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Technical Guidance Document: Application of Film Forming Substances in Industrial Steam Generators

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Summary

This Technical Guidance Document addresses the use of film forming substances in the water/steam cycles of industrial steam generating plants.

In order to control corrosion throughout the water/steam circuits of industrial steam generating plants, it is essential for the operator of the plant to choose and optimize a chemical treatment scheme that is customized to that plant. IAPWS has provided guidance on the use of volatile treatments as well as for phosphate and caustic treatments; this document addresses the use and application for the range of chemicals referred to as film forming substances (FFS). As well as providing background information on FFS, the document includes guidance in Section 8 for determining if a FFS should be applied, the tests required before application, the locations for the addition, the optimum dosage level, and tests to determine the benefits of applying FFS. It is emphasized that this is an IAPWS guidance document and that, depending on local plant requirements, the application of FFS will need to be customized (Section 9) for each industrial plant depending on the actual conditions of operation, the equipment and materials installed, the condenser cooling media, and applicable regulations.

This Technical Guidance Document contains 58 pages, including this cover page.

Further information about this Technical Guidance Document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS (Dr. R.B. Dooley, bdooley@iapws.org) or from http://www.iapws.org.

Contents

1. Nomenclature and Definitions

Term	Alternative or Acronym	Definition
Air-Cooled Condensers	ACC	System to condense steam from a turbine by air cooling
All-Volatile Treatment	AVT AVT(R) AVT(O)	Conditioning regime in which only volatile alkalizing agents are added to the feedwater (commonly ammonia, but volatile amines may also be employed) May be either: Reducing conditions (added reducing agent) or Oxidizing conditions (residual oxygen present)
Alkalizing Amine	Neutralizing Amine	Amine added to the water / steam cycle to raise the pH in the water and steam phase
Chemical Abstracts Service Number	CAS-No.	Internationally used number to identify chemical substances
Condensate		Water that derives from condensation of steam after expansion in a steam turbine and passage through a condenser or process heat exchanger
Condensate Polishing Plant	CPP	System containing ion exchange resins to purify condensate. Can also include a filtration system
Condensate Pump Discharge	CPD	Outlet of condensate pump (typically at over-pressure)
Conductivity	Specific Conductivity Direct Conductivity	Electrical conductivity of the water sample as measured directly [1]
Conductivity After Cation Exchange	CACE Cation Conductivity Acid Conductivity	Conductivity of a water sample after passage through a strongly acidic cation exchanger in the hydrogen form
Caustic Treatment	CT	Involves addition of NaOH to the boiler or HRSG evaporator
Degassed Conductivity After Cation Exchange	Degassed Cation Conductivity DCACE	Conductivity after cation exchange of a sample from which volatile weak acids (predominantly carbonic acid) have been stripped
Dissolved Organic Carbon	DOC	A measure of dissolved organic components in the water or steam
Feedwater		Water that is being pumped into a boiler or HRSG to balance the steam production

Term	Alternative or Acronym	Definition
Film Forming Amines	FFA	Defined chemical with film forming properties based on an amine. (The three FFA are defined in Section 3)
Film Forming Amine Product	FFAP	Commercially available products containing a film forming amine (FFA) as the FFS
Film Forming Substance	FFS	Defined chemical with film forming properties which could be amine-based or non-amine-based
Film Forming Product	FFP	Commercially available products containing film forming substances which are not amine-based
Flow-accelerated Corrosion	FAC	Accelerated corrosion of carbon steel components in fossil plant feedwater systems and HRSG evaporators and economizers as result of the flow-induced thinning of the protective oxide (magnetite) on surfaces
Heat Recovery Steam Generator	HRSG	Plant that generates steam using heat transfer from the exhaust gas of a combustion (gas) turbine
Industrial Plants		Examples: refineries, pulp and paper, chemical industry, food processing dairies, sugar industries, hospitals, and other delineated in Section 5
Once-through boiler or HRSG	Benson Boiler	Boiler in which output steam is generated from input water by complete evaporation. There is no recirculation of boiler water
Oxygenated Treatment	OT Combined Water Treatment, CWT	Conditioning regime in which alkalizing agents and oxygen are added to the feedwater
Phase-transition Zone	PTZ	Region in low pressure steam turbine where superheated steam changes to moisture
Phosphate Treatment	PT	Conditioning regime for drum boilers in which alkalinity is achieved by dosing a sodium phosphate compound or blend of compounds to the boiler water
Total Organic Carbon	TOC	A measure of total organic components in the water or steam

2. Introduction: Purpose of Document and How to Use It

The purpose of this IAPWS Technical Guidance Document (TGD) is to provide guidance on the application of Film Forming Substances (FFS) to assist industrial steam generator plant operators in choosing, applying, monitoring, and ensuring optimum usage of these chemicals in minimizing the risk of possible equipment damage and loss of efficiency, and in maximizing plant reliability. Section 8 contains this guidance. Section 9 indicates how to customize the guidance to many different industrial plants. The other sections provide important background information.

This TGD must not be taken as IAPWS support for any commercial products. The guidance document can form the basis of, but should not restrict, other derivative guidelines around the world.

Previously, IAPWS has published a number of Technical Guidance Documents (TGDs) for fossil and combined cycle plants [2-7]. These provide guidance for instrumentation/control, volatile treatments (AVT and OT), phosphate and caustic treatments (PT and CT), steam purity, corrosion product sampling and monitoring, and carryover. There is also a TGD on Application of Film Forming Amines in Fossil, Combined Cycle, and Biomass Plants [8]. Using these TGDs, the development of optimum cycle chemistry guidance can be achieved for fossil and combined cycle / HRSG plants as well as for biomass plants. Each TGD contains a number of base cases for the most common plant configurations and equipment; importantly, the documents also include a number of customizations that may be required for each plant.

This TGD includes new guidance for the application and uses of film forming substances (FFS), which are being applied to industrial steam generation plants worldwide. There is currently much misunderstanding, lack of clarity, and concern about their application for continuous operation as well as for shutdown/layup protection. This TGD includes not only some of the important scientific background but also the key guidance steps in Section 8 for applying FFS to these plants, and a number of customizations to the base cases in Section 9.

It is emphasized that this is an IAPWS Technical Guidance Document representing the cumulative experience of the IAPWS Power Cycle Chemistry (PCC) Working Group (with representation from 24 countries), and as such should be regarded as consensus guidance for the application and usage of film forming substances (FFS) in industrial steam generation plants. Section 8 of this document provides guidance for the user/operator on determining if these products can be applied to a plant, how they should be applied and monitored, and the procedures that can be used to determine the benefits of the application. This guidance document can form the basis of, but should not restrict, other derivative guidelines around the world from equipment manufacturers and chemical supply companies. Experience has indicated that, depending on local requirements, the normal or target values for volatile, phosphate, and caustic treatments presented in the tables of the previous TGDs [4, 5] will provide good reliability and plant availability if they are customized for each plant depending on the actual conditions of operation, the equipment installed, the materials used in different parts of the cycle, and the condenser cooling media.

It is emphasized that, although this TGD provides guidance for the application of FFS to these industrial plants, the IAPWS guidance should not be considered as manufacturer's or chemical supply company's guarantees. Each manufacturer and supplier should provide guidance representing the plant as designed and the FFS chemical composition as manufactured, and these may be slightly different than the operating guidance provided in this document. Also, Section 9 of this document provides a number of customizations for varying industrial plant designs, equipment, and materials.

The application of FFA/FFAP in fossil, combined cycle, and biomass plants is covered in detail within the IAPWS Technical Guidance Document TGD8-16 [8]. It should also be mentioned that FFS are frequently used for the conditioning of closed cooling or heating systems, but that application is not included in this TGD or in TGD8-16.

3. Terminology

IAPWS recognizes that film forming substances (FFS) have been cited in the literature as both chemical substances with specific hydrophobic film forming properties and commercial products containing these chemical substances. In the past film forming substances were sometimes misleadingly referred to as film forming amines even when they were non-amine-based. This has led to much confusion and misunderstanding in the literature, so IAPWS has standardized the following terminology:

- Film Forming Substance (FFS): Film Forming Substances describe defined chemicals with film forming properties. They adsorb onto the water/steam surfaces of a plant. FFS could be amine-based or non-amine-based.

- Film Forming Amines (FFA): defined group of organic substances with specific functional groups. Because the chemical definition covers a wide range of amine molecules, this TGD lists three substances, which have been the subject of intensive research, and where significant application experience is available. The FFA listed in this TGD are the following three chemicals that are defined with a unique numerical identifier assigned by Chemical Abstracts Service (CAS):

Octadecylamine	(ODA)	CAS-no.:	124-30-1
Oleylamine	(OLA)	CAS-no.:	112-90-3
Oleyl Propylenediamine	(OLDA)	CAS-no.:	7173-62-8

- Film Forming Amine Products (FFAP): Commercially available products which contain a FFA as the FFS. They can also contain further substances such as alkalizing amines, emulsifiers, reducing agents, and dispersants (e.g., polycarboxylates). The operator will need to ask the supplier of the commercial product whether the FFA is included in the listing above.

Examples of alkalizing amines are listed below. They are defined with a unique numerical identifier assigned by CAS:

2-Aminoethanol (Monoethanolamine)	CAS-no.:	141-43-5
Cyclohexylamine	CAS-no.:	108-91-8
2-Amino-2-methylpropanol	CAS-no.:	124-68-5
2-Diethylaminoethanol	CAS-no.:	100-37-8
Morpholine	CAS-no.:	110-91-8
3-Methoxypropylamine (MOPA)	CAS-no.:	5332-73-0

- Film Forming Products (FFP): This term was used in IAPWS TGD8-16 [8] to summarize all commercially available products in this class which do not contain film forming amines (FFA). The exact chemistries of these FFP are proprietary and can cover a wide range of molecules. Therefore, specific chemical guidance, e.g., with regard to analysis or dosage, cannot be fully provided in this TGD for industrial plants, and the guidance delineated specifically for FFA/FFAP may not be applicable to FFP. Also, in the past FFP were referred to generally as film forming amines so the reader must be careful when reading literature.

4. Introduction to Film Forming Substances (FFS)

IAPWS TGDs [2-8] are applicable for most fossil, combined cycle, and biomass power plants and for the conventional treatment methodologies of volatile (AVT and OT) and solid alkali (PT and CT) and film forming amines. Alkalizing amines have been applied worldwide as extensions to these treatments or as standalone treatments. Film forming substances (FFS) have been introduced into the market, and their use is continuing to increase. Unfortunately, because there are no international guidelines or limits for successful application for these chemicals to industrial steam generation plants, there has been much misunderstanding and confusion for the operators of exactly what these chemicals can achieve when applied. In some cases, there has been damage and failure of generating equipment due to misapplication and/or lack of monitoring and control. If plants have not previously made thorough assessments of the chemistry used, the consequences of using a FFS cannot be clearly demonstrated. This IAPWS TGD is aimed at filling this gap and providing answers to the most common and most important questions asked by industrial plant operators.

The technology provided in this TGD is applicable to industrial steam generation plants.

Objectives of this TGD

- To provide guidance on whether a FFS can be used and is an option for a particular industrial steam generation plant;
- To provide guidance on how to choose a FFS for a particular situation (operation or shutdown);
- To provide guidance on how to use, optimize, and monitor FFS in industrial steam generation plants;

- To consolidate the knowledge and experience gained from using FFS in the 24 countries associated with IAPWS;
- To provide initial general advice and suggestions for application in industrial steam generators.

Questions and Confusion Associated with the usage of FFS (e.g., possible technical risks)

As already mentioned, there is currently confusion and no international guidance on deciding whether to use a FFS in an industrial steam generation plant and whether there will be any consequences, impacts, or influences on plant operation.

