Cycle water chemistry based on film forming amines at power plants: evaluation of technical guidance documents

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Abstract. Efficiency and reliability of the equipment in fossil power plants as well as in combined cycle power plants depend on the corrosion processes and deposit formation in steam/water circuit. In order to decrease these processes different water chemistries are used. Today the great attention is being attracted to the application of film forming amines and film forming amine products. The International Association for the Properties of Water and Steam (IAPWS) consolidated the information from all over the World, and based on the research studies and operating experience of researchers and engineers from 21 countries, developed and authorized the Technical Guidance Document: "Application of Film Forming Amines in Fossil, Combined Cycle, and Biomass Power Plants" in 2016. This article describe Russian and International technical guidance documents for the cycle water chemistries based on film forming amines at fossil and combined cycle power plants.

1. Introduction
In order to decrease the corrosion rate and the deposit formation in steam/water circuit of fossil and combined cycle power plants, it is important to use the cycle water chemistry appropriate for operating conditions of particular equipment. Due to the fact that the equipment damages are heavily impacted by cycle water chemistry [1], the main analysed parameters should be identified and controlled within the recommended limits during different operational conditions for each water chemistry. Today at fossil and combined cycle power plants, the number of applications using water chemistry based on film forming amines is increasing [2-5]. This water chemistry for fossil power plants is now used as alternative to conventional cycle chemistry with ammonia or hydrazine and ammonia for feedwater treatment and phosphates or NaOH for boiler water treatment. The advantages of using blended products with film forming amines are: reduction of the number of dosed products (usually one product is used); the reduction of blowdown; the reduction of corrosion rate and deposit formation; no need for additional lay-up of the equipment during shut downs [6-7].

The power plants of Russia and other countries (Germany, Holland, Belgium, Austria, Republic of Belarus, Kazakhstan, Rumania, Great Britain, USA, New Zealand, Republic of South Africa, UAE and others) applied the following film forming amine based products: Helamin, Cetamine, Finamin, Anodamine. Even though the blended products using film forming amines are used in power industry, there's a lack of technical norms for their applications. The main difficulty in elaborating norms for blended products is that they contain several substances. For example, one or several components to maintain the pH, other components to prevent deposit formation and to form the hydrophobic
protective layer on the metal surface. The blended product producers don't divulgate the product composition which makes more difficult the developing of technical guidance documents.

2. Russian technical guidance documents
Based on provisional regulations of RAO "EES Russia" developed by OAO "Firma ORGRES", OAO "VTI" and OOO "Helamin project" in 2002 [8], in 2012 OAO "Firma ORGRES" authorised the standard of organisation (STO) for Helamin water treatment of the coolant of boilers with pressure 1,4-13,8 MPa [9]. This standard has a summary of Helamin capabilities, its main components and possible dosing points in water/steam circuit. This document doesn't contain direct recommendations on the quality of water and steam. The standard stays that during stable conditions the concentration of polyamines determined with polyamine-test in feed water, boiler water, steam and condensate should be within the range of 1-5 ppm. Higher concentrations may increase the risk for copper-alloy corrosion when they're used in condensate path.

In 2008 OAO "VTI" have developed and then NP INVEL in 2009 authorized the standard of organization [10] which includes the norms for so called "amine containing water chemistry" which are described in this STO as water chemistry "using amine containing reagents, that consist of the blend of neutralizing and film forming amines". According to this document when dosing products that consist of neutralizing and film forming amines, we should determine the concentrations of polyamines in following point:

- for the fossil power plants with drum boilers and desalted water as make up, the polyamine concentration in clean and salted section of the drum should be > 2 ppm;
- for the fossil power plants with drum boilers and chemically cleaned or partially desalted water, the content of polyamines for the boilers with pressure 3,9 MPa should be > 2ppm;
- for combined cycle power plants the content of polyamines in the boiler water is limited to ≥ 2 ppm.

This technical guidance document for "amine containing reagents" doesn't indicate the norms for polyamine concentration in the feed water of once through and drum boilers of pressure above 4,0 MPa; for HRSGs the content of polyamines is not set for the feed water either for turbine condensate. It is not clear, why the concentration of polyamine in the boiler water should be ≥ 2 ppm as well as in the feed water when used at power plant with combined schemes containing both once through and drum boilers. The maximum acceptable values of polyamines in the steam/water circuit is not indicated either. Another question is why when dosing any kind of film forming amines, we should control only the concentration of polyamines and which methods should be used for such control.

3. International technical guidance document
In 2016 the International Association for the Properties of Water and Steam developed a technical guidance document (TGD) for the application of film forming amines (FFA) and film forming amine products (FFAP) in fossil, combined cycle, and biomass power plants [11]. In this document, film forming amines are defined as a group of organic substances with specific functional groups. The list of FFA includes only octadecylamine, oleylamine and oleyl propylenediamine. FFAPs are commercially products containing FFA but they can also include other substances such as alkaizing amines, emulsifiers, reducing agents and dispersants (f.ex. polycarboxylates).

Due to the fact, that the exact compositions of FFAPs are confidential, the document [11] noted that the following information should be provided by the company-producers of the chemical:

- does the product contain FFA from the list mentioned in the document;
- what other components are included in the blended product;
• the list of the thermal decomposition products of the FFAP and the influence of these decomposition products on the conductivity after cation exchange (CACE) and the pH of the first condensate especially at low moisture;
• the influence of the product at ion exchange resin;
• the results of other researches.

