on corrosion and deposition in cooling towers and steam boilers that are part of heating, ventilating, and air conditioning (HVAC) systems at five military facilities were also reported [38]. Environmentally friendly water treatment formulations were investigated. Smart monitoring and control technology provided continuous corrosion monitoring of all systems and also adjusted corrosion inhibitors based on actual corrosion results. This report addresses five important HVAC issues: scale protection, control of algae and bacteria, cycles of concentration, corrosion protection, and water usage and cost. The nonhazardous corrosion inhibitors and the smart control systems resulted in a longer, energy-efficient service life, lower life-cycle operating costs, and reduced risk of environmental contamination.

EPRI is currently conducting research on use of film-forming amines and other barrier coatings or inhibitors to protect exposed metal surfaces by preventing interaction of air or moisture with the metal surface. According to the EPRI view, such alternative offline preservation techniques may offer significant benefits over the current techniques, because they do not require significant capital expenditures and complicated operating procedures, and they are flexible to changes in outage duration period. Current research has demonstrated that the development of a protective barrier on the metal surface, established by the formation of a hydrophobic polyamine barrier, inhibits corrosion and pitting activity in the presence of aggressive chemical species and moisture. Use of the alternative layup technology involving this filming amine resulted in reduced corrosion product transport on startup. This capability allows for more rapid startup, lengthens the interval between chemical cleaning, and minimizes the potential for under-deposit corrosion in boiler/high-pressure evaporator tubing [41].

In the following sections, data on the effect of film-forming amines on uniform and localized corrosion, oxide film formation and restructuring will be presented and discussed in more detail.

7.2 Uniform corrosion and oxidation

Systematic studies on the corrosion inhibition of film forming amines (FFA) applying both electrochemical and weight loss experiments in cooling system simulations have shown a dependence of the corrosion protection on carbon steel on the chemical structure of the inhibitor [42-46]. According to the results, FFA are efficient corrosion inhibitors on carbon steel. It could be noted that the number of amino groups influences the anticorrosion efficiency which decreases with increasing number of amino groups. In contrast to this, there is a limited impact of the type of the investigated alkyl chains [42].

The effects of advanced amine 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU), compared to ammonia (NH_3), dimethyl amine (DMA), ethanolamine (ETA) and morpholine on solution pH in the presence of $FeCl_2$ was assessed in combination with a characterization of oxide morphology on steel exposed to amine containing solution [36]. Aerated solutions containing 100 ppm of DMA or ETA showed the highest room temperature solution pH. DMA containing solution showed the highest resistance to flocculation as indicated by the longer time required to flocculate. A solution containing 100 ppm DBU did not show any flocculation. Oxide morphology on steel samples exposed to an acidic 100 ppm DBU containing solution showed fine round (about 0.1 μm in diameter) oxide particles.

The corrosion behavior of carbon steel and nickel based alloy 690 in solutions with different ETA concentrations was investigated [43]. Corrosion morphology was observed using scanning electron microscope (SEM) and composition of the oxide analyzed by X-ray photoelectron spectroscopy analysis (XPS) and X-ray diffraction (XRD). It was found that the oxide formed on carbon steel was a duplex Fe_3O_4 oxide. Oxides formed on alloy 690 contained mainly of a single layer of chromium oxide after immersion in 40-80 mg/L ETA solutions. Electrochemical experiments at 280 °C showed that the corrosion current of carbon steel exposed to 80 mg/l ETA decreased 9 times, and that of alloy 690 - 3 times, compared with those in 20 mg/L and 40 mg/L ETA solution, coupled with the corresponding increase in the polarization resistance. In case of carbon steel the lower corrosion rate was coupled with a clearly lower corrosion potential and thus it may be difficult to discern between the effect of the corrosion potential and the true inhibiting effect of ETA.

Two WWER-440 plants (Armyanskaya, Armenia) were urgently shut down after the December 1988 earth quake. As the expected extent of repair period was uncertain, it was decided to preserve the secondary side equipment and pipelines with octadecylamine (ODA) injection [35]. Preservation was performed at almost full power (420 and 430 MW) by injecting 2% ODA water emulsion to the suction of feed pumps. Injection lasted for 100 and 160 h (Unit 1 and Unit 2, respectively), resulting in measured ODA concentrations downstream of HP heater PVD 8 of 1 mg l^{-1} initially and 5-8 mg l^{-1} in final stage. Corrosion rate reduction (based on coupons exposed in the steam bleed-off pipelines using both electrochemical and weight loss techniques) was 80 to 85%. During the re-commissioning of Unit 2 in 1995 after 69 months preservation, satisfactory water chemistry indices were met in much shorter time than before the outage, indicating successful long term functioning of the ODA treatment as a preservation method.

Weight loss and electrochemical tests were used to determine the anticorrosive behavior of octadecylamine (ODA) on carbon steel, brass, and austenitic stainless steel [44]. Coupons were first exposed to steam above an aqueous solution containing 100 ppm ODA at 130°C and 3 bar pressure, for a period of 8 h. Corrosion tests were performed in an aerated pH = 9 solution at T = 85^{o}C up to 1100 h. Corrosion inhibition was estimated to be 94.5%. Additionally, experiments were carried out with a heat exchanger by circulating soft pH = 8.27 water (1 ppm Fe, 240 ppm Cl, 445 ppm Na, 4 ppm K, 0.5 ppm PO_4^{3-}, 5.75 ppm O_2, 730 ppm SO_4^{2-}, 1270 ppm TOC, 280 ppm HCO_3^-, 2 ppm Ca, and 2 ppm Mg) at T = 140 ^{o}C, p = 4 bar, v = 5 m/s and containing 10 ppm ODA. The ODA application was run until the rate of decrease of the concentration of ODA was no more than 10% in 4 h. After this initial ODA application, the corrosion inhibition efficiency of different ODA concentrations was studied. At $C_{ODA} > 0.2$ ppm, the efficiency reached 96%. Further increase in C_{ODA} did not increase the corrosion inhibition efficiency.

In addition, the optimal conditions for the maximum corrosion inhibition effect of ODA-treated iron samples in electrolytes containing chloride, sulfate and carbonate ions were established using electrochemical impedance spectroscopy [45]. The most protective ODA film was formed on the surface after the carbon steel samples were treated in steam at 220 °C in an autoclave for 1 h, using an ODA concentration of 40 mg/L in the water at the bottom of the autoclave. Samples exposed at T = 220^{o}C for 3 h to water with 5 ppm ODA showed a corrosion inhibition factor of about 60%, whereas those exposed to the steam phase above showed a corrosion inhibition factor of about 98%. The effect of temperature and ODA concentration on corrosion inhibition of carbon steel are shown in Figure 13. From the Auger electron spectroscopic analysis, it was inferred that the surface layers of the ODA-treated samples consisted of one of the following structures: at ODA concentrations <20 mg/L: iron<iron oxide<mixed ODA–iron oxides; at ODA concentrations >20 mg/L: iron<iron oxide<mixed ODA–iron oxides<ODA.