Some of the key questions being asked internationally and that will be addressed within this IAPWS TGD include the following:

- What are FFS and what can they accomplish for industrial steam generation plants? (See Section 5)
- What may be the consequences of moving from the conventional treatments of AVT(O), OT, and AVT(R)? (See Section 8.1)
- Is FFS treatment compatible with other treatment programs? (See Section 8.1.1)
- What needs to be monitored before application of FFS (how to conduct a baseline test to determine whether any benefits will accrue)? (See Section 8.2)
- How to monitor and control FFS treatment. (See Sections 5.1.6, 8.3, and 8.5)
- How to determine if the FFS is successful and providing the intended benefit. (See Section 8.6)

5. Background Information

This section provides some of the available background information relating to the use of film forming substances in industrial plants. An exhaustive listing of industrial plants cannot be provided, but some identified in Section 9 include: refineries, petrochemical, pulp and paper, chemical industry, food processing, dairies, sugar industry, hospitals, universities, laundries, steel and metal mills, electrode boilers, ammonia, waste incineration plants, and district heating. Before applying any product, the legal requirements of the chemicals should be verified.

It is intended to give a fairly comprehensive survey of the available information and of the application experiences. The section distinguishes between film forming amine (FFA) and products (FFAP) (5.1), and film forming products (FFP) (5.2). The literature cited in this TGD has been selected for this purpose but does not claim to be exhaustive.

5.1 Background Information on Film Forming Amines and Products

This section gives a fairly comprehensive survey of the available scientific information on FFA, such as the recent report on FFA in the water/steam cycle [9], and of the application experiences.

5.1.1 Definition of Film Forming Amines

Film forming amines (FFA), which are a family of chemical substances, are misleadingly referred to as fatty amines or polyamines [10-12]. Polyamines are molecules with a saturated carbon chain containing more than two (poly) amino groups. The term “fatty amine” refers to the fact that this group of chemicals is derived from fatty acids [13]. So, the term polyamine refers to the nomenclature of the molecular structures, fatty amine describes the derivation of the compounds, and the term “film forming amine” describes the characteristics of the substances. “Film forming amine”, “polyamine”, as well as “fatty amine” summarize a group of organic molecules which overlap partially, but their definitions are completely different. Film forming amines typically contain the following functional groups:

- One or several primary and/or secondary amine groups
- Aliphatic carbon chain (10 to 22 carbon atoms long), saturated or unsaturated.

With regards to FFA, this TGD is referring only to the substances listed in Section 3, which have been the subject of intensive research and where significant application experience is available. The information and suggestions given in this TGD may not be directly transferrable to all FFS delineated in Section 3.

5.1.2 Application

Film forming amines are solid or paste-like materials and they are sparingly soluble in water. They are applied as solutions, emulsions, or suspensions in water and can be blended with alkalizing substances, such as ammonia, alkalizing amines, sodium hydroxide, or phosphate. The dosage can be as a single component or as a blend of different substances.

The objectives of a FFA treatment include:

- Corrosion reduction in continuous operation;
- FAC minimization (single- and two-phase variants);
- Minimization of corrosion product transport from corrosion and FAC situations;
- Formation of clean, smooth heat transfer surfaces;
- Corrosion protection during shutdown/layup.

The formation of hard scales such as calcium carbonate or silicates due to poor water purity cannot be prevented, and it is currently not clear whether such scales can be (partially) removed with a treatment of FFA/FFAP alone.

5.1.3 Advantages and Benefits

Not all advantages and benefits are applicable to both FFA/FFAP and FFP, and it is not possible to provide generalizations. When a specific issue in the plant needs to be addressed, the chemical supplier of the product should be able to show detailed results from other plants and/or research results.

Some of the possible advantages and benefits of using FFA can be delineated as follows:

- Clean and smooth heat transfer surfaces;
- Removal of loosely bound existing deposits from heat transfer surfaces and steam turbine blades; however, the transport of these deposits must be managed or else they could result in increased deposits and failure in evaporators;
- 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;
- Lower concentrations of corrosion products, e.g., in feedwater (the reader is referred to Section 8 where monitoring is required to confirm);
- Reduction of FAC, including two-phase FAC in HRSGs and ACCs;
- Lower release of corrosion products during startup;
- Applicability to many different systems;
- Improvement of heat transfer.

Some of these are discussed further:

FFA as Corrosion Inhibitors
The inhibitor effect is accomplished by the formation and maintenance of a very thin non-wettable film on the surface of the industrial steam generator plant equipment. In general, the film acts as a barrier between the metal surface and the water/steam phase. Several reports are summarized in [14-17] which show that FFAP have an impact on several corrosion mechanisms. Laboratory test data as well as field tests have demonstrated that for uniform and localized corrosion (flow-accelerated corrosion and crud-induced corrosion [18]) FFA/FFAP may have a protective effect. Furthermore, reduction of chemistry-influenced tube failures has been reported in practical applications [19, 20].

Supporting the Formation of the Metal Oxide Layer
In all power generation applications where metal surfaces are exposed to water/steam, there will be a protective oxide layer which will vary in composition **depending on the equipment material and the operational conditions**. FFA adsorb onto the metal oxide surfaces and thus form a physical barrier between the metal oxide/deposit and the water or steam, providing additional protection for fossil, combined cycle, and biomass power plants, and also other industrial plants.

Reduction of Corrosion Product Transport
The impact of a FFA-based treatment on corrosion product transport can be monitored by quantitative and qualitative criteria. The measured iron and/or copper levels at key sampling locations should be reduced or at least kept to the same level as with the previous treatment (see Sections 8.2 and 8.6). Inspections of the system should result in improved cleanliness and appearance of the systems. A simple test for hydrophobicity during downtime inspections can be an indicator of general corrosion protection in a particular

area of the system. The use of other methods, including corrosion coupons, can help determine on-line / off-line effectiveness. It should be noted that non-hydrophobicity does not necessarily mean non-protection.

Due to the interaction of the amino groups with oxides, FFA will gradually remove loose material (corrosion products) from metal surfaces and provide cleaner surfaces. This oxide transport has been reported in many practical applications [21, 22].

Other Benefits
FFA may provide **improved protection** during normal operation and limited short-term benefits during abnormal operational circumstances. These conditions could be ingress of contaminants, from the demineralized water plant due to malfunction during resin regeneration or from surface water condenser leakage. Both require immediate action to minimize asset damage. It should be noted that **the limits of protection strongly depend on the specific conditions**.

5.1.4 Disadvantages / Critical Aspects

Some of the disadvantages for FFAP can be delineated as follows:

- Thermal degradation and formation of low molecular weight organic acids and the risk of masking anionic contamination (such as chloride and sulfate from a condenser leak) measured by CACE in condensate, feedwater, and steam;
- Lack of knowledge on the impact on condensate polishing plants (see Section 9.10);
- Lack of knowledge on the impact on reverse osmosis (RO) (see Section 8.1.2).
- Incomplete scientific knowledge;
- Risks related to overdosage;
- Increased levels of deposits on boiler/evaporator surfaces and tube failures due to under-deposit corrosion.

Some of these are discussed further:

Degradation Products (see also Section 5.1.5)
Organic substances such as FFA and organic components in FFAP are susceptible to thermal degradation at high temperatures. This results in low molecular weight organic impurities, mainly organic acids and carbon dioxide. It is known that both can reduce the pH of condensed steam, and, if this is not compensated for by a proper water treatment program, a higher rate of corrosion may occur, including stress corrosion cracking [23].

The impact of low molecular weight acids on corrosion due to possible pH reduction has been investigated. It was concluded that the specific corrosion effect of organic acids and carbon dioxide is less relevant for real service conditions if the local pH is maintained sufficiently [23]. However, these acids can lead to increased level of CACE, which is discussed in the next section.

High CACE

FFAP under boiler/steam generator conditions are susceptible to thermal degradation, and the low molecular weight organic acids will contribute to CACE. Depending on dosage levels, their application (together with thermolysis of alkalizing amines) may lead to CACE levels that are higher than the suggested IAPWS Steam Purity limits [6] and the guidance set by the steam turbine manufacturers.

FFAP may also temporarily increase the CACE by enhancing the release of impurities accumulated within the surface oxide layers. This effect is also often seen when changing chemistries, for example from AVT(R) to OT.

Overdosing

The dosing and control of the FFA and FFAP are critical aspects (see Sections 8.3 and 8.4 for guidance). The key to the control of freely available FFA is to keep its concentration constantly low. Several physical properties of the aqueous phase will change when micelle formation begins at the critical concentration [24, 25]. It has also been reported that constant overdosing of FFA can lead to the formation of "gunk" balls (clumps of gel-like material) which have the potential to form blockages of vessels or tubes [19, 26].

5.1.5 Basic Properties / Mode of Action

Alkalinity

FFA, as all amines, are bases and therefore increase the pH and conductivity by dissociation in water. Due to the low concentration of FFA required, the impact on pH and conductivity is negligible compared to alkalizing agents (ammonia, alkalizing amines, etc.) [27, 28].

Adsorption

The intended effect of FFA is the strong adsorption on metal oxide surfaces [14, 28-30] by a combination of physical and chemical bonding, and thus modification of the oxide properties.

The adsorption takes place on metal oxide surfaces of steel, copper, stainless steel, as well as aluminum. The results of studies suggest a rapid initial adsorption of a very thin layer (mono molecular layer) followed by a second slower adsorption step and the formation of a multilayer. The amount of FFA adsorbed onto the surface is dependent on the FFA molecular structure, temperature, and composition of the surface [31-33]. The adsorption isotherm has been described with the Langmuir model [30], whereas the Henry model has been applied in other studies [29, 34].

Furthermore, FFA adsorbs onto metal oxides as has been indirectly demonstrated [35]. Suspensions of magnetite particles and stainless steel particles were cationically stabilized over a broad pH range, as shown by zeta potential measurements. At low concentration of FFA a reduction of magnetite deposition occurs, whereas at high concentrations a coagulation of the particles can be observed, illustrating the importance of avoiding overdosing of the FFA.

It is generally accepted that the long alkyl chain forms a hydrophobic barrier between the metal oxide surface and the water. The corrosion protection has been studied by electrochemical techniques as well as the film formation, demonstrated by characteristic two-loop Electrochemical Impedance Spectra [15-17, 36]. The hydrophobic barrier film has been confirmed on the surface of laboratory samples by spectroscopic methods, especially Infrared and Photoelectron Spectroscopy [25, 30, 37, 38], and on samples from water/steam cycles [39-41].

FFA will also adsorb on many plastics and glass surfaces, which must be taken into consideration for analysis by grab samples. It will also adsorb onto surfaces of on-line instruments and may compromise measurements (see Sections 5.1.6 and 8.1.4).

Stability of the Film

The durability of the film under the different conditions encountered in the water/steam cycle is not completely understood, but practical experience shows that a system with an established film is protected for a shutdown period of several weeks under wet storage.

Several studies in the laboratory under controlled conditions are available on the corrosion protection of FFA. The film formed on the oxide surface is stable and not significantly removed from stainless steel, carbon steel, and copper substrates after several days of exposure to oxygenated FFA-free de-ionized (DI) water [14]. Exposed surfaces showed no sign of corrosion. A sharp reduction was reported of the corrosion rate by ODA in DI water [42] both for metallic blank samples and samples with an oxide layer. Furthermore, corrosion under slightly acidic conditions (oxygenated water at 80 °C) was significantly reduced for a steel specimen prefilmed with FFA compared to untreated ones. Prefilmed steel coupons were exposed to three different air storage conditions: dry, constant temperature; dry, varying temperature; and humid, varying temperature. In contrast to the untreated steel coupons, the prefilmed coupons did not show any corrosion after one year of storage.

Volatility

FFA are steam volatile, and their volatility depends on their chemical structure with monoamines being less volatile than diamines [40, 43]. Due to their volatility, FFA can protect evaporator surfaces, the condensate system, and the steam turbine at locations with high steam moisture. It is not fully confirmed whether film formation also takes place in areas of superheated steam; sometimes steam circuits are found protected possibly because of the presence of water in the steam during startups and shutdowns. Studies in a pilot boiler under controlled conditions clearly showed the presence of FFA on tubes exposed to superheated steam, thus strongly indicating the adsorption of FFA on metal surfaces also from the gas phase [41].