The document [11] describes also the main advantages and benefits of using FFAP:
• slow removal of existing deposits from heat transfer surfaces and steam turbine blades;
• insensitivity to load transients, frequent start/stop operation, and during shutdown periods;
• improved wet and dry conservation during shutdown/layup;
• lower sensitivity during upset conditions, e.g., contaminants, pH excursions;
• reduction of flow accelerated corrosion (FAC), especially two-phase FAC in heat recovery steam generators (HRSGs) and air cooled condensers;
• lower corrosion products during startup;
• improvement of heat transfer;

The document [11] also specifies some disadvantages and critical aspects when using FFAP:
• thermal degradation and formation of low molecular weight organic acids;
• lack of knowledge on the impact on condensate polishing plants;
• risks related to overdosage.

Also according to [11] it is important to know what FFA is used and what other compounds are included in FFAP (alkalizing amines, dispersants etc). Without knowing the exact chemical composition and the decomposition products, it is impossible to know if any damage or failure might be associated with the applied FFAP.

One of the aspects analysed in document [11] is the influence of FFAP on ion exchange resins. It is mentioned that due to the variety of FFAP compositions, a general statement on the impact of FFAP on the functionality of a condensate polishing plant cannot be provided. Therefore, in the case where a FFAP is intended to be continuously applied in a water/steam cycle, the corresponding technical information should be requested from the supplier of the FFAP. The key indices of the condensate polishing plant performance should be monitored before the change to the FFA-based treatment and compared to the same indices determined in an analogous way when the FFAP is applied. If a power plant equipped with a condensate polishing unit intends to apply a FFA/FFAP for preservation during a shutdown only, the condensate polishing plant should be bypassed during the period of FFA/FFAP dosage.

In TGD [11] the attention is also brought to safety and environmental issues. FFA and FFAP are chemicals, and thus they should be handled as described on the Material Safety Data Sheet (MSDS), which should be provided by the chemical supplier. The MSDS should be fully compliant with current legislation. The discharge regulations for waste waters containing FFA/FFAP has to take into account that FFAP can contain carbon- and nitrogen-based materials that can further increase the TOC and total nitrogen content of the blowdown.

One of important question when applying FFAP is the impact it has on the functionality of sensors [12]. This is due to the fact that FFA may create a film on the surface of sensors used for automatic
chemistry control. Under laboratory conditions, the impacts of three FFAP were studied. With all three FFAP, no interference was observed for pH, sodium, as well as for the Clark-type oxygen probe [11]. Oxidation reduction potential (ORP) probes were affected by all the FFAP tested, and it has also been observed two out of three tested FFAP showed coating effects on conductivity probes [11].

The main requirements for the quality of water and steam when using FFA and FFAP is that it should be within limits of other IAPWS technical guidance documents [13-18]. In cases where FFA is used with other alkalizing amines AVT(F) [19], the water and steam chemistry limits should be those in the IAPWS TGD on AVT(O) [15, 20].

Prior to the application of FFA/FFAP it is suggested to

- analyse the internal surfaces of the water/steam circuit on the presence of deposits and effectuate a chemical cleaning if needed;
- analyse the quality of the coolant before FFA/FFAP application, especially the concentrations of iron as well as copper and aluminium if its alloys are present in the circuit.
- The following locations and parameters should be monitored as a minimum: feedwater pH, oxygen, and CACE; drum pH and CACE; and main, reheat, or HP steam sodium and CACE.
- The sampling and analyses of corrosion products may be effectuated with respect to the document [18]. According to this TGD the samples should be taken only during steady high load conditions that have been maintained for at least 3-4 hours and not at the same time each day.

According to the technical guidance document of IAPWS [11], the FFA residual should be controlled at all available sample points because of the different distribution ratios, volatility, and adsorption/desorption processes. The following spectrophotometric methods are proposed in order to analyse the FFA concentrations: methyl orange extraction and xanthen dye reaction (Rose Bengal, Eozyn).

Another important question is the dosage level of the reagent. As FFA are adsorbed as a hydrophobic film onto the available steam/water internal oxide surfaces, the objective of a treatment with FFA/FFAP is to establish as complete a film as possible on these internal surfaces. The required initial dose of the reagent will depend on metal surface properties especially the presence of deposits, the FFA concentration in the reagent, and thermal decomposition of other components of FFAP at high temperatures. Usually the inner surface of the water/steam cycle can only be estimated, therefore the dosage should be regulated according to the concentration of FFA in turbine condensate. The FFA/FFAP are advised to be fed proportionately to the feed water (or make up water) flow. The location of dosing points of FFA/FFAP is determined by the type of power plant and the cycle scheme. For most of power plants single injection point at the condensate pump discharge is used. The alternative dosing location may be at the boiler/HRSG feed water pump inlet. However, if FFAP contain non-volatile components such as polycarboxylates, sodium hydroxide, or phosphate according to this technical document [11] the dosage of the reagent should not be effectuated into the feedwater because this is the source for attemperation water. In these cases, they should be dosed into the drum.

4. Conclusion
The evaluation of the current technical guidance documents on the application of FFA/FFAP shows that the most complete description of the properties of film forming amine products, the conditions of its application and the required qualities of water and steam are included in [11], before the implementation of any FFAP it is necessary to have the information about the comportment of all its
components in water/steam circuit; the dosage of FFAP depend on the composition of the reagent, the plant equipment and its operational conditions.

5. References

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