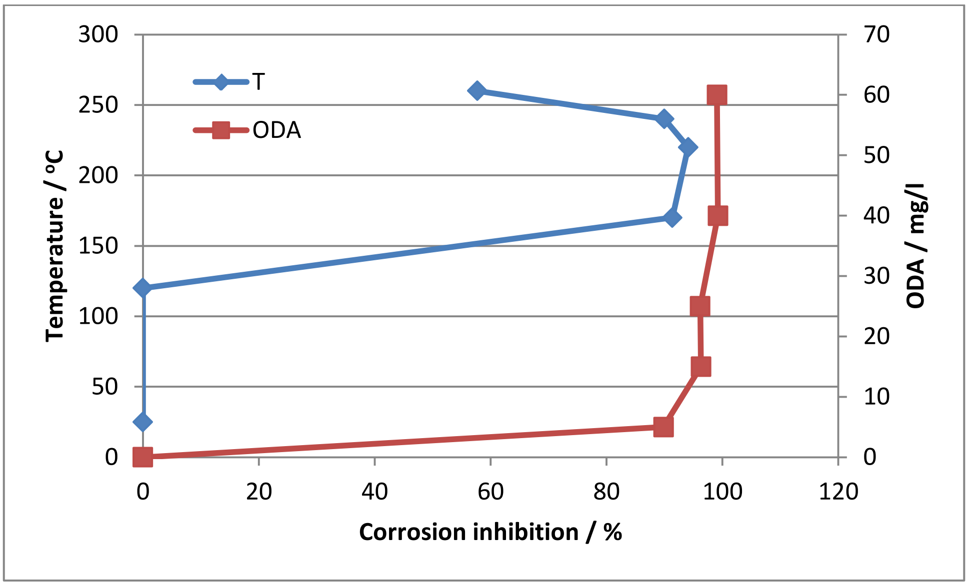

Figure 13 Effect of ODA concentration (exposed for 3 h in steam at T = 220 °C) and exposure temperature (exposed for 3 h at 5 mg/l ODA) on corrosion inhibition efficiency of carbon steel. Modified from [45].

A very recent study on gas-fired plants focused on the film-forming characteristics of octadecylamine (ODA), to estimate the feasibility of shutdown protection using ODA at high temperatures, and to determine the optimum process condition of shutdown protection for units under full load [46]. An autoclave was used to simulate the water-vapor environments at 350-560 °C in the water-steam system of power plants. The decomposition rate of ODA was investigated and the ODA film-forming characteristics were studied for furnace tube materials used in gas-fired power plants. Results showed that ODA had a decomposition equilibrium and the decomposition products did not contain harmful organic substances such as low molecular organic acids. ODA would form a satisfactory protective film in the range of 350-560 °C with the best film at 480 °C. The protection effect of the film formed by ODA at 560 °C was much stronger than was that of its oxide film, which showed the feasibility of shutdown protection using ODA for gas-fired power plants operating under full load. The optimal conditions of shutdown protection under full load were as follows: the temperature was 560 °C, the concentration of ODA was 80 mg/L, the pH was 9.5 and the exposure time was 2 h. From the experimental results of X-ray photoelectron spectroscopy, it was known that the surface film on the specimens was composed of a compound of ferro-ferric oxide and ODA, and the film-forming mechanism was chemical adsorption between N in the ODA and Fe. It was found that ODA has a good film-forming effect at high temperatures and it is practicable to implement shutdown protection for base-load units. The research results can provide theoretical guidelines for shutdown protection of gas-fired power plants.

Aliphatic tertiary di-amine (ATD) was synthesized and tested by gravimetric and electrochemical methods as a film-forming inhibitor of hydrogen sulfide corrosion [47]. Both H_2S-induced general corrosion in the vapor (80°C) and liquid (20± 2°C) phases and hydrogenation were inhibited by ATD more effectively than by aliphatic tertiary amines and commercial corrosion inhibitors. The data obtained were confirmed by comparative autoclave tests simulating the operating conditions of gas mains. Aliphatic tertiary di-amine causes no emulsification or foaming and meets requirements imposed by gas industry on the protective and technological properties of film-forming inhibitors of hydrogen sulfide corrosion.

An extensive EPRI-funded project to evaluate the current PWR steam generator lay-up guidance based on corrosion mitigation of steam generator components was reported [48]. Phase 1 of this project included an extensive literature review of the corrosion test data, and development of a gap analysis to determine additional data needed to update the current guideline recommendations. Phase 2 was a corrosion test measurement program to evaluate the general corrosion rates of several SG materials under wet lay-up conditions. In the test program, weight loss measurements were made in varying concentrations of oxygen scavengers with solutions containing <20 ppb dissolved oxygen and the pH controlled to >9.0. Additional tests were performed in initially air saturated and nitrogen purged solutions with and without oxygen scavengers. The oxygen scavengers tested in this work included hydrazine, carbohydrazide and diethyl hydroxylamine (DEHA). Phase 3 completed additional corrosion tests including localized and galvanic corrosion under steam generator lay-up chemistries. Phase 3 used the same oxygen scavengers as tested in Phase 2 under more controlled conditions.

The inhibitory effects of Anodamine on the corrosion behavior of 1018 Mild Steel (MS) in deionized water were investigated using immersion tests and electrochemical methods [49]. It was found that the corrosion of 1018 MS is significantly mitigated when the concentration of Anodamine is as high as 100 ppm. The hydrophobic layer of absorbed inhibitor preformed in solution containing 100 ppm Anodamine is still sufficiently resilient to mitigate the corrosion of MS when the concentration of Anodamine is gradually decreased to 0 ppm. With increasing concentration of Anodamine, the passive range of MS in deionized water is gradually expanded. However, after de-passivation by anodic polarization, pitting occurs and the current density increases rapidly. The adsorption of Anodamine can be enhanced by gradual anodic potentiodynamic polarization whereas cathodic polarization induces desorption. Once de-passivation had occurred, Anodamine was not re-adsorbed onto the corroding sample surface and the corrosion process was even catalyzed in the presence of Anodamine.

In a further paper, electrochemical impedance spectroscopy has been used to explore the corrosion and electrochemical behavior of 1018 MS in deaerated, deionized water containing different concentrations of Anodamine [50]. The Point Defect Model (PDM) was optimized on the EIS data using the newly-developed procedure to study the mitigation mechanism of Anodamine. The optimization results suggest that, as the concentration of Anodamine increases, the pore resistance of the adsorbed inhibitor, the charge transfer resistance, and the Warburg coefficient associated with the trans-port of redox species through the porous outer layer of the passive film increase, with the latter being the primary cause of inhibition. Accordingly, the hydrophobic layer of adsorbed Anodamine becomes more protective and the inhibitory effect of Anodamine is enhanced as its concentration increases. In addition, within the passive range, increased applied anodic potential enhances the adsorption of Anodamine and hence enhances its inhibitory effect.

A key benefit of film-forming amine is improved corrosion protection during frequent startups and shutdowns. This allows for high steam quality during startup to be achieved much quicker with consequent economic benefits. No evidence of any of the problems related to oxide layer removal or magnetite deposits have been found [51].