Thermal Decomposition Products

The thermal stability in aqueous solution of two of the three FFA molecules listed in Section 3 has been studied and published. The thermal effect of ODA starts at a temperature of 80 °C. At temperatures above 450 °C, the molecule completely decomposes to carbon dioxide, methane, hydrogen, and ammonia [24]. ODA also combines to form di- and tri-ODA by elimination of ammonia. OLDA has been reported to be stable at approximately

300 °C. No organic acids, such as acetic or formic acid or lower organic amines, could be detected. The thermal stability of OLDA was also studied with thermogravimetric analysis and pyrolysis gas chromatography mass spectrometry. The maximum temperature was 500 °C. No evidence of decomposition was reported [44].

Besides FFA, FFAP can contain organic alkalizing agents and dispersants. This makes the prediction of potential degradation products more complex. The thermal degradation of a number of organic alkalizing amines (ethanolamine, morpholine, cyclohexylamine, dimethylamine, and 3-methoxypropylamine) has been systematically studied, and these amines are sometimes used as alkalizing agents in FFAP. It has been found that these amines undergo a cationic as well as an anionic degradation. The main product of the cationic degradation is ammonia, while anionic degradation leads to the formation of acetic and formic acids. Minor breakdown products were propionate and glycolate [45].

The main decomposition products may vary depending on the different components of the FFAP and the system conditions (temperature, pressure, and exposure time). The reported decomposition products are carbon dioxide, small organic acids, ammonia, low molecular weight amines, octadecylamine, and substituted diamines. Minor breakdown products may be propionate, glycolate, oxalate, citrate, and benzene [46].

Besides these studies, some detailed measurement programs were performed using Liquid Chromatography – Organic Carbon Detection (LC-OCD) and ion chromatography (IC) to measure thermal decomposition products in steam generators treated with FFAP [28, 47-49]. The main decomposition products found were carbon dioxide and glycol. Small organic acids were only found in traces and were predominantly acetic acid.

As discussed in Section 8, prior to a new application, each FFAP supplier should provide the operator with the FFAP decomposition products and, more importantly, the impact of these products on the steam CACE and on the pH of early condensate especially at low steam moisture.

Heat Transfer

FFA form a film on the inner surfaces of the water/steam cycle and thus also on the heated surfaces. Due to their surface active properties, FFA feature a theoretical potential for improving the heat transfer in nucleate boiling near metal surfaces. The intensifying impact of FFA on bubble evaporation was qualitatively demonstrated [35] and quantitatively measured compared to phosphate-based water chemistry [50]. Significantly higher heat transfer coefficients have been determined for FFAP-treated steel tubes compared to phosphate-based treatment.

The heat transfer coefficient was determined on copper surfaces as a function of ODA concentration [51]. An improvement in heat transfer coefficient was measured over the tested concentration range. Furthermore, an improvement of heat transfer was reported in the condensation process [52] due to the improved droplet formation on the hydrophobic surfaces in the condenser.

The influence of FFA on theoretically possible boiling crisis (burn-out) in steam boilers has been studied independently [53, 54]. There was no significant influence of FFAP on the critical heat flux density at 2 bar operating pressure compared to phosphate treatment or without treatment. Both metallic tubes and tubes with a magnetite layer were examined [54].

Subcooled boiling after cold and warm starts was studied over time and as a function of FFA dosage, applying a heat flux density up to 1000 kW/m^2. The curves for tube temperature and heat flux density as a function of time show the same form for FFAP as obtained during analogous tests carried out with phosphate treatment, or with FFA overdosage.

5.1.6 Monitoring Concepts

Monitoring and Control of FFA Dosing
FFAP dosing rates should be monitored by measurement of the residual FFA concentration in the sampled water. Different test methods are available to accurately determine the amount of FFA in the water. In industrial plants, organic ingress can take place that might lead to an interference. In Section 8.5.1 of this TGD, the two most applied methods are described. The FFA residual should be controlled at all available sample points because of the different distribution ratios, volatility, and adsorption/desorption processes. Due to the intended adsorption of the film forming amine on the metal oxide surfaces, there is no straightforward correlation between the FFA added to the system and the resulting concentration in the water sample. Nevertheless, most FFA and FFAP are dosed as a function of flow.

Control of the cycle chemistry using pH, conductivity, or TOC (total organic carbon) measurement is not accurate enough for monitoring dosing of FFA.

Qualitatively, the presence of a film can be demonstrated by the lack of wettability of the metal surface. This is the most common and easiest method to qualitatively detect the FFA on a metal/oxide surface. However, hydrophobicity sometimes cannot be observed, e.g., in case of a rough surface with porous iron oxide deposits, even though FFA is present on the oxide surface. Reference [41] describes a laboratory method to semi-quantitatively determine FFA on the inner surfaces of water-steam cycles. This non-destructive method can be applied during system outages. The time until complete film formation depends on many parameters and cannot be predicted. Some further discussion is in Section 8.3.

Total Iron/Copper Monitoring
In the IAPWS TGD6-13(2014) *Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants* [7], sampling strategies as well as several analytical methods are described. The presence of FFA as well as FFAP does not interfere with the analytical methods described in [7] for the determination of total iron/copper, nor do the analytical methods change the FFA/FFAP in the sample. In Tables 6 and 7 of that TGD, AAS (Atomic Absorption Spectroscopy) and ICP-AES/MS (Inductive Coupled Plasma followed by Atomic Emission Spectroscopy or Mass Spectroscopy) are listed as suitable analytical

methods. The colorimetric reaction based on ferrozine is not disturbed by FFA/FFAP if a previous digestion step is performed.

Conductivity and pH Measurement

Among the main tools to control the cycle chemistry in general, as well as during dosage of FFA and FFAP, are conductivity and pH measurement. If FFA or FFAP is dosed, the following impacts should be considered:

- Impact of the FFA on the measurement equipment. Laboratory experiments with three different FFAP showed that pH measurement using a glass electrode was not affected [55]. But for some FFAP, the coating effect of the conductivity probe led to drift in the reading. These effects are discussed in more detail in Section 8.1.4.
- pH calculation errors due to unknown composition of FFAP. Temperature compensation of conductivity measurement and pH calculation is discussed in this Section.

The result of a conductivity measurement is always expressed as a temperature-compensated value at 25 °C. Most transmitters use fully automatic temperature compensation models. Such models normally assume a dominant ion pair in the water. For example, a temperature compensation model for "ammonia" expects that only the ammonium ion will be present, besides the dissociated water ions (H_3O^+, OH^-). FFAP sometimes contain mixtures of alkalizing agents or the FFA is dosed together with ammonia. So, using FFAP leads to a more complex mixture of different ions in the water.

A comprehensive study concluded that temperature compensation models within the range from 25 °C to 50 °C depend only slightly on the chemical composition of the sample. The reason for this is that the quotients of the compensated and temperature-dependent equivalent ionic conductivity of all ions have similar values [56].

However, if conductivity measurement is used to calculate the concentration of an ion, knowledge of the chemical composition is mandatory. For example, pH calculation using differential conductivity measurement is one such application. The pH calculation uses the total conductivity and the CACE under the assumption that:

- Only one alkalizing agent is present;
- Contamination concentration is small compared to that of the alkalizing agent.

Additionally, such a calculation is only applicable within a narrow pH range from 8.0 to 10.5. FFAP can contain a high concentration of strong alkalizing agents other than ammonia. As mentioned in other sections of this TGD, it is most important to know the concentrations of all alkalizing agents in the dosed FFAP. Only with this information is it possible to apply the calculation [28, 57].

The concentration of freely available FFA in the water/steam cycle is generally small compared to the alkalizing agents and does not influence the calculation model.

5.2 Background Information on FFP

It is emphasized again that the information in Section 5.1 is specifically in reference to the use of FFA/FFAP. There is not the same detailed open or publicly available literature for most of items covered in Section 5.1 for the other FFS delineated in Section 3. This is particularly applicable to the FFP that are not amine-based. There is, however, significant application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFS for any application, then it behooves that plant to ask for literature backup and the same critical questions so that this knowledge is available before application. Answers should be provided by the supplier on each of the items in Section 5.1.

As discussed in Section 8, prior to a new application of any FFS, each supplier should provide the operator with substantive information on the properties of the FFS, such as the FFS decomposition products, volatility, adsorption behavior, and, more importantly, the impact of these products on the steam CACE and on the pH of early condensate, especially at low steam moisture. Especially, the supplier must provide all necessary information on the impact of the FFS on humans, plant parts, etc. in case of any sensitive use, such as in the food industry (see Section 9). Furthermore, the supplier must give a method for control and analysis of the FFS dosage.

Most importantly, the procedures provided for guidance in Sections 8 and 9 must be carefully evaluated for all FFS if applicable and, if necessary, adapted to the individual FFS chemistry. Alternatively, the operator who does not follow this guidance is potentially at risk of future failure and damage. As FFP cover a variety of chemical substances, the same potential risks exist.

5.3 General Suggestions on Legal Compliance

FFS are chemical substances or chemical preparations, and thus they are the subject of numerous regulations. When using FFS-based products, it is most important to be in full compliance with all relevant regulations. As these regulations vary from country to country, a detailed description of the regulatory aspects cannot be given in this Technical Guidance Document. Some important regulations cover the following aspects:

- Chemical inventory (e.g., REACH, TSCA);
- “Black” list (e.g., Substances of very high concern);
- Discharge;
- Working safety;
- Food application (e.g., for steam having direct contact with food, such as FDA 21CFR173.310).

It should be emphasized that this list is not exhaustive.

It is most important for the user of FFAP and FFP that the supplier of the product provides all necessary information in order to ensure regulatory compliance of the chemicals applied.

6. Description of Applications

FFS can be added to plants for a number of different reasons. This IAPWS TGD is applicable to all-ferrous industrial steam generation plants including a steam turbine, without a condensate polishing unit, and without sensitive use of steam: these represent the base cases. Plants that contain copper or copper-based alloys and other variants are addressed through customization in Section 9. The two main applications that are covered are continuous application when the plant is operating, and the conservation mode when the plant has to go into short-term or long-term shutdown/layup.

7. Chemistry Limits

The IAPWS guidance for plant control limits when using FFS is the suite of IAPWS TGDs [2-7]; the chemistry treatment will depend on the individual plant. The use of any FFS should not require a change of the IAPWS basic guidance except for the customization that should always be applied to any plant. There will be of course the need for monitoring and analysis before and after an application, as covered in Sections 8.2 and 8.6 of this TGD.

As already mentioned, the inclusion of alkalizing amines within FFS often causes an increase in the CACE especially in steam to the turbine, which relates mainly to the decomposition products as discussed in Sections 5.1.5 for FFA and should be considered for any FFP not amine-based as suggested in Section 5.2. Frequently, FFS are applied in combination with alkalizing amines only. The chemistry limits for the combinative treatment of film forming substances and alkalizing amines will be those in the IAPWS TGD on AVT(O) and OT [4].

8. Operational Guidance for Continuous Addition of a FFS

This section provides guidance for operators when applying FFS to industrial steam generating plants as a supplement to, or as a replacement for, the current chemistry regime. This is the base case for this IAPWS TGD, and it is applicable to all-ferrous industrial steam generation plants including a steam turbine, without a condensate polishing unit, and without sensitive use of steam. As such, the corrosion product sampling and analysis will for example only relate to the monitoring of total iron as per the IAPWS TGD [7]. If the plant contains copper alloys, then the base case should be customized through the use of Section 9.5. Other customizations in Section 9 include: a) plants operating with different temperatures and pressures; b) multi-types of steam generators; c) cooling water systems containing aluminum; d) plants with chloride contamination including seawater-cooled plants and plants providing steam for desalination; e) plants with air-cooled condensers; f) special boiler types; g) sensitive usage of steam; h) dilution steam treatment; and i) others.