Effects of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which is a strong base with a pKa of 13.4, were compared to dimethylamine (DMA) concerning oxidation kinetics and oxide phase formation/transformation of AISI 1018 steel at 120 °C [52]. Low carbon steel samples were exposed to steam in an autoclave containing amine added aqueous solution at pH of 9.5 for 1, 2, 4, 6, 8, and 12 h. Control samples exposed to plain steam and amines showed the highest and lowest weight loss respectively. Fourier Transform Infrared Spectrophotometry (FTIR) showed that DBU containing steam favored formation of magnetite (Fe_3O_4) while steam with DMA formed more α and γ-FeOOH. Transformation of magnetite to hematite (α-Fe_2O_3) was the fastest for morpholine. Analysis of oxides morphology was done utilizing Scanning Electron Microscopy (SEM). Oxides formed in plain or DMA containing steam exhibited acicular particles of goethite/hematite (α-FeOOH/α-Fe_2O_3) compared to DBU containing steam that showed equiaxed particles of magnetite/ maghemite (Fe_3O_4/γ- Fe_2O_3). Morpholine containing steam promoted agglomeration of thin sharp platelets into coarse flakes of hematite.

After discovering the benefits from Italian fossil plant experience, Comanche Peak Nuclear Power Plant (CPNPP) augmented morpholine chemistry in the secondary system with dimethylamine (DMA) chemistry [53]. As a result of the operational success with DMA, CPNPP began searching for alternative amines that may provide greater benefit. The amine discovered to have the most favorable potential benefits was found to be DBU. Corrosion and compatibility testing was performed in reference to existing amines and followed the pattern of the qualification testing performed for implementation of DMA. Testing was performed on carbon steel for BOP considerations and Alloy 600 steam generator tubing material. Also described is an unexpected finding from the testing. One test regime indicated a corrosion protection benefit of DBU beyond a simple pH effect which may be the result of surface modification or surface reaction with the carbon steel oxide.

Further research [54] involved more detailed deposit characterization by studying the samples collected from different units in secondary side system at CPNPP. Electrochemical impedance spectroscopy and polarization curves were used to study the interaction mechanism between DBU solution and alloys 600 and 690 at steam generator operating temperatures and pressures. Of all the amines used in this study (DMA, DBU, ETA, and morpholine), DMA was more effective at keeping the passive film formed on the alloy 600 surface from failing at both ambient and high temperatures. Morpholine was found to result in higher corrosion resistance compared to the other amines in case of alloy 690.

In plant applications, the corrosion inhibition of closed cooling systems can be a quite challenging task because of the very long holding time. As a consequence, contaminations entering the water remain inside the system and gradually accumulate. This potential risk was claimed to be overcome if corrosion protection is realized by adsorption of the film forming amine on the metal surfaces [55]. 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 of a changeover of the treatment program from molybdate to film forming amines show a significant improvement of corrosion inhibition reflected in a marked 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. In addition, much lower conductivities in the cooling water were reported with FFAs compared to corrosion inhibition programs based on inorganic inhibitors (nitrite, molybdate).

7.3 Flow-accelerated corrosion

A program of experimental tests has been conducted to assess the potential for using corrosion inhibitors in liquid–solid flows, where erosion and corrosion occurs, to control material degradation [57]. Tests were conducted using the submerged impinging jet (SIJ). Both mass loss and in situ electrochemical corrosion tests were conducted on carbon steel. Two commercial inhibitors showed a peak-value phenomenon for erosion–corrosion mitigation; for inhibitor A, the optimum concentration is 50 ppm and for inhibitor B, it is 100 ppm. The chemical packages were reported to be based on combinations of proprietary complex blends of phosphorus, nitrogen and carboxylic acid containing corrosion inhibitors, film forming inhibitors and other organic constituents. Erosion and corrosion components were characterized as a proportion of the total material loss. The mechanisms by which chemical inhibitors reduce material loss were discussed. The following conclusions were drawn from the results:

- Both of the inhibitors tested with SIJ have peak-value phenomena; for inhibitor A, the optimum concentration is 50ppm and inhibition is mainly attributed to the inhibitor molecules working positively with the corrosion products.
- For inhibitor B, the optimum concentration is 100ppm according to erosion–corrosion results. Erosion–corrosion inhibition is mainly due to the inhibitor film formed on the metal surface.
- For inhibitor A, the optimum concentration under erosion–corrosion was the smallest concentration required for general corrosion protection. For inhibitor B, the optimum concentration under erosion–corrosion is also the optimum concentration for reducing general corrosion.
- It was clear that corrosion is a controlling parameter in erosion–corrosion and the trend in corrosion align to the trends in erosion–corrosion for both inhibitors even though erosion is a significant part of the total damage.

Several pressurized water reactor (PWR) plants have switched to ethanol-amine (ETA) injection to reduce iron transfer in the steam generator [58]. ETA injection is supposed to reduce the rate of flow accelerated corrosion (FAC) by increasing the pH of the secondary system. However, the effect of ETA injection on FAC rate has not been studied systematically. To assess the influence of ETA injection on FAC rate, first the water chemistries in secondary systems were calculated considering thermal decomposition of hydrazine in SG and vapor/liquid distribution of ammonia, ETA and hydrazine in SG and moisture separator-re-heater. Then change in FAC rate was evaluated using magnetite solubility changes before and after ETA injection. Evaluation from calculated magnetite solubility shows that ETA injection reduces the FAC rate of the secondary system. In some portions of the secondary system, the FAC rate was also measured experimentally by the rotating disk test to examine the effect of ETA injection. The peak of FAC rate shifted to a higher temperature after ETA injection. At 274°C, the FAC rates were nearly the same under the conditions of high pH of ETA and conventional low pH of all volatile treatment (AVT). Same pH dependence was observed in ETA and ammonia treatment.

Results obtained from putting in use a technology for making the tubes of heat recovery boilers in combined-cycle plants more resistant to erosion–corrosion wear with the aid of film-forming amines were recently reported [59]. Preserving the heating surfaces of heat-recovery boilers using film-forming amines was proposed to allow, on one hand, the problems of reducing local operating erosion–corrosion to be solved in a comprehensive way and, on the other hand, the surface of tubes to be reliably protected from shutdown corrosion even if there was residual moisture. This method for control of corrosion has been put into use in a co-generation station almost from the commencement of operation, and it was demonstrated to have a favorable effect on the reliability of power unit operation. Figure 14 shows the concentration of iron in the boiler water of high- and low-pressure circuits during startups carried out after long-term outages (from 3000 to 8000 h) prior to which preservation with FFA had been carried out. The concentration of iron with preservation was much lower than without and did not exceed the guideline levels.

Considerable plant and laboratory data on flow-accelerated corrosion (FAC) exists for temperatures below 225°C, but there is little relevant data for the higher temperatures experienced in steam generators. In addition, recent testing has suggested that the FAC rate may be a function of the specific amine used for pH control beyond that predicted based on the pH_T alone. Results from a series of tests on carbon and low alloy steels at temperatures above and below 225°C further investigating specific effects of pH at the operating temperature and amine on the FAC rate were presented and discussed together with limited data on the effects of hydrazine concentration on the FAC rate at 256°C [60].

Erosion-corrosion tests were conducted in autoclaves and on a pilot steam generator (SG) design to look into the impact of ODA [61]. To accelerate corrosion, process tests were conducted in a more aggressive environment as compared to actual operating conditions, including high chloride concentration and stress levels. It is not only important to reduce deposition growth, but also to wash out deposits previously formed on heat exchanger surfaces. This allows one to reduce the risk of local corrosion and corrosion cracking development. A number of WWER plants have conducted full-scale testing that confirmed the impact of ODA micro-additions on local corrosion mitigation [63]. Some PWR plants are testing injection of surface active dispersants to loosen SG deposits. Multiple studies proved ODA ability to remove chlorides from smooth surfaces which allowed to reduce the rate of micro-crack growth. Trial testing has shown that the rate of corrosion cracking on SG tubes was reduced by 60-70% owing to ODA injections. Such effect was due to significant reduction in chlorides absorption by the metal surface during the year of ODA injection.

Tests on a pilot SG design [61] have shown that ODA could be used for partially wash out deposits from a heating surface. Testing was conducted for 560 h with C_{ODA} ~0.07 ppm in boiler water under P=7.2 MPa, T=256°C and q=150-170 kW. Initial deposits on the tube bundle were formed by repeated evaporation of boiler water artificially contaminated by the impurities. During the ODA treatment the deposit removal efficiency was from 50 to 75%.

Additional experimental studies were conducted to check the possibility of SG Type PGV-440 tube bundle cleaning after long-term WWER-400 plant operation. Specimens were cut from different areas inside the tube bundle with specific contamination in the 20-100 g/m^2 range. The 500 h cleanup test in water phase of trial SG with C_{ODA}=0.5 ppm showed more efficient washing for specimens with higher level of contamination. Cleanup efficiency with ODA treatment was 88%, 55% and 17% for contamination levels of 100, 50 and 24 g/m^2, respectively.

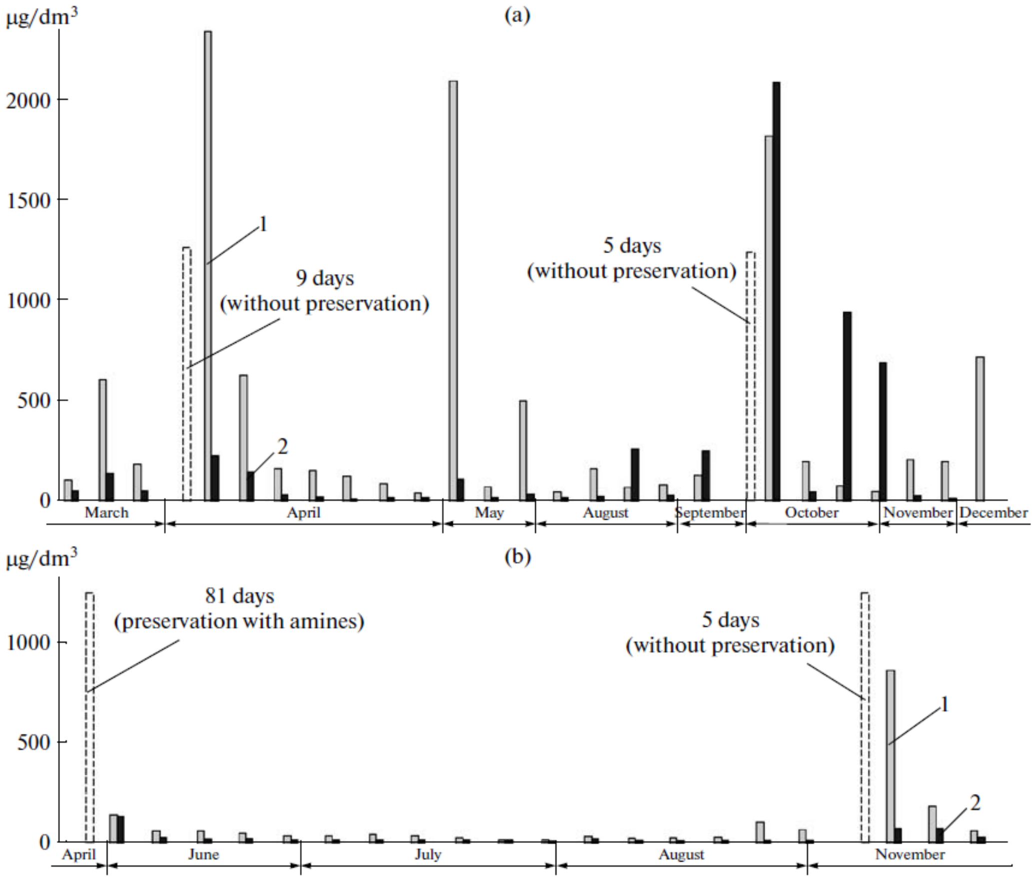

Figure 14 Content of iron oxides in the boiler water of the low- (1) and high-pressure (2) circuits of a cogeneration station: (a) start-ups without, and (b) with preservation.

The tests showed that ODA micro-additions remove chlorides from micro-cracks and crevices on SG tubing spacer grids. The ability to wash out previously formed deposits allows to reduce risk of local corrosion and cracking. The abilities of micro-additions of film-forming corrosion inhibitors identified through the above mentioned testing could be used under the WWER plant life extension program. The experience of the Kola NPP showed long-term reliable SG operation owing to ODA treatment even without routine chemical cleaning. Such effect was due to significant reduction in chlorides absorption by the metal surface during ODA injection. Hide-out data comparison during shutdown of Kola Unit 2 prior to and after implementation of secondary water chemistry with ODA injection revealed reduction of chloride release to SG bulk water with factor 15, sulfates with factor 3, acetates with factor 6. The above mentioned experimental fact confirmed improvement of SG tube corrosion status and reduction of SG tube contamination after ODA treatment implementation. Results of laboratory investigations of ODA effect on local corrosion processes have also been validated in the course of commercial tests at Nord Unit 4 (Germany) and Kola Unit 2.

7.4 Crevice and crud-induced corrosion

Very recently, coupling current measurements were performed on 1018 mild steel and type 410 SS in a sodium chloride solution with the addition of as-received Anodamine [62]. In such experiments, the crevice is electrically coupled to the bare external surface via a zero-resistance ammeter (ZRA), and as the crevice becomes active due to the establishment of a differential aeration cell, a positive current flows through the solution from the crevice mouth. The addition of the inhibitor at a concentration of 20 mg L^{-1} significantly affected the crevice corrosion behavior of 1018 mild steel, but not that of 410 SS (Figure 15). However, when a sufficient amount of polyamine exists in the solution, crevice corrosion of 410 SS can also be inhibited due to the formation of a protective film decreasing the rate of the cathodic reaction on external surfaces (Figure 16). Thus the film-forming amine is an effective inhibitor of crevice corrosion for both mild and stainless steel, provided a sufficient concentration of it is present in the solution.