As indicated in the IAPWS Steam Purity TGD [6], the FFS composition, including its percentage contribution in the commercial product, as used in a plant should be known by the operators. However, in most cases the FFAP and FFP composition is considered to be a commercial secret or proprietary information. A chemical supplier may not reveal the complete product and thus the composition may not be known 100%, so it is difficult to evaluate potential risks and the likely effect on the steam/water cycle limits (IAPWS TGDs [4, 5]). An alternate approach is to determine by sampling and analysis the decomposition products and evaluate if these might have a negative impact on the operation of the unit/plant.

Suppliers of FFS should have conducted independent materials and performance testing of their particular FFS blends that demonstrate their effectiveness in controlling the cycle chemistry as intended for a particular plant if applied under the recommended supplier instructions. This does not lessen the need for the supplier to provide the composition of the FFS. Information on the toxicity and ecotoxicity of the product should also be provided to ensure the operator understands any environmental aspects and to ensure legal compliance. These items are covered in Sections 5.3 of this TGD.

It is most important for the plant operator to know which film forming molecule is being applied and also any other compounds (alkalizing amines, dispersants, reducing agent, etc.) included in a blend, the purpose for their inclusion, and the result/benefit expected for the plant. As with any major treatment regime change, there is also a major requirement for an initial assessment of the plant prior to the use of an FFS (Section 8.2). For example, special care should be taken to develop an understanding of internal deposits on HRSG HP evaporators or conventional boiler waterwalls. Lack of such knowledge and poor monitoring and control can lead to failure, such as under-deposit corrosion (UDC), especially where heavy deposits were not identified or removed by chemical cleaning. This applies for any major change of chemistry and it is not specific for FFS treatments.

Some film forming substances are surface active and may slowly remove loose deposits but should not be used as a means of cleaning up heavy deposits in an operating boiler or HRSG because uncontrolled metal oxide transport is a major risk to future boiler reliability and tube failures. There may be risk of overdosing of FFS. For FFA/FFAP it is known and discussed in Section 5.1.4. The requirement to understand the level of internal deposits in terms of possible under-deposit corrosion and the need to chemically clean prior to an application of any FFS is discussed in Section 8.2. Therefore, if the condition of the water/steam cycle is not well known, an assessment prior to application of FFS treatment is needed, as discussed in Section 8.2. This baseline assessment is used to evaluate the success of the FFS treatment program.

The remaining sub-sections provide direct advice and guidance to the operator of a plant who is interested in changing to a FFS treatment. These subsections are directly valid for FFA/FFAP. For the use of FFP, careful evaluation of the applicability and, if needed, adoption to the specific chemistry of the FFP is an indispensable precondition.

8.1 Evaluating the Potential Benefits and Side Effects of Adopting a Plant Chemistry Program using FFS

The plant operator should ask a series of questions prior to changing to a FFS treatment regime. The first and foremost question should be "why is there a need to change?" If the plant is operating successfully within internationally accepted industrial plant guidance, and particularly meeting the corrosion product transport levels [7], then there should be an associated operating or economic benefit for the plant to change. This could relate to a change in the mode of operation with more starts and shutdowns. For industrial plants that do not operate within the IAPWS TGDs and/or have higher levels of corrosion products, there might be a corporate goal for future improved reliability, better shutdown protection, or long-term layup. In all cases there is a need to determine the possible benefits that will or could accrue and, most importantly, to acquire information relating to the concerns delineated in Sections 4 and 5 of this TGD. Sections 5.1 and 5.2 are particularly important if consideration is being given to application of a FFA/FFAP or to a FFP, respectively. Once a decision has been made to consider the use of a FFS, the important questions are: does the proposed commercial product contain an FFA listed in Section 3? If it does not, the information given in Section 5.1 is not valid. Furthermore, is it blended with a neutralizing amine and/or a dispersant, and/or other components? Questions should be asked about the thermal stability of any component contained within the blended product and whether it will be suitable under the operating conditions (temperature and pressure) of the plant. Not asking such questions or not receiving satisfactory answers from the supplier can result in an unknown chemical or chemicals being added to the steam/water cycle. The basic IAPWS rule is that if an unknown chemical with unknown degradation products is used at the plant, then relaxation of normal limits and action levels [4-6] is not allowed. One of the primary goals of this IAPWS TGD is to assist in this understanding.

8.1.1 Are FFS Treatments Compatible with other Treatment Programs?

FFS can be used as a standalone treatment or in combination with other treatment programs. When a FFS-based treatment is applied as a supplement to another treatment program, it is very important for the user to know if there are any incompatibilities and how such incompatibilities could affect the system to be treated.

The FFS may contain a wide variety of different chemical substances, as outlined in the introduction to Section 3 and in Section 9.2. Therefore, it is emphasized that a general statement of compatibility with other programs cannot be given in this TGD. The supplier of the FFS should provide this important information. The overriding actions for an operator are to know the composition of the FFS and to conduct a careful monitoring and assessment of the treatment program.

8.1.2 What Effects do FFS have on Plant Equipment and Processes?

Impact of FFS on Ion Exchange Resins
Information on the impact of FFS on ion exchange resins can be found in Section 9.10 of this Technical Guidance Document.

Impact of FFS on Reverse Osmosis (RO) Membranes
Reverse osmosis (RO) can be used for preparation of makeup water. In cases when the condensate is returned to the makeup water treatment plant, there is potential for the FFS to come in contact with the RO membranes. Studies on the impact of FFS on reverse osmosis membranes are not available. The adsorption of the FFS molecule on the membrane could cause membrane fouling. The supplier of the FFS should provide information on any detrimental effects of the FFS in contact with the membrane. Studies on the effect of FFS are pending.

8.1.3 Are there Special Safety and Environmental Issues?

FFS are chemicals, and thus they should be handled as described on the Safety Data Sheet (SDS), which should be provided by the chemical supplier. The SDS should be fully compliant with current legislation.

FFS contain organic molecules and, therefore, will contribute to the total organic carbon (TOC), and if they also contain amines there will be total nitrogen levels associated with the blowdown from the water/steam cycle. FFS can also contain other carbon- and nitrogen-based and eventually further heteroatom-based materials that can further increase the TOC, total nitrogen content and the relevant heteroatoms of the blowdown. The discharge regulation has to be taken into account accordingly (Section 5.3).

8.1.4 Impact on Functionality of Sensors

The application of a FFS results in the formation of a protective layer on the equipment surfaces. So, it is expected that the analytical equipment used to monitor and control the water/steam cycle will also be coated.

Film forming amines

Some field reports described problems with some measuring equipment and concluded the reason to be the filming/adsorption effect of FFAP [58].

Under laboratory conditions [55], the impacts of three FFAP on the following instruments were studied:

- Specific conductivity (SC);
- Conductivity After Cation Exchange (CACE);
- Degassed Conductivity After Cation Exchange (DCACE);
- Calculated pH (differential conductivity measurement);
- pH (ion-selective electrode);
- Oxidation-reduction potential (ORP);
- Sodium (ion-selective electrode);
- Oxygen (Clark-type sensor).

With all three FFAP, no interference was observed for pH, sodium (both ion-selective electrodes), as well as for the Clark-type oxygen probe. Oxidation-reduction potential (ORP) probes were affected by all the FFAP tested, and a coating effect was deemed to be responsible for the loss of sensitivity and the speed of response of the instrument. It has also been observed under laboratory conditions that FFA/FFAP can coat conductivity probes. Three FFAP were tested where one FFAP was based on ODA and two FFAP contained OLDA as the FFA. The two tested FFAP containing ODA and OLDA showed coating effects on conductivity probes. Surprisingly, no such coating effect could be observed with another tested FFAP also containing OLDA as the FFA. It appears that it is not necessarily the

FFA alone that can promote filming effects on conductivity probes but the combination with other substances in the FFAP. For CACE and DCACE measurements, the main observation was the early breakthrough of the cation exchange resin. It should be kept in mind that the error due to the coating of the probe for certain applications was negligible. However, the loss of sensitivity as well as response time on ORP probes warrants attention.

Other important sensors for plant operation, such as flow and level measurements, may also be affected by FFA/FFAP, but these effects have not been studied systematically.

Film forming products

It is emphasized that the information in the preceding sub-section of Section 8.1.4 is specifically in reference to the use of FFA/FFAP. There is not the same detailed open or publicly available literature for most of items covered in Section 8.1.4 for the other FFS delineated in Section 3. This is particularly applicable to the FFP which are not amine-based. There is, however, significant application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFP for any application, then it behooves that plant to ask for literature backup and the same critical questions so that this knowledge is available before application. Answers should be provided by the supplier on each of the items in the preceding sub-section.

8.1.5 Complete and Comprehensive Documentation

The supplier of the FFS product has to provide safety information, e.g., SDS, fully compliant with local, regional, and national regulations, and comprehensive technical documentation covering the relevant aspects, e.g., handling, dosage, storage, composition, analytical control, application, and discharge (see also Section 5.3). This documentation should be delivered in the country language or at least in English.

8.2 What does an Operator need to do before Applying a FFS?

It is extremely important that the key objectives and performance indicators are identified and monitored prior to and during the application of a FFS, just as it is for any major chemistry change on any plant. Historically, this has been the most common missing aspect in the application of FFS and has led to concern as any improvements and benefits provided by the FFS could not be quantitatively validated.

Furthermore, good knowledge of the current plant condition is important, such as the presence of thick porous oxide layers or contaminants, in order to judge the risk related to the intended change of treatment regime, as mentioned in the introduction to Section 8. Good knowledge of the plant condition as well as careful monitoring and control is essential in order to avoid failures and damage, as has happened in plants where no prior assessment had been made of such important aspects as deposit loading on boiler waterwalls and other inner surfaces.

The best way of determining the baseline is through measurement of the key indices for the cycle chemistry, especially total iron (and total copper and/or aluminum if the plant contains these metallurgies) under the conditions of the chemistry before the application of the FFS treatment. The key parameters from the IAPWS Instrumentation TGD [3] should be monitored in parallel and recorded. It is recognized that industrial plants might not have this level of instrumentation and will only be able to use grab samples. 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; condensate iron and copper and aluminum, if applicable.

Without the results from the baseline tests, there will be no ability for the plant to validate quantitatively that the addition of a FFS has provided any benefit. There could be an improvement or, in some cases, the key indicators of the plant chemistry could be worse.

Thus, the sampling and analytical facilities for monitoring total iron (and total copper) should be in agreement with the IAPWS TGD for Corrosion Product Sampling and Analysis [7]. IAPWS Target Values have been established for total iron (and for copper in mixed-metallurgy units) at various locations around the cycle. IAPWS Target Values for total iron (and total copper) at some of these sample points are provided for fossil, combined cycle, and biomass plants in Section 5 of the TGD [7] and could be applied also for industrial steam generators. The required analytical procedures are also delineated in Section 9 of [7]. The Corrosion Product TGD [7] suggests that the samples 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. The monitoring should last for at least one month prior to the FFS application to ensure that the metal/oxide surfaces within the various circuits are stabilized with respect to the previous chemistry program. This monitoring will take longer in a cycling plant. The frequency of sampling for monitoring should be considered with once per week as the minimum. Comparison of the measurements of total iron (and total copper) to the Target Values provides baseline values and an indication of the effectiveness or otherwise of the current treatment being applied and to be replaced with a FFS. The whole monitoring process with examples has been published [59]. Results of the baseline series of tests serve as the starting point from which effects of subsequent changes in treatment (addition of a FFS) can be compared and evaluated, both against the baseline readings and the Target Values for optimized treatment programs. In some cases, the Target Values for optimized treatment [7] may not be attained unless all the iron oxides are digested prior to analysis to overcome any FFS–oxide interaction. But even in these instances, improvement, as indicated by lower concentrations of total iron (and total copper) in the cycle, should be observed after the FFS regime is started.

IAPWS also recognizes that a number of organizations worldwide have used on-line monitoring of suspended solids using particle counters or turbidity measurement to provide an indicator of particulate iron. The relationship between online methods and the IAPWS TGD 6-13(2014) [7] methods are currently being investigated by IAPWS for flexibly operating plants. These methods could be used as trend monitoring for before and after application of a FFS.

Besides the baseline monitoring of the plant's water and steam circuits as indicated above, the condition of the internal surfaces of boiler waterwalls and other relevant inner surfaces of the water-steam cycle in terms of internal deposits should be assessed. It is well understood that thick deposits can lead to under-deposit corrosion (UDC). Poorly monitored and controlled applications of FFS have led to increased transport of iron in the cycle from these deposits. Applying FFS treatment without knowledge of the deposits on the high heat transfer surfaces could lead to problems if the precautions delineated in Section 8.3 of this TGD are not respected. Thus it is suggested, as with any major chemistry change, that samples be removed and analyzed prior to the application, and that consideration be given to chemical cleaning if necessary. The emphasis for this suggestion becomes most important for boilers/evaporators that have already experienced an UDC mechanism [60-62]. An IAPWS TGD [63] covers this aspect comprehensively for HRSG HP evaporators.

Additionally, with regard to inspections of the plant prior to application of a FFS, the condition of the water/steam cycle should be evaluated and recorded with regard to the following:

- Appearance and color of internal parts and surfaces;
- Occurrence and frequency of boiler tube failures;
- Amounts of sludge and loose deposits in drums, headers, deaerators, and condenser hotwells;
- General cleanliness of drums, evaporator tubes, turbine blades, etc., and identification of any tubercles and pits on the internal surfaces of pressure vessels;
- Time needed for startup after shutdowns and layup;
- Level of staining of produced goods in direct contact with steam;
- Performance of specific plant parts such as catalysts.

There is a large variety of parameters of importance for industrial steam generating plants. The above list is indicative but does not claim to be exhaustive.

Some other aspects that should be recorded prior to the application of FFS which can then be used after the start of an application for direct comparison and assessment of benefits:

- If the plant has experienced any form of FAC [64], the locations and wear rates should be known and recorded. As a FFS will influence the FAC mechanisms in single- and two-phase flow, these will provide important indicators for comparison and of benefits following the application. Positive results from FFS applications have been observed worldwide, especially for two-phase FAC in HRSGs and air-cooled condensers (ACC), but usually there has not been any quantification of the damage reduction.
- For units with ACC, the condensate total iron levels should be included in the baseline monitoring. A quantitative indicator of the FAC in the transport ducts and especially at the tube entries in the upper ducting should be known and recorded using the ACC corrosion index (DHACI) [65].

- If there is a condensate polisher in the plant cycle, then the key indicators of performance such as pressure drop should be documented.

It should be emphasized that, without the results from a baseline assessment, there will be no ability for the plant to quantitatively identify benefits and drawbacks of the addition of a FFS. Thus, the validation of the new chemical treatment program would have to be based on qualitative parameters only.

8.3 Determining Product Dosage Levels and Initial Usage of a FFS

As the FFS are currently supplied as proprietary chemicals, it is to be expected that each chemical supplier, even supplying the same basic chemical, e.g., FFA, delineated in Section 3, will have product formulation differences and different recommended dosages. This sub-section provides some general guidance for the plant operator.

As FFS, if the film forming molecule is steam volatile, are adsorbed as a film onto the available steam/water internal oxide surfaces, the objective of a treatment with FFS is to establish as complete a film as possible on these internal surfaces. For FFA the volatility is known (Section 5.1.5), but the volatility may not be postulated a priori for all other FFS. The required initial dosage is determined by the available surface oxide/deposit area, the surface properties such as porosity and roughness, the concentration and chemistry of active FFS injected, and the estimated thermal decomposition of the active chemical in high temperature/pressure plants. Because not all of these parameters are known, the exact quantity of FFS needed to establish the protective film cannot be accurately predicted. In many plants, the inner surface area of the water/steam cycle can only be estimated. Therefore, the analytical proof of the FFS in the water, e.g., condensate, is used to verify the distribution of FFS. If the dosage is not sufficient, the film formation will remain incomplete. This may also be the case for FFAs with no or very low volatility.

The cycle pH should be corrected, if necessary, with an adjunct feed of ammonia and/or alkalizing amine if used to maintain the feedwater pH within the IAPWS guidance [4] or other industrial plant guidance.

8.3.1 Film Forming Amines and Film Forming Amine Products

The control of dosage is carried out via the determination of the residual free FFA in the various samples taken around the steam/water circuit. Dosage of the FFAP has to be adjusted to achieve the specified value in the control samples, predominantly in the condensate. The dosage should be adjusted accordingly if the measured concentration is outside of the specified target range.

The following are some of the key features that operators should be aware of in developing an optimum dosage rate and during early operation with a FFA/FFAP:

- For most cycles, it is suggested that the FFA/FFAP is gradually introduced and increased to the target dosage. The initial dosage is usually based on a supplier's laboratory research studies including corrosion, volatility, basicity, etc., combined with practical experience. The results of these should be reviewed with the chemical supplier prior to initial application. This is to make sure that the FFAP to be used relates to the specific plant and to the materials contained within the condensate, feedwater, and boiler/evaporator circuits (all-ferrous or mixed-metallurgy).

- The FFA/FFAP should be fed proportionately to the feedwater (or makeup water) flow by an automatic dosing pump.
- The initial target dosage will probably be at the low mg/L (ppm) level as FFAP based upon feedwater flow. If an industrial power plant is starting a treatment based on FFA, it is quite normal that, for a time dependent on the plant, mode of operation, and dosage, no FFA will be detected in the condensate due to the adsorption of the FFA onto the metal / metal-oxide surfaces. The actual product demand will depend on the chemistry treatment (AVT(O), AVT(R), PT, or CT) being used prior to the application of the FFA/FFAP. The period also depends on the operational mode of the plant, i.e., whether it is operating continuously or cycling.
- It must also be noted that for mixed-metallurgy systems with copper alloys there is a large difference between an application of FFA/FFAP to a system which has been operating previously under oxidizing conditions due to poor air in-leakage control (high oxygen levels), and those systems which have operated optimally under reducing conditions with low levels of condensate oxygen as per the IAPWS TGD [4]. Very careful baseline monitoring (Section 8.2) for total copper needs to be conducted for the former case.
- Porous oxides or deposits in the plant could be partially removed from the surfaces by the moderate cleaning effect of the FFA. This is the main reason why it is suggested to begin with a dosage rate that is lower than the estimated final dosage for continuously operating plants. During the initial period of treatment, an increase of particulate iron and/or copper oxides (if copper alloys are included in the cycle) will be measured, indicating the above mentioned cleaning effect. Usually, this effect is limited in duration. The effect of the FFA dosage on the iron and copper must be evaluated after this first cleaning period is finished to make a comparison with the IAPWS TGD on corrosion products [7].
- Following the initial system demand, the feed of the FFA/FFAP should be increased to the desired target (as product) until it is determined that all monitored parameters as delineated in Section 8.2 are stable. This is typically achieved over a period of 3-4 weeks as a minimum in most systems, but it can vary as indicated above with the prior chemistry treatment, the materials of construction, and the operational mode of the plant. The initial target dosage is then maintained contingent on the total iron (and total copper) monitoring levels being less than those in the baseline and/or those target levels in the IAPWS TGD [7]. This typically takes up to three months. If a FFAP is applied without an alkalizing amine, the former alkalizing agent, e.g., ammonia, should be monitored to maintain the desired pH control that is in agreement with the IAPWS guidance [4]. If a FFAP is applied that also contains an alkalizing amine, the pH should be monitored, and the feed of the previously used alkalizing agents can be reduced and/or stopped. The feedwater pH control range should be in agreement with the IAPWS guidance [4].

- It is most important that the total iron (and total copper) concentration be monitored across the cycle using the procedures in the IAPWS sampling TGD [7] with full digestion and as outlined in Section 8.2. This ensures that, in case of large amounts of corrosion products, they are identified by the operator and not allowed to flow around the cycle. In the case of elevated concentrations of corrosion products, the operator may need to reduce or stop the addition rate.
- If necessary, and based on these iron/copper monitoring results, increase the boiler/evaporator blowdown rate to maintain the iron and copper levels within the appropriate control guidelines [7].
- The FFA residual should be monitored using a spectrophotometric test such as discussed in Section 8.5. This test should be performed daily at a minimum until a stable active FFA residual is achieved in the boiler/evaporator feedwater. Also, pH should be monitored continuously.
- An overdosage of FFA for a long period of time must be avoided. Overdosing increases the risk of higher metal oxide transport and the formation of sticky deposits especially in strainers, filters, steam traps, and small pipes. There will also be a detrimental effect on the condensate polishing plant if installed on the industrial plant (see Section 9.10).
- Plant operators using a phosphate-based treatment (preferably only PT as per the IAPWS TGD [5]), prior to dosing a FFA/FFAP should maintain the phosphate level during the initial "film-forming amine demand" period [5]. The phosphate addition is continued to maintain internal boiler protection until the FFA protective hydrophobic film is formed. Once the targeted value of FFA residual is achieved and maintained in the feedwater, and FFA is measured in the fossil boiler water or HRSG evaporator water, the phosphate feed may be carefully discontinued. In high pressure boilers/evaporators, the solid alkali may be required for boiler pH management in association with blowdown. In the LP circuits of HRSGs, the phosphate feed is often needed to control two-phase FAC [5, 64] and should be maintained until confirmation that the FAC has been reduced or eliminated by use of the FFA/FFAP.

8.3.2 Film Forming Products

It is emphasized that the information in the preceding Section 8.3.1 is specifically in reference to the use of FFA/FFAP. There is not the same detailed open or publicly available literature for most of items covered for the other FFS delineated in Section 3 that are not amine-based. There is, however, application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFP for any application, then it behooves that plant to ask for literature backup and the same critical questions so that this knowledge is available before application. Answers should be provided by the supplier on each of the items in the preceding sub-section.

8.4 How and Where to Dose the FFS

Commercial compounds containing non-volatile components such as non-volatile FFS, polycarboxylates, sodium hydroxide, or phosphate must not be dosed into the feedwater because this is the source for attemperation water. In these cases, they should be dosed into the drum.

In the case of plants equipped with an ACC, depending on the volatility and decomposition rates of the applied FFS, the dosage or additional dosage of the FFS into the steam exhausting line from the low pressure turbine to the condenser should be considered in order to directly provide the FFS to the large iron-containing surfaces of the ACC. A uniform distribution of the FFS in the water/steam mixture has to be achieved.

Dosing should be done by a properly controlled dosing system which is preferably controlled externally. External control should be done proportionally to feedwater or condensate flow. Recordings must be made of product consumption and water flows in order to be able to calculate the average product dose rate.

The chemical feed system must be compatible with the FFS.

8.4.1 Film Forming Amines and Film Forming Amine Products

It is generally suggested to feed the FFAP into the system undiluted (i.e., as shipped). If a dilution of the commercial product is desired, the supplier of the chemical should give advice on the stability of such dilutions. For most applications, one single point of feed is adequate to introduce the FFA/FFAP to the cycle with the ideal location being into the condensate at the condensate pump discharge (CPD) or at the condensate polisher plant (CPP) outlet if a CPP is installed on the unit. An alternative feed point is at the boiler/HRSG feedwater pump inlet. It is not advisable to add the FFA/FFAP into the drum or steam headers, as the high temperature superheated steam will result in significant thermal degradation of the FFA/FFAP and any neutralizing amines contained in the product.

For the chemical feed system for FFA/FFAP, the following materials are frequently used:

- PTFE membrane;
- EPDM seals;
- Polyethylene and stainless steel tubing.

Due to the variety of materials, this IAPWS TGD cannot give a full list of materials suitable or not suitable to be used in the dosing system. However, incompatibilities have been reported frequently for Viton and for some elastomers. Therefore, it is suggested to avoid these materials, or the supplier of the FFAP should provide the necessary information.

8.4.2 Film Forming Products

It is emphasized that the information in the preceding Section 8.4.1 is specifically in reference to the use of FFA/FFAP. There is not the same detailed open or publicly available literature for most of items covered for the other FFS delineated in Section 3 which are not amine-based. There is, however, application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFP for any application, then it behooves that plant to ask for literature backup and the same critical questions so that this knowledge is available before application. Answers should be provided by the supplier on each of the items in the preceding sub-section.