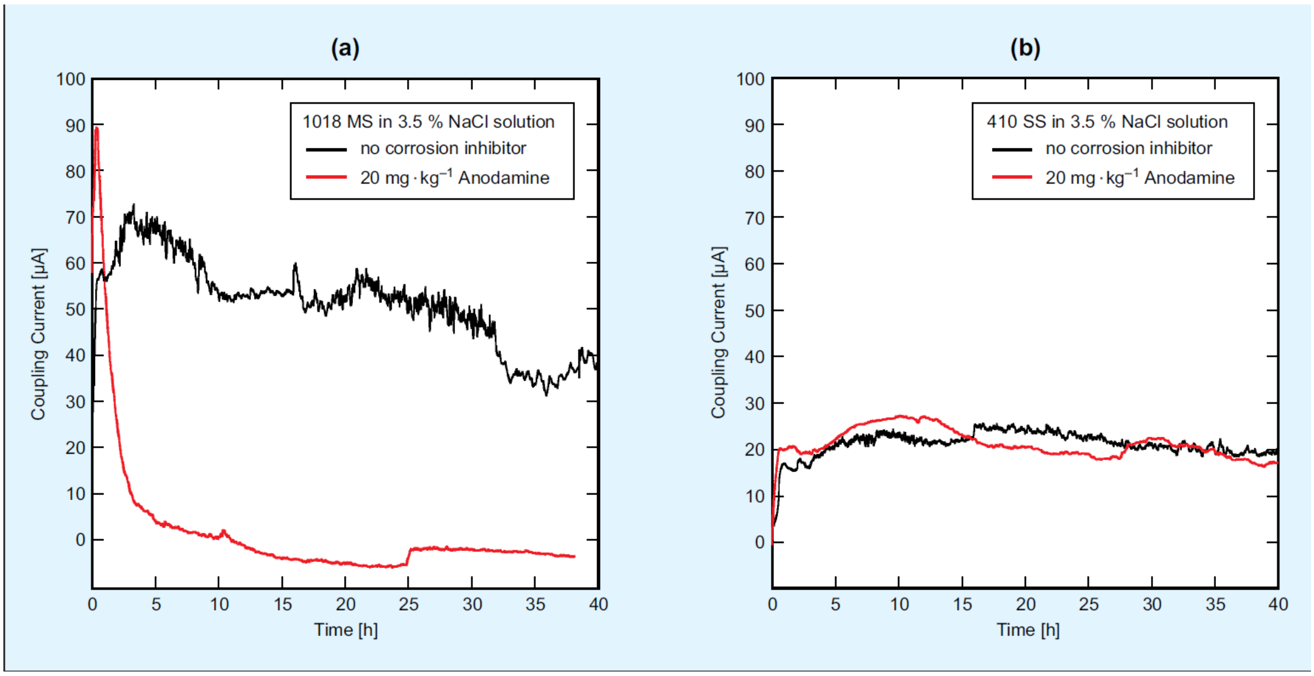

Figure 15 Plots of the coupling current measured with (a) 1018 steel and (b) 410 SS in 3.5% NaCl solution with and without 20 mg L^{-1}Anodamine.

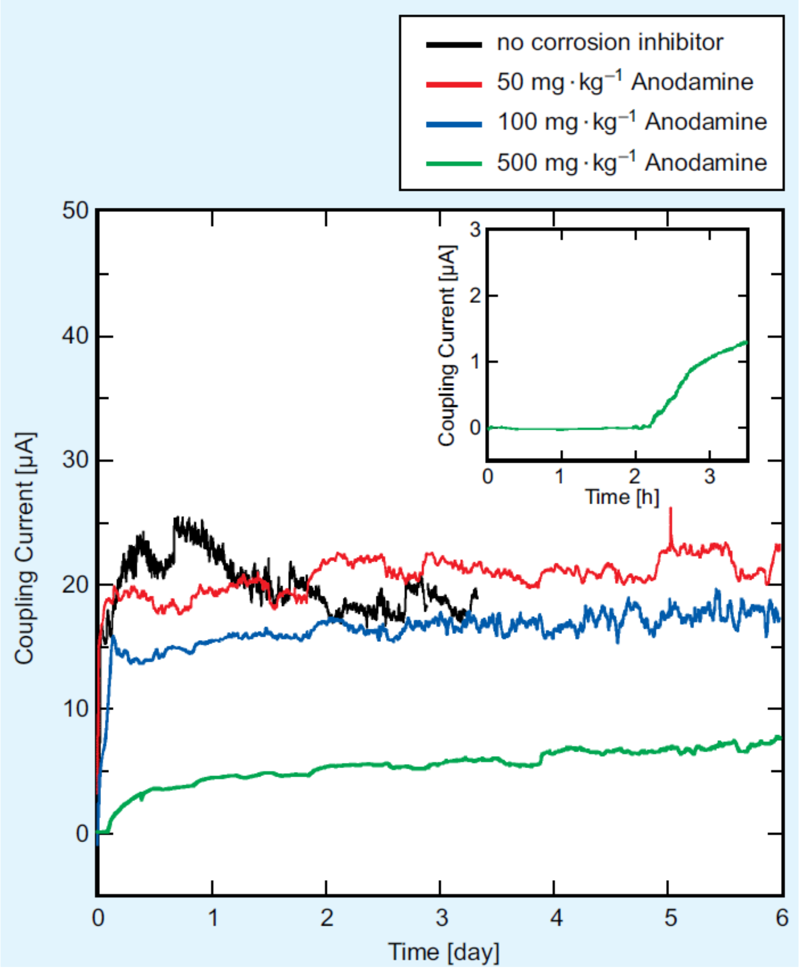

Figure 16 Plots of the coupling current measured with 410 SS in 3.5% NaCl containing different concentration of Anodamine.

8 Influence of Film-Forming Amines on deposition processes

Almost without exception, the degradation that affects the safety and performance of the SG is related in one way or another to the accumulation of deposit on various components on the secondary side of the SG, e.g., the tube bundle, tube support structure, tube-sheet and steam separators. A corollary of this statement is that a properly designed SG should not fail by any of the abovementioned degradation mechanisms provided that the SG remains clean, i.e., free of deposits. Thus, the key to mitigating degradation of the SG is the ability to mitigate the accumulation of unwanted deposit, or fouling, of the surfaces of critical components within the SG.

Reliable experimental data on the effect of film-forming amines on deposition processes in the secondary circuit that are available in the open literature are significantly scarcer than those concerning corrosion inhibition. In the following, some examples of such studies are cited. It is once again important to stress that due to the fact that the very recent EPRI programs concerning dispersant and filming amines are not yet available to the public, they are not discussed here. In general, it is presumed that the formation of an adherent hydrophobic temperature resistant film leads to release of adsorbed or adhered particulate iron oxide deposits and ionic impurities on the surface can be released to variable extent (Figure 17).

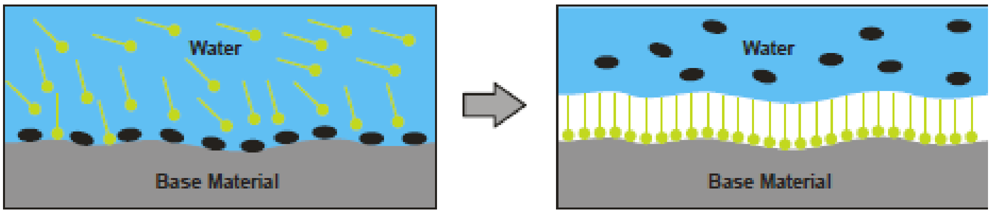

Figure 17 A simplified scheme of the action of film-forming amines (yellow) on the release of impurities from surfaces (black).

EPRI and AECL have been jointly conducting a program to optimize water chemistry for mitigation of steam generator (SG) fouling [64]. Within the frames of this study, loop tests showed that dodecylamine (DDA) inhibits fouling by magnetite particles under conditions representative of recirculating SGs. These results were summarized in Figure 18.