8.5 How to Analyze the Content of FFS within the Cycle

8.5.1 How to Analyze the Content of FFA within the Cycle

Where and How to Sample (Container Material and Storage)
FFA are surface-active substances; therefore, all sampling lines will be coated as well. It is preferable to have constant sample flow on the extraction line.

If the FFA concentration is measured by a grab sample method, the use of PTFE as the sample storage material together with the addition of acetic acid to adjust the pH will prevent a decrease of FFA concentration over time. Normally, the amount of acetic acid used for this sample pre-treatment is negligible compared to the sample quantity and will not affect the measurement of FFA by dilution. However, unnecessary dilution steps and long storage times should be avoided.

If storage materials other than PTFE are used, they should be silicone-coated. If the storage time is relatively short (few hours), typical laboratory plastic materials and glassware are also suitable.

As good laboratory practice, a sample containing a high concentration of FFA should be stored at room temperature. Due to the low water solubility of FFA, cold storage temperatures should be avoided.

Detergents should not be added to increase storage time. Detergents of all kinds strongly interfere with colorimetric methods such as those based on methyl orange extraction or xanthene dyes [55]. Sample vessels which are used repeatedly should be cleaned with solvents in order to remove FFA residues and to avoid cross contamination.

The locations to be monitored include those delineated in Section 8.2 which are the IAPWS TGD suggested sampling locations [3].

Methods of Analysis
Numerous analytical techniques have been developed for the determination of FFA concentration. The most dominant approaches are those using two different spectro-photometric analyses:

- Methyl orange extraction;
- Xanthene dye reaction.

The methyl orange extraction method uses the abilities of long-chain primary amines to form a water-insoluble colored complex with methyl orange. This complex is extracted in an organic solvent (e.g., chloroform, dichloromethane). The concentration of FFA present in the sample is proportional to the color formation. This method is described in a British Standard document [66].

Xanthene dyes are a class of molecules related to fluorescein. Two examples are Eosin Y (2′,4′,5′,7′-Tetrabromofluorescein disodium salt) and Rose Bengal (4,5,6,7-Tetrachloro-2′,4′,5′,7′-tetraiodofluorescein sodium salt). The sodium salts of the dyes form a water-soluble colored complex with FFA. This complex is measured without further treatment [67, 68].

The fact that the xanthene dye method does not require a toxic organic solvent makes this analysis easier and safer to handle. Approaches for online measurement of FFA normally use the xanthene dye reaction [69, 70]. The experiences obtained with two prototype on-line monitors in an industrial water-steam cycle have been reported [71]. Moreover the application of on-line monitoring of OLDA and ODA-based FFAP has been described [72].

Both methods described are applicable to the three FFA molecules listed in Section 3.

A commercially available test kit or online measuring system should fulfill the following requirements:

- Expression of the result as a mass fraction (e.g., mg/kg) of ODA, OLA, or OLDA;
- Wide measuring range (avoids dilution steps);
- Detection limit: the method should have a detection limit to measure traces of free FFA. This means a detection limit preferably lower than 0.1 mg/kg as ODA, OLA, or OLDA.
- No interference by short-chain amines (normally present as alkalizing amines) or ammonia.

Analysis of decomposition products
The main anionic decomposition products are short-chain organic acids (acetate and formate) together with carbon dioxide. These breakdown products will increase the CACE and DCACE. A selective measurement of all ionic thermal degradation products can be performed with ion chromatography. These low molecular weight acids may mask the presence of undesirable anionic contamination (e.g., chlorides and sulfates) identified by the CACE monitoring.

8.5.2 How to Analyze Film Forming Products (FFP) within the Cycle

It is emphasized that the information in the preceding Section 8.5.1 is specifically in reference to the use of FFA/FFAP. There is not the same detailed open or publicly available literature for most of items covered for the other FFS delineated in Section 3 which are not amine-based. There is, however, application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFP for any application, then it behooves that plant to ask for literature backup and the same critical questions regarding application so that the concentration of the FFS is known and can be adjusted.

8.6 Determining Optimum Usage

After a FFS is applied to a plant, the operator will need to determine as soon as possible whether it is accomplishing the desired effect, and then be able to assess the benefits of the application. This is a crucial process which basically follows on from the baseline monitoring and inspections (Section 8.2), and from the data obtained after the operation of the water/steam cycle with the FFS running properly, i.e., the targeted values have been achieved (Section 8.3). Before this, the data can only provide a first indication.

If the baseline aspects have not been determined or the verification step is not completed as the FFS is applied, then the operator only has qualitative indicators of success. Without careful monitoring and control, the operator would have no idea of an arising problem or may notice it too late. This could lead to failure and damage, as with any chemistry change in any industrial steam generation plant. Therefore, as outlined in Section 8.2, a second monitoring campaign must be conducted to monitor the new chemistry once a FFS is added to the plant. The important aspect is to be able to compare these results directly with those from the baseline series of tests. To accomplish this, the same total iron (and total copper) monitoring protocol as developed for the baseline series of tests should be adopted by monitoring the same locations and parameters around the cycle (Section 8.2). It is suggested that at least three months will be needed to record the total iron (and total copper) levels which can be compared with the baseline tests. Sample lines should be inspected if possible after an extended treatment period and checked for organic/oxide fouling to assist in understanding, disputing, or validating reductions in oxide transport.

As mentioned in Section 7 of this TGD, application of a FFS should not be expected to change the major operating chemistry parameter limits for the plant customized from the other IAPWS treatment TGDs [4, 5] or from the OEM's guidance.

At the first opportunity after an FFS application, the opportunity should be taken to compare the internal inspection results with those outlined in Section 8.2.

9 Customization

As with the other IAPWS TGDs, this customization section is most important so that the IAPWS Guidance in Section 8 can be customized to accommodate a very wide range of industrial plants with different configurations, materials, cycle chemistries, and operating requirements including various shutdown/layup situations. The previous sections of this document have provided general guidance for the base cases of all-ferrous industrial steam generation plants with a steam turbine, without condensate polishing and without sensible steam usage, which cover an important portion of plants around the world where FFS may be used. **However, it is emphasized again that this is an IAPWS Technical Guidance Document and that, depending on local requirements, the guidance and analytical**

processes will need to be adapted and customized for some plants, as there cannot be one set which can be applied to every plant worldwide. It is also emphasized that IAPWS does not advocate or support use of any specific commercial FFS products in the applications discussed in Sections 9.1 to 9.18.

This customization step for every plant is very important to ensure that: a) the FFS is chosen correctly for that plant; b) baseline testing, monitoring, and inspection is conducted; c) the FFS is added at the correct location/locations; d) the optimum level of FFS is added; e) there is adequate instrumentation and monitoring; and f) the benefits and efficacy of the new chemistry is ascertained through a second monitoring program where the results can be directly compared with the baseline. Thus, the emphasis of this section is to provide guidance on steps that the operator must take if the plant is not configured or operated as the base plants in the previous sections of this TGD. The most common of these features constitute the topics in Sections 9.1 to 9.18, which relate to units with mixed metallurgy including copper and aluminum alloys, different temperatures and pressures, plants with seawater cooling or desalination equipment, plants with ACCs, plants that will be shut down for various periods, systems with specific boiler types, plants using poor makeup water quality, plants with sensitive usage of steam, plants without steam turbines, systems with foreign steam usage and foreign steam supply, and dilution steam systems. This section also provides general guidance on the wide range of FFS combined blends, e.g., with alkalizing amines and dispersants.

9.1 General Comments on FFS Chemistry Differences

In general, the predominant and reactive functionality of FFS molecules make their interaction with the oxide to metal surface non-selective. However, FFS differ in their mechanism of operation and their interaction with the type of alloy, virgin metal, the semi-protective porous oxide, and protective oxide boundaries. The location, mode, and tenacity of protective film formation vary by product, molecular type, their orientation, and respective abilities to isolate a surface from the cooling medium. Some FFS combination products utilize mixtures with alkalizing amine compounds (Section 9.2), and these additional organic additives not only exhibit different volatile-to-liquid partition ratios to the FFS active compounds themselves, but they also have their own thermal degradation products. Some of the blended products contain dispersants. It is most important that the operator and/or prospective user of any FFS is provided with full disclosure on the composition and compounds of the FFS blend and of the limitations and potential consequences in the steam/water cycle.

9.2 FFS in Combinative Mixtures

FFS can be blends of different treatment chemicals such as alkalizing amines (e.g., ammonia, monoethanolamine), reducing agents (e.g., hydrazine, carbohydrazide, hydroxylamines, sodium sulfite), dispersants (mainly polycarboxylates, e.g., polyacrylates), and solid alkalizing agents (e.g., sodium hydroxide, alkali phosphates).

Compounds containing non-volatile components such as non-volatile FFS, polycarboxylates, sodium hydroxide, phosphate, or sodium sulfite must not be dosed into the feedwater because this is the source of attemperation water. They must be dosed into the drum. It should be noted that the thermal stability of polycarboxylates (dispersants) is strongly dependent on their chemistry, and thus it is very important to use a polycarboxylate which is suitable for the conditions (temperature and pressure) in the boiler. The supplier of the FFS should provide this information accordingly.

FFS that are a mixture of the active ingredients listed above can be used in conjunction with other treatment products or as a single, stand-alone "all-in-one" treatment product to protect the whole steam/water circuit. The contents of the FFS may dictate the application location in the steam/water circuit to ensure effective system protection while maintaining steam purity. There must be discussion on the location, and the operator should not simply use the injection equipment and location for the previous and on-going chemistry program. Numerous problems have occurred because insufficient time was spent in ensuring the correct location of addition as discussed in Section 8.4.

The fact that many of these materials are organic and contain varying amounts of carbon in their chemical structure will lead to an increased level of lower molecular weight compounds in the steam/water circuit after exposure to the high temperature/pressure sections of the system. The level to which these compounds will affect steam purity, particularly conductivity after cation exchange (CACE), will depend on the molecules used, the application location, and the dose rate to achieve the required effect in the steam/water circuit. These effects must be identified by the monitoring programs outlined in Sections 8.2 and 8.6.

9.3 Influence of Unit Pressure and Temperature

The relative volatility, thermal stability, and thermal degradation products of FFSs depend on many variables, but predominantly upon the molecular architecture of the chosen FFS and the other compounds in the product, and the thermo-hydraulic conditions. These variables include but are not limited to the effects of pressure, temperature, water quality, contaminant excursions, metallurgies, and oxygen levels. As a general rule, the degradation increases with temperature and residence time. The influence of pressure on degradation is less pronounced and can depend on the molecule. It can be expected that degradation takes place predominantly in the superheater and reheater sections and in drum boilers with longer residence times. Details on the degradation products formed can be found in Sections 5.1.4 and 5.1.5 of this TGD for film forming amine products (FFAP) and in Section 5.2 of this TGD for other film forming products. The FFS should be suitable for the conditions of the specific water-steam cycle.

FFS-based treatment options can work as a replacement to treatment programs documented in international guidelines including the IAPWS TGDs [4, 5], but can also provide a possible additional layer of protection. Local pressures and temperatures will determine the presence and relative ability of the film forming molecule to protect metal. Protection will vary by location and conditions which exist in the steam/water cycle, and by the properties of the FFS molecule. These effects must be identified by the monitoring programs outlined in Sections 8.2 and 8.6, and the requirements within the IAPWS Steam Purity TGD [6] must be adhered to as mentioned in Section 9.2.

9.4 Application to Multi-Type Steam Generation Plants

Industrial steam generation plants can consist of different kinds of steam generators (drum boiler, waste heat boiler, HRSG) and can have sections of different pressure feeding the same steam system, usually a header system. The operating regime of the individual steam generators may be different. An example of such a system is described in [21].

For multi-type industrial steam generation plants, it is important to note that the temperature and pressure effects in Section 9.3 will be most applicable, and that each pressure circuit will need to be monitored according to the guidance outlined in Sections 8.2 and 8.6.

The volatility of FFS compounds included in the commercial product individually depend on temperature, and thus their distribution between steam and water phase changes for steam generation plant sections with different operating temperatures and pressures. Special care must be taken in the selection of alkalizing amines to achieve the desired pH control in both drums and steam.

The injection points of the chemicals in multi-type steam generation plants must be carefully selected in order to ensure rapid distribution of all components in the complete water/steam cycle and to achieve stable conditions within a short period of time. Therefore, as discussed in Section 8.4.1, FFAP dosing should preferably be into the condensate pump discharge or before the main feedwater pump. Dosing of FFP will need to be defined by the properties of the FFS applied based on the information provided by the supplier of the treatment chemical.

Dosing into one boiler drum in a multi-drum system is not suggested due to the uneven distribution of the components resulting from the differences in volatility. The only exception to this was discussed in Sections 5.1.2 and 8.4 with regard to FFAP-containing non-volatile components and the concern for attemperation if they are dosed in the feedwater. Components with low distribution ratio will accumulate in the drum, whereas components with high volatility are enriched in the steam phase.

When applying FFA/FFAP to a multi-type industrial steam generation plant, the same baseline monitoring and inspection aspects as described in Section 8.2 will need to be conducted prior to application. The key monitoring locations for total iron (and copper) will be in the feedwater (usually at the outlet of the boiler feed pumps) and in each of the steam generation drums. The instrumentation required and parameter(s) to be recorded will be as delineated in the IAPWS Instrumentation TGD [3]. From a failure/damage point of view, it is important to have recorded the details of steam generator tube failures. This includes the locations of any FAC (single- and two-phase) so that any improvements can be noted after the FFS application, and may also be accompanied by a reduction in total iron corrosion products. If a steam generator has experienced UDC or has extracted tubes with heavy deposits, then particular care must be given to the application of any FFS in terms of careful total iron monitoring to ensure that there are no long-term increased levels. It is much better operating practice not to dose any FFS until the root cause of the UDC has been addressed and the heavy deposits removed by chemical cleaning.

9.5 Systems with Copper-Containing Materials (Industrial Plants with Mixed-metallurgy Feedwater Systems)

Generally, the corrosion of industrial steam generator plant feedwater copper-based alloys and the transport of copper oxides increases with oxygen concentration (increasing ORP) under AVT chemistry. In short, this involves a continued growth of cupric oxide on the copper alloy as oxide is removed from the surface and the base metal continues to corrode [73]. There is a risk for cupric and cuprous oxide release, transport, and re-deposition in the feedwater and generating sections as well as the threat of possible copper hydroxide (cupric and cuprous) volatilization and transport through the superheater and to the steam turbine [73]. The accepted international protocols for mixed-metallurgy feedwater systems, as outlined in the IAPWS TGD for Volatile Treatments [4], should be applied in order to minimize these risks.

The interaction of FFS with copper or alloys containing copper is dependent on the chemistry of the FFS. For FFA/FFAP, the adsorption of FFA onto copper surfaces has been shown (see Section 5.1.5); for FFP, the supplier of the product should provide the needed information, accordingly.

When FFS containing alkalizing amines are applied for pH control instead of ammonia, the risk of ammonia grooving in the tubing of copper alloy-based condensers due to the formation of cupro-ammonium complexes can be significantly reduced in low oxygen environments.

It is thus extremely important that monitoring campaigns are adopted for baseline conditions (no FFS) and after FFS addition for units with mixed-metallurgy feedwater systems and those with copper alloys such as desalination equipment. For these, total copper must be monitored before and after the addition using the protocols and procedures delineated in the IAPWS TGD [7] and outlined in Sections 8.2 and 8.6.

9.5.1 Film Forming Amines and Film Forming Amine Products

The reactive functionality of FFA molecules is such that the amino group will directly interact with metal ions and their oxidation state (protective or semi-protective oxides); see Section 5.1. Thereby, a protective layer is formed, which acts as a barrier between the water and the metal / metal-oxide surface and can promote the passivation of the component surface. There is a complex formation between FFA molecules and metal / metal oxides that may lead to increased metal-oxide transport in case of overdosing. Therefore, the concentration of FFA has to be carefully determined and monitored as outlined in Sections 8.3 and 8.5 of this TGD.

Although there are indications that the target values for Oxidation-Reduction Potential (ORP) and oxygen concentration of AVT(R) could be relaxed when applying FFAP, the user should respect these and should ensure routine analysis for total copper and copper transport using the protocols and procedures delineated in the IAPWS TGD [7]. It should also be noted that there is serious impact of FFA/FFAP on the ORP measurement (Section 8.1.4) which might preclude its use.

9.5.2 Film Forming Products

It is emphasized that the information in the preceding Section 9.5.1 is specifically in reference to the use of FFA/FFAP. There is not the same detailed open or publicly available literature for most of items covered for the other FFS delineated in Section 3 which are not amine-based. There is, however, application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFP for any application, then it requires that plant personnel ask the critical questions regarding application in systems containing copper alloys. The levels of total copper will need to be monitored before and after application of the FFS.

9.6 Systems Containing Aluminum

Cooling Systems with Aluminum Tubes. This customization relates to units with a jet-spray condenser and a dry-cooled heat exchanger tower with aluminum tubes. Units that have these systems require strict pH control to ensure compliance with published guidelines for these metals (see IAPWS TGD on Volatile Treatments [4]). Interaction of FFS with the aluminum surfaces and thus possible protective properties of FFS depends on its molecular structure. The adsorption of FFA onto aluminum surfaces has been shown (see Section 5.1.5); for FFP, the supplier of the product should provide the needed information, accordingly. The utilization of FFS formulations that exhibit molecular basicity and especially those with alkalizing amine combinations should be carefully evaluated, due to inherent highly alkaline product pH restrictions and limitations of the chemicals dosed. Furthermore, the impact on the localized pH of the film that contacts the oxide-to-metal interface has to be considered, which could substantially increase corrosion of aluminum alloys. The user should also be aware of the partition coefficients of alkalizing amine combinations that will predominate in the low pressure saturated steam sections and especially in the potential two-phase FAC locations. Only FFS that ensure compliance with published guidelines, especially concerning pH, for these metals may be applied with care for aluminum protection in air-cooled condensers. The user should exhibit care and ensure routine analysis for soluble aluminum oxide release, transport, and re-deposition in the feedwater and steam generating sections as well as the possible metallic oxide volatilization and impact on steam turbine integrity [6]. Plants with aluminum cooling systems need to include the monitoring of aluminum in the baseline testing and compare the results to the suggested levels in the IAPWS TGD on Steam Purity [6].

It is known that aluminum oxide/hydroxide has a significant volatility in steam and thus may transport into the steam turbine and deposit on the blade surfaces as the steam expands. Aluminum-based oxides/hydroxides have low solubility and are therefore hard to remove chemically from generator heat transfer surfaces. These concerns are supported by experience of steam turbine fouling in plants that contain aluminum [6].

As there is not a large amount of experience in applying FFS to plants containing aluminum, it will be most important for an operator to conduct a thorough assessment of the equipment around the cycle before application. This should include tube sampling from the steam generating tubes to assess any aluminum deposition. It will also be necessary to monitor total iron and aluminum before and after the addition using the protocols and procedures delineated in the IAPWS TGD [7] and outlined in Sections 8.2 and 8.6.

9.7 Systems with Air-Cooled Condensers (ACC)

Unlike water-cooled condensers made of corrosion-resistant alloys like red or yellow metal, stainless steels, or titanium grades, ACC tubes are normally fabricated in carbon steel. They add a vast steel surface area to a water/steam cycle, typically of the order of thousands of square meters, and hence constitute a major potential source of total iron corrosion products.

Furthermore, unlike water-cooled condensers, ACC cannot be placed directly underneath steam turbines. This necessitates the use of relatively long transport lines for the two-phase mixture of water and steam exhausting from the LP steam turbine.

It should be emphasized that the protection of the ACC requires the application of a FFS containing a film forming molecule with a sufficiently high steam volatility under the conditions of the industrial steam generation plant.

In this case, the dosage of the FFS into the steam line from the turbine to the condenser can be considered in order to directly provide the FFS to the very large iron surfaces of the ACC. A good distribution (fine spray) of the FFS in the water/steam mixture should be achieved.

Conditions both in the transport lines and at the tube entries of the ACC make them susceptible to FAC [64], with the tube entries in the upper ducting operating under the most severe two-phase FAC conditions [65]. If the cycle chemistry control for units with ACCs is not in essential agreement with the IAPWS Volatile Treatment TGD [4] with pH levels close to 9.8, then the international experience indicates that very large levels of total iron will be measured in the condensate and feedwater [65]. Most often, plants operate with condensate filters to assist in the removal of the total iron particulate. There is an ACC Corrosion Index (DHACI) [65] which has been applied to ACCs worldwide so that a unifying indicator can allow qualitative comparisons before and after the application of the FFS.

It is most important that monitoring of total iron in the condensate is conducted before and after the FFS application to units with ACCs in accordance with the protocols and procedures delineated in Sections 8.2 and 8.6. These must be accompanied by the application of the DHACI so that improvements can be easily semi-quantified.

There are now an increasing number of reports on the experiences of applying FFAP [26, 48, 74] and FFP in water/steam cycles equipped with ACCs. Furthermore, some good results have been presented at the ACC User Group (ACCUG) meetings (http://acc-usersgroup.org/). But often when FFS have been added to units with ACCs there has been no baseline comprehensive monitoring of total iron or inspections of the ACC tube entries using the DHACI [65]. This has not permitted a comprehensive assessment of the improvement after treatment.

9.8 Units with Seawater Cooling or Desalination Equipment

The use of seawater cooling for industrial steam generation plants always creates a higher risk for damage and failure of major components, so any treatment program must include operating and chemistry procedures on how to deal with ingress of the contaminant, chloride. Unfortunately, no condenser or condenser material is totally resistant to failure. The IAPWS TGDs on Volatile [4] and Solid Alkali [5] Treatments cover such events in detail; this is applicable to condenser tubing manufactured in titanium, stainless steel, and copper-based alloys. Some desalination plants include brine heaters, heated by LP steam, and dump condensers cooled with seawater. The tubes in both cases are fabricated with copper-based alloys (usually Cu/Ni alloys). Multi-effect desalination plants (MED) also mostly rely on copper alloy tubing. Tubes in both desalination systems sometimes leak because it is very difficult to operate with chemistries that provide protection to these copper alloys and at the same time to the all-ferrous materials in the generating source (HRSGs or boilers).

These plants can operate on the chemistries included in the other IAPWS TGDs [4, 5] or on blends of alkalizing amines. They can convert to the use of a FFS containing alkalizing amines and maybe dispersants. But in all cases, it is most important that tubes are removed from the steam generating sections (HRSG HP evaporators and boiler waterwalls) to determine the internal deposits prior to changing the chemistry to a FFS so that a chemical clean can be performed if necessary before the conversion. As also discussed in Section 8.2, monitoring is most desirable before the addition, but often in the past this has not been accomplished.

The choice of which FFS to use has been covered in Section 8.3 as well as the key questions that need to be asked. The methodology of determining how much FFS to use and how to monitor whether the FFS is successful has also been covered in the base cases of Sections 8.4 and 8.5.

Irrespective of whether the plant is using FFS, the plant operator must always be prepared for a sudden leak of seawater from a condenser or dump condenser or MED tubing, or of concentrating brine from a brine heater. Such major incidents of leakage can cause significant chloride ingress into the boiler/steam generation system. Consequently, the CACE for the condensate, boiler feed water, boiler water, and steam will increase within a very short period of time. However, it should be noted that if the leak is very small then CACE may not be sufficient to identify the leak because of increases in CACE from the application of some FFS. IAPWS strongly suggests [3] that these plants also have sodium analyzers in the condensate at the condensate pump discharge (CPD) and in steam (see Section 8.1.4). Most importantly, the pH for all boilers/HRSGs will decrease rapidly after the leakage and thus subject the boiler/HRSG to conditions which could lead to under-deposit corrosion. The primary reactions to such a situation have been covered in other IAPWS TGDs [4, 5] and will require the unit to be shut down immediately if the boiler or evaporator water pH continues to decrease below 8.0.