The improved water chemistry with DDA needed to be field tested. Accordingly, qualification efforts for a trial run in a pressurized water reactor (PWR)-type steam cycle were attempted [65]. The DDA qualification program assessed the following issues: analytical assay for DDA, the possible effect of DDA on the electrochemical behavior of the SG tubing, compatibility of DDA with ion exchange resins, hydrothermal stability of DDA, the method of addition of DDA into the steam cycle, and the effect of DDA on flow boiling heat transfer. The results to date supported a DDA field trial.

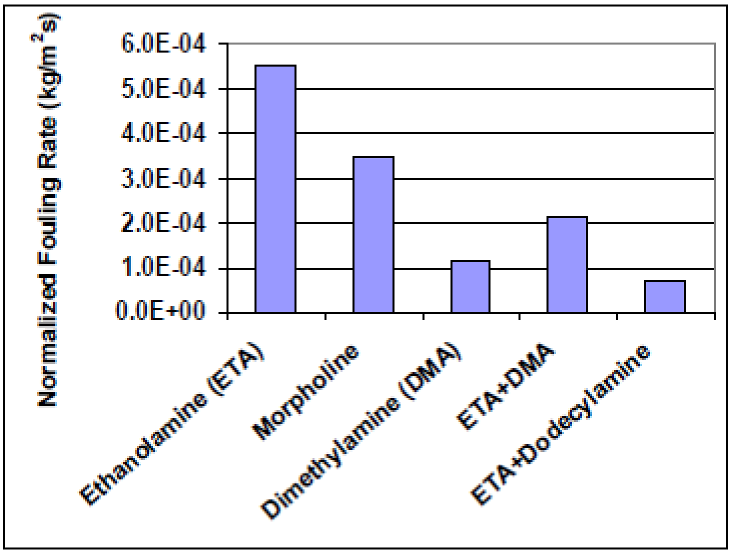

Figure 18 Influence of amine used for pH control on the fouling rate of magnetite particles under flow-boiling conditions

Results of a study of tube specimens cut from hot-water boilers show that film-forming ODA used in the process of preservation removes deposition from the surface of the metal [66]. An ODA film was preserved on the surface after repeated washing of the latter with hot water. The concentration of chlorides at the surface of the metal after treatment with ODA was lower than before the treatment. The following conclusions were drawn:

- Analysis of the state of surfaces of hot-water boilers protected from corrosion by ODA, which was made after operation for a heating season, showed that an ODA layer was preserved on most of the surfaces.
- After preservation the distribution of admixtures in the scale varied over the scale layer; chlorides, calcium, and SiO_2 displaced from the surface of the metal to the upper zones of scale. This caused decrease in the concentration of corrosion-active admixtures (chlorides) at the surface of the metal and lowered the intensity of corrosion processes.
- The use of ODA lowered the intensity of formation of scale in the season of autumn and winter maximum loads.
- The use of ODA for preservation of delivery water decreased the vulnerability of the tubes to damage, decelerated the growth of scale, and stabilized the temperature difference.

Very recently, Gasnier and Lister [67] compared the effects of a commercial film-forming amine (FFA) to polymeric dispersants – two types of poly-acrylic acid (PAA) and sodium polymethacrylate – on particulate magnetite deposition from suspension in water at 100 °C onto heated Alloy 800 during sub-cooled and bulk boiling. It was demonstrated that PAA was the most effective in preventing magnetite deposition. Of particular interest, however, are the zeta potential measurements that indicate that the zeta potentials of both magnetite and Alloy 800 are significantly altered in the presence of film forming amine (Figure 19-Figure 20). The concentrations of the polymers were adjusted to correspond approximately to the same amount of carboxylic groups per gram of magnetite/Alloy 800. In order to account for losses of FFA due to the coating of the sample cell and the immersed electrode during measurements, FFA was added in excess, and the concentration shown in the figures is that measured after determination of zeta potential. FFA increases the zeta potential of both magnetite and Alloy 800 and maintains it at positive values in the whole investigated pH range. Thus FFA could also provide an electrostatic repulsive force over a large range of pH in analogy to the polymeric dispersants.

Since the FFA molecule was reported to contain both primary and secondary amino groups, its protonation should lead to positively charged species. One of the amino groups was probably the anchor point of the molecule to the Alloy 800 or magnetite surface. The authors concluded that if FFA is used in a high-pH coolant circuit, the main concern could be that contrary to polymeric dispersants that provide extra negative charges to surfaces that are already negative at high pH, FFA will shift surface charges to completely positive, which could lead to effects that merit further investigation.

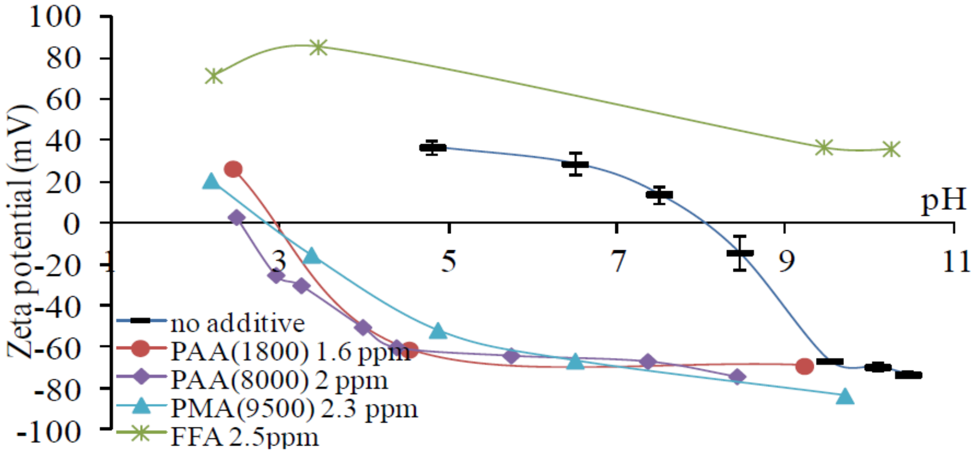

Figure 19 Effect of additives, including a film-forming amine, on the zeta potential of magnetite.

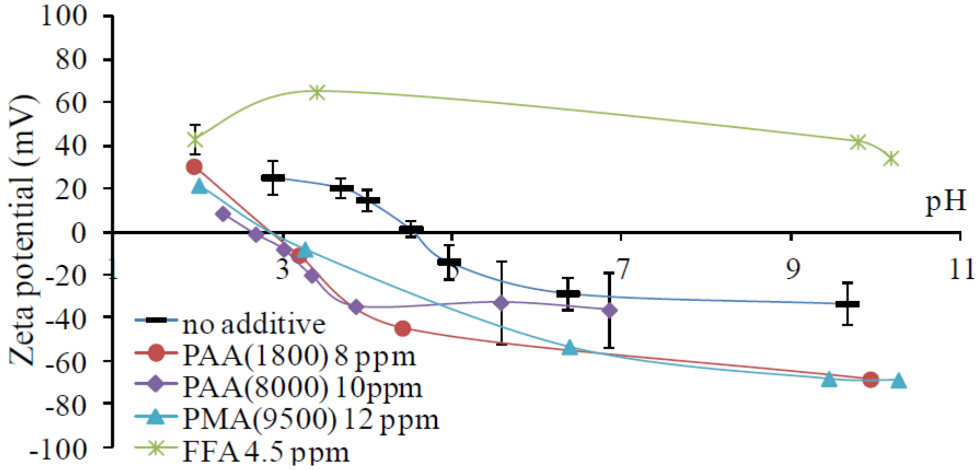

Figure 20 Effect of additives, including a film-forming amine, on the zeta potential of alloy 800.