Although the film formed by the FFS provides an additional protection to the surfaces, it must be emphasized that the identification and elimination of the leakage is a priority measure. Longer term operation outside of the recommended specifications set forth in the IAPWS guidance must be avoided [4, 5]. A major problem with seawater ingress is the deposition of sodium chloride onto the steam turbine.

It is known that FFA improves the general cleanliness of turbines, but it is not fully clear if a FFA provides benefits on the mitigation of salt deposits in the steam turbine.

If the pH does not depress below the shutdown limit, then to counteract the effect of this corrosive chloride contaminant the dosing of the alkalizing agent, e.g., FFS which contains alkalizing amines, should be increased while increasing the boiler blowdown rate. Alkalizing agents will help to neutralize the acid generated by the chloride contaminant, and higher boiler blowdown will help to reduce the accumulation of chloride contamination in the boiler/evaporator water. It is important to ensure sufficient buffering is achieved, as an extreme low pH will risk under-deposit corrosion [60]. Of course, the boiler/HRSG should be shut down when the pH continues to drop below 8, and, as with phosphate (PT) or NaOH (CT) additions in conventional treatments, the chloride remains in the boiler/evaporator and is equally harmful in the alkalized form. As a general rule, the concentration of FFS which contains alkalizing amines should be temporarily increased until the boiler water pH recovers to at least 9.0. Once the pH reaches 9.0, the dosing of FFS blended with alkalizing amines can be gradually normalized as long as the leak has been eliminated.

The boiler/steam generator internals should be inspected as soon as possible after the event. Particular emphasis should be given to whether the boiler/HRSG internals are found to be hydrophobic in nature due to the fact that FFS can protect metal surfaces against corrosive chloride. Depending on the seriousness of the chloride in-leakage, any steam turbine included in the cycle may also need to be inspected and chemically cleaned.

9.9 Shutdown and Layup

During shutdown and layup, air ingress will lead to an accumulation of oxygen and carbon dioxide in the water/steam cycle. In water-filled areas, oxygen and carbon dioxide will be dissolved in the water. This can result in electrochemical corrosion. Additionally, the pH will be reduced by carbon dioxide, so the existing protective layer may not remain stable.

In drained and emptied areas, the oxygen may react with the surfaces if the relative humidity in the system is not kept below 30–40 % according the Vernon curve [75]. This can happen from the first minute of shutdown, so corrosion protection should start immediately during the shutdown process. The use of a steam-volatile FFS can be an effective way to protect the main parts of the water/steam cycle against corrosion during these shutdown periods. With injection of a FFS before the shutdown, most of the internal surfaces should be covered with a protective layer which remains stable during shutdown irrespective of whether or not the system is filled with water. As discussed in Section 5.1.5, film formation on superheated surfaces has sometimes been shown for FFA. This has also been shown for some FFP.

9.9.1 Film Forming Amines and Film Forming Amine Products

To customize the FFA application, there is a major difference between industrial plants in cycling and intermittent operation, and those with continuous operational periods interspersed with long shutdown periods that might last for months. In some cases, industrial plants have fossil plants located within them, whereas in others there is steam generation inside process equipment. This can include decoking, auxiliary/package boilers, campaign industries, etc.

Cycling and intermittent operation is often characterized by short operation times with starts and stops daily, mostly unscheduled and often with short notice. The duration of the shutdown periods cannot be predicted. For these industrial plants, a continuous injection of FFA during operation is preferable because of the short time of operation. Depending on the chosen FFA (Sections 8.3 and 8.4), the injection has to be made in addition to the normal water chemistry or as a substitute for the conventional chemicals.

Industrial plants with longer shutdown periods, which need to return to service within a short time period, could increase the dosage prior to shutdown so that a higher concentration of FFA can be measured in the water. Section 5.1.4 provides discussion on the risks of overdosing. During the shutdown period, the water should be recirculated and the following parameters measured in the water once every two weeks. The trend of the data is more important than the absolute value:

- pH;
- Conductivity;
- Film forming amine (FFA) concentration;
- Chloride and sulfate;
- Total iron;
- Total copper (in cases where copper alloys are used).

A specific value for total iron and total copper cannot be given, since iron and copper uptake of the water is dependent on the metal / metal-oxide surface to water volume ratio.

In cases when the FFA concentration drops below the value specified by the supplier, additional product should be dosed and the water recirculated.

The conservation of the equipment in the water/steam cycle can be supported by an increase of pH in the water.

The film on the surfaces does not need to be removed before returning the plant to normal operation. The water chemistry should be returned to the normal operational conditions. In the case that the water level in the boiler, e.g., in the drum, has been increased, the water should be drained to the normal level of operation. Furthermore, the dosage of FFA should be reduced or stopped until the measurable FFA concentration is within the desired range for continuous operation (Section 8.3). This can be accelerated by a temporary increase of water discharge. The cycle chemistry parameters should return to normal levels, typically within one week, during which time the parameters should be carefully controlled.

When carrying out repair work, such as welding, the formation of fumes caused by the thermal decomposition of the FFA has to be taken into consideration, and suitable personal protection should be worn accordingly.

Industrial plants going into a planned shutdown/layup after a long period of continuous operation (for example for seasonal reasons such as heating plants, sugar industry, capacity reserve) do not need a continuous injection of FFA. To make sure that all areas of the water/steam cycle are covered with a protective FFA layer, the injection of the FFA has to start at a defined period before the shutdown. This period depends on the chosen FFA, the design of the water/steam cycle, and the steam capacity. Also in this case the maximum concentration is commonly higher than during continuous FFA treatment (Sections 8.3 and 8.6). Plant protection is complete when the specified concentration of the FFA can be measured in the system for the specified period of time.

Industrial plants with a condensate polishing plant should bypass it during the FFA application, as the ion exchange resins will remove the FFA and alkalizing amine molecules from the condensate. Although the evidence that FFA damages the resin is not conclusive, a higher amount of FFA will be needed and could cause a loss of capacity of the resin.

In the case where a plant is applying a FFA for preservation only, the film established on the surface will be slowly removed during normal operation. The influence of the removed film on cycle chemistry is negligible.

For film forming amines, laboratory data performed with conductivity probes showed that the coating effect caused by the FFA was washed away shortly after stopping the addition of the FFA. However, ORP probes lost their sensitivity and response time irreversibly after one exposure to FFAP [55].

Plants that are to be emptied for preservation should be drained warm and dried as much as possible by the residual heat from the plant. Draining temperature, therefore, should be as high as possible. Observing whether there is any surface protection can be done visually. After draining, the surfaces should show a hydrophobic, water-repellant character, which should remain during the shutdown period. For these dry layup situations, there is not enough information available on how long the film will last.

For film forming amines, good preservation of the metal surfaces has been obtained in practice [14, 42] and in the laboratory for more than one year.

9.9.2 Film Forming Products

FFP have also been used to provide shutdown/layup protection of fossil plants. Some examples are provided in references [76, 77] (*for these references, the reader is referred to Section 3 which describes the incorrect nomenclature used for FFP at that time*).

9.10 Systems Containing Condensate Polishing Plants (CPP)

Condensate polishing units, e.g., using ion exchange resins or active carbon, are important to achieve the desired high water purity needed for proper operation of the water/steam cycle. Therefore, it is important for the user to know the impact of FFS on the components, such as ion exchange resins or active carbon bed, of the condensing polishing plant if they are used in industrial plants.

Due to the variety of compositions, a general statement on the impact of FFS on the functionality of a CPP cannot be provided. Therefore, in the case where a FFS is intended to be continuously applied in a water/steam cycle, operators should request technical information related to the interaction of the components with the CPP from the supplier of the FFS, in order to be able to judge whether there will be a risk related to the application of the FFS. The key indices of the CPP performance should be monitored as a baseline according to the principles outlined in Sections 8.2 and 8.6 of this TGD before the change to the FFS treatment and compared to the same indices determined in an analogous way when the FFS is applied.

9.10.1 Film Forming Amines and Film Forming Amine Products

A few papers have been published on experiences with a CPP as part of water/steam cycles treated with film forming amines [26, 49, 78]. They describe proper operation of the CPP. A decrease in the regeneration frequency has been reported [26] after the change of a conventional AVT treatment program to FFA, but the reason for this was not mentioned. Diminished cation exchange resin capacity in the CPP was reported, which was attributed to resin fouling by hydrocarbons [74].

Laboratory studies on the impact of FFA on ion exchange resins show that the FFA molecules are almost completely removed by the strongly acidic cation resin [79, 80] and are removed from the resin by the normal regeneration process. High FFA dosages led to a reduction of total cation ion exchange capacity [80] and mass transfer coefficient, which could be recovered by an additional regeneration. Regeneration of a resin exposed to ODA could not fully recover exchange capacity.

If an industrial steam generator plant equipped with a condensate polishing unit intends to apply a FFA/FFAP for preservation during shutdown only, then generally the CPP should be bypassed during the period of FFA/FFAP dosage. Generally, in this case the operator will need to apply higher dosages of FFA/FFAP in order to establish the protective film on the surfaces (see Section 9.9 and Section 5.1.4 on overdosing).

9.10.2 Film Forming Products

There is not the same detailed open or publicly available literature for the effect of FFP on condensate polishing or ion exchange resins. There is, however, application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFP for any application, then it requires that plant personnel ask the critical questions regarding application in systems containing condensate polishers.

9.11 Systems with Special Boiler Types

Whereas boilers constitute the core of a fossil power station around which everything else is built, the opposite is the case in industrial plants. Here, requirements imposed by the process on the one hand and space limitations on the other hand often make for very high heat fluxes, unconventional geometries and deviant construction materials in relation to boiler systems.

Examples of process-specific requirements include rapid cooling to arrest chemical reactions or different operating regimes, e.g., in relation to catalyst bed reduction or decoking of coals. Vertical so-called Quench Coolers or Transfer Line Exchangers of tunnel-flow or double-tube design in ethylene plants may be qualified as unconventional boiler geometries from a fossil industry perspective. The same holds for waste heat boilers in, for example, caprolactam, formaldehyde, hydroxylamine, and mineral acid manufacturing. As to construction materials, various solutions are applied in steam generators in ammonia plants to combat nitriding and metal dusting, failure mechanisms that are not prevalent in electric power generation.

None of the boiler systems alluded to above includes a mud drum from which loose deposits can be released. By contrast, in many industrial steam generators the area of highest heat flux coincides with a physical low point susceptible to buildup of fouling, and, hence, under-deposit corrosion. Only a few have intermittent blowdown facilities to remove foulants from bottom tube sheets or headers. This needs to be taken into careful consideration in view of the increased iron oxide transport observed particularly in older systems when FFS are first applied.

Industrial auxiliary boilers may be fired with natural gas or oil, but also with tar-like residues emanating from a chemical process. The risk of localized overheating with the latter may be greater. Especially in the Nordic countries, it is not unusual for electrode boilers to help satisfy peak demand in a steam grid at an industrial site.

For wider acceptance of FFS in industrial steam generation, it is important to discuss application of film-forming chemistries with the process technology licensors, catalyst suppliers, and boiler system OEMs concerned. Risk assessments must include an evaluation of (potential) effects of contamination of process/product streams with FFS.

Some important industrial boiler types and their main operational characteristics are described in this section.

Large Water Space Boiler
The operational conditions in large water space boilers may be combined with critical conditions with regard to thermal heat transfer, especially after long standby periods. Severe local superheating causing permanent damage up to total failure of the heating surface may be the consequence. Heat transmission and the mechanisms of boiling during particular operational conditions (cold start, warm start, sudden pressure change) can be influenced by the water chemistry in a positive but also in a negative way. Boilers with two fire tubes and insufficient