9 Mechanism of the Action of Film-Forming Amines

9.1 General remarks

It is often claimed that reliable corrosion protection by inhibitors on all metallic materials is based on a molecularly thin film coating on the metal surface. In water-steam cycles, and therefore in neutral to weakly alkaline conditions, there is no clean (oxide- or hydroxide-free) metallic surface to which the film-forming amines would have a particular affinity. Thus it was proposed that the theory of membrane inhibition could be applied to corrosion inhibition under the latter conditions. This presumes the formation of a three-dimensional membrane which is formed between the corroding substrate and the electrolyte and consists of corrosion products, which are difficult to dissolve, and the inhibitor [68].

A large number of organic substances, most often aromatic compounds or macromolecules with linear or branched chains, serve as corrosion inhibitors [69]. These inhibitors adsorb onto the surface of the metal and thus slow the rate of corrosion. In many cases a continuous film formation can occur. The inhibition efficiency in a given application depends on the molecular structure of the inhibitors and on their concentration. As mentioned already above, an organic inhibitor molecule typically includes a hydrophobic non-polar part that contains mostly carbon and hydrogen atoms, and one or several hydrophilic functional groups such as -NH2 (amine), -SH (mercapto), -OH (hydroxyl), -COOH (carboxyl), -PO3 (phosphate) or their derivatives. The polar functional groups permit dissolution of the inhibitor in water and they link the inhibitor molecule to the metal surface. The non-polar part, which takes up a much greater volume, partially or fully blocks the active surface area. Inhibitors generally chemisorb on the surface. The effectiveness of the inhibitor therefore is the better, the greater the tendency of the functional groups to form bonds with the metal by acting as electron donors. For organic molecules which differ only by their functional groups, the inhibition efficiency varies inversely with the electronegativity of the functional atoms. The molecular structure of the non-polar part can also influence the ability of the functional atoms to donate electrons. The general picture given here applies only to the simplest kinds of molecules. Often other factors, in particular steric effects, influence the adsorption behavior of organic molecules. In that case, there is no simple correlation between the electron density at the functional group and the inhibition efficiency. The same is true if the inhibitor forms surface films of more than one atomic layer, or if it undergoes an oxidation, reduction or polymerization reaction at the surface.

9.2 Mechanism of film formation and inhibition efficiency

The inhibitive properties of fatty amines in neutral and/or alkaline media are usually attributed to their hydrophobic character [21,22,70]. Experimental results show the influence of the amino groups in each compound and more precisely the number of nitrogen atoms [71]. In fact, it seems that corrosion suppression efficiency decreases when the number of N atoms increases, which could be explained by the increasing difficulty to form a homogeneous film on the material surface because of steric hindrance effects. On the other hand, repulsion between free electron pairs of each N atom is also worth considering. In addition, the interaction of nitrogen with the surface could lead to the formation of a complex of low solubility with divalent or trivalent iron dissolving from that surface which would provide a supplementary barrier to corrosion. In contrast to the number of amino groups, the alkyl chain has a limited influence, e.g. the difference in corrosion inhibition between a saturated and unsaturated chain seems to be not relevant even if the layer formed on the surface is different due to the different chain polymerization reaction.

Studies of the hydrophobic character of the filming amine layers at different temperatures are of utmost importance to assess the mechanism of their interaction with both oxidized surfaces and suspended oxide particles. The differences in wettability of the amine films on the oxide surfaces of thermally treated metals are attributable to differences in closeness of packing of the adsorbed amine molecules [72]. This conclusion is derived in the case of octadecylamine films on iron from the critical surface tension determinations. Oxide films were first formed on iron samples by exposure at different temperatures to flowing He-gas with 200 ppm O_2 at $p = 0.3…0.4$ mm Hg. After cooling to $T = 25^oC$ the surface was let to react with the amine containing solution overnight. The amine film adsorbed on iron at 25°C had a critical surface tension which corresponds to a surface of close-packed methyl groups. The amine molecules were judged to be densely packed and oriented with the hydrocarbon chains pointing away from the metal surface. The surface tension of films formed at 180°C indicated that in this case the amine molecules exposed a significant portion of methylene groups as well as methyl groups to the wetting liquid. The nature of the thermally induced changes in the metal oxide layer (e.g. loss of strongly bonded water at the metal surface) might be responsible for the observed differences in packing of the amine molecules and hence alteration in their hydrophobic properties. For films formed between 200 ° and 300°C, the solution contact angle increased with increasing pretreatment temperature. This regime of behavior appears to be associated with a different degree of surface oxidation from that which occurs below 200°C.

9.3 Interaction with suspended iron oxides

Recent investigations [73,74] showed that the shape and porosity of hematite particles, produced from a hydrolysis reaction, were controlled by using the so-called surfonamines of the type CH_3-(PEO)x-(PPO)y-NH_2). The hydrophilic L-100 amine of this group resulted in the fabrication of spherical, whereas L-200, L-207 and L-300 which were of hydrophobic character, provided pseudo-cubic hematite particles. The uniformity of these particles was improved by an increase in their concentrations. The pH values of these systems indicated that the surfonamine molecules act as a buffer agent and led to the formation of pseudo-cubic particles. Not only the morphology but also the pore size of hematite particles was controlled from nonporous to micro-porous by using surfonamines.

Very recently, the morphology of hematite particles prepared by a hydrothermal method assisted by octadecylamine was assessed [75]. The binding ability of amine to Fe^{3+} was also reported [76]. Based on the analyses performed, it was concluded that the presence of ODA is an important factor for α-Fe_2O_3 particles morphology evolution (Figure 21). As the amount of ODA increased, the protonated amine could increase the pH value and accelerate the nucleation process. At the same time, the long alkyl groups of ODA molecule acted as an adsorption-inhibiting agent to retard the growth of nano-particles in the reaction process. The above increased nucleation rate and the decreased crystal growth rate led to smaller particle size. In comparison with the neutral surfaces of {100} and {010} planes, the {001} facets of α-Fe_2O_3 have a net ionic charge on the surface [77]. When the α-Fe_2O_3 nuclei were formed in the solution, the ODA were specifically adsorbed on {001} faces via the lone pair of electrons on N atoms. When the amount of ODA was insufficient (5 mol %), the crystal growth rate on these facets decreased. This resulted in the formation of nano-ellipsoidal particles with characteristic constriction. With increasing ODA to 12 mol%, its molecules were also adsorbed on the {012} faces, on which weak specific adsorption of chloride restrained the growth leading to polyhedral structures [74]. With further increase of ODA to 30 mol%, the ODA adsorbed on α-Fe_2O_3 particles became sufficient, enabling the particles to grow into nanospheres.

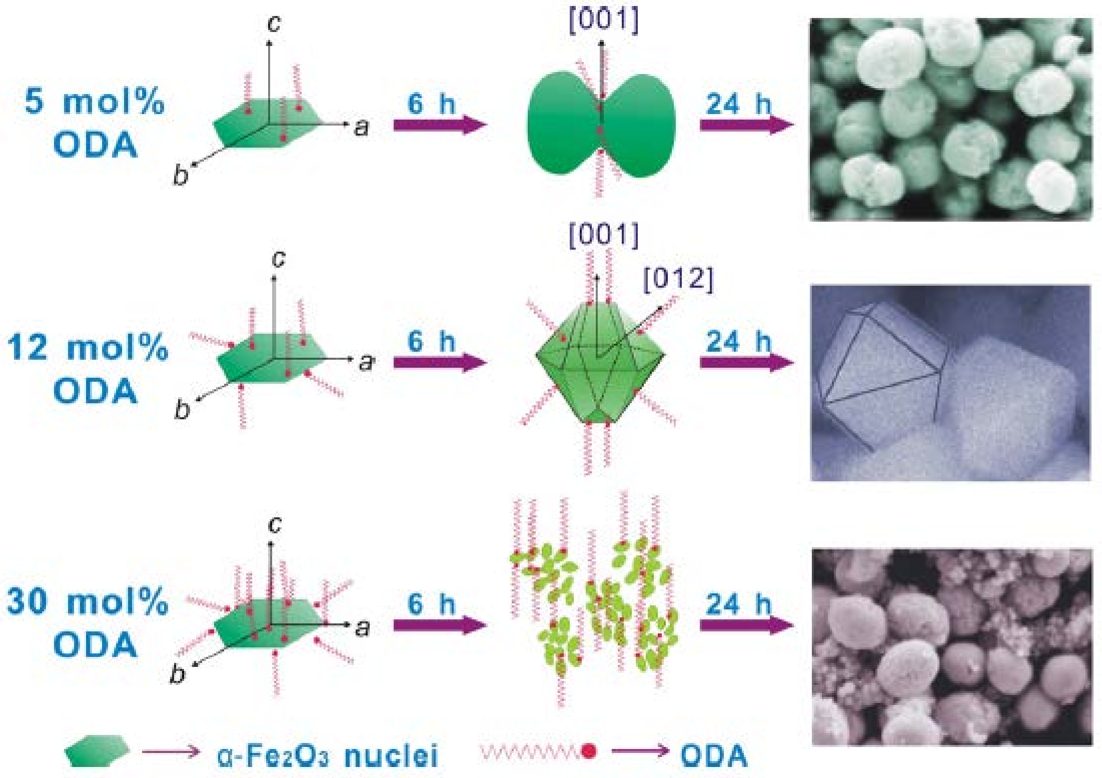

Figure 21 Formation mechanisms of hematite particles depending on ODA concentration.

10 Conclusions and outlook

In recent years, the effect of film forming amines on corrosion and associated fouling processes in process industry and conventional power plants has been thoroughly studied in lab scale by electrochemical methods, as well as in pilot plants closely simulating practice-like conditions. According to these results at least the same or better corrosion protection can be achieved in comparison to well established corrosion inhibitors like molybdate or nitrite. The mechanism of corrosion inhibition is 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 done by colorimetric determination of the free film forming amine concentration in the cooling water. A concentration above 1 mg L^{-1} is generally recommended. Due to the intended adsorption of the film forming amine on the surfaces there is no straightforward 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 to deliver satisfying treatment results. Water consumption and effort for maintenance could be reduced. Thus considerable savings could be realized. FFA based programs are suitable for various metals, such as carbon steel, copper and aluminum alloys. Much lower conductivities in the cooling water can be achieved with FFAs compared to corrosion inhibition programs based on inorganic inhibitors. This can be important for special applications in systems where the conductivity is limited by the process or safety related regulation.

Concerning the SGs of nuclear power plants, especially plants with a non-optimal Balance-of-Plant design that are restricted in the use of high-all volatile treatment, a complementary and continuous dosing of less volatile amines might be needed to avoid FAC due to the difficulty in establishing a sufficiently high pH. The non-continuous and controlled dosing of film forming amines could lead to significant reduction of corrosion product transport generation and transport into the SGs, as well as significant reduction of impurities on the inner surface of the steam-water cycle. The application of FFAs in that cycle of a PWR was judged to be a useful supplement to the existing water chemistry for removal of impurities from the secondary cycle surfaces, protecting the surfaces in the wet steam areas and contributing to an optimized pH control strategy. A refreshment application of FFAs in the cycle could be required in case of increasing iron concentration in the feed-water, as well as a change in the heat transfer efficiency of SGs due to impurities. Furthermore, the use of film-forming amines in lay-up strategies has been recommended since during outages the wet surfaces and moist condensation will result in general corrosion of carbon steel components, as well as localized corrosion at anodic sites in the presence of impurities. Thus establishing a hydrophobic film on the metal surface would ensure their stability without additional measures for outage lay-up.

According to the EPRI point of view, use of the alternative layup technology involving a film forming amine reduced corrosion product transport on startup. This capability allows for more rapid startup, lengthens the interval between chemical cleaning, and minimizes the potential for under-deposit corrosion in boiler/high-pressure evaporator tubing. In addition, steam-touched surfaces (tubing, piping and turbines) are protected from pitting, which is a precursor to stress corrosion cracking and corrosion fatigue on low-pressure turbines and oxygen corrosion and failures in steam tubing and piping. Film forming amines form a hydrophobic film on the metal surface and provide a barrier against water and gases, and the protective barrier remains intact after the dosage is stopped. The filming amine has a low toxicity, and environmental approval has been straightforward at the locations seeking to use these products. Unlike any other method, this technique is implemented in advance of the unit outage while the equipment is still operating, not after the unit is removed from service or even during the process of removing the unit from service. This characteristic ensures the equipment is continuously protected from corrosion.

However, concerning the mechanism of interaction of film-forming amines with oxidized metal surfaces which is all-important in future design of novel formulations for corrosion protection in both fossil and nuclear plants, comparatively little is known besides the general framework for film formation. Clearly further mechanistic investigations are needed in order to transform the empirical search for better compositions to a deterministic endeavor guided by a deeper understanding of the elementary physical and chemical processes involved in the interaction of the fatty amine molecule with oxides on construction material surfaces.

11 Summary

Corrosion products in the secondary side of pressurized water reactor, as well as the steam-water cycle of fossil plants and process industries primarily deposit on the steam generator tubes. These deposits can inhibit heat transfer, lead to thermal-hydraulic instabilities through blockage of tube supports, and create occluded regions where corrosive species can concentrate along tubes and in tube-to-tube support plate crevices. The performance of the SGs can be compromised not only through formation of an insulating scale, but also through the removal of tubes from service due to corrosion. The goal of the present task is to report a literature study on the use of film-forming amines in nuclear reactor secondary side and in conventional power plants with regard to their composition, structure, thermal stability, and interaction with deposits during their formation and consolidation. The mechanisms of interaction of film forming amines with structural materials and deposits, their chemical stability and degradation, as well as the efficiency of their action during laboratory and in-plant tests are reviewed in detail. The review of the use of filming amines presented in this report consists of the following parts. First, the composition and structure of film-forming amines, their physical and chemical properties, surface activity and interaction with structural materials are described. Second, their role as corrosion inhibitors in combination with other chemicals to form suitable compositions is discussed. Third, the effect of film-forming amines on fouling mitigation is considered. Finally, in a short outlook chapter, the mechanism of action of such amines is discussed and further areas of research in the field are outlined. On the basis of the literature data, conclusions on the prospective application of film-forming amines in existing and newly commissioned plants are drawn.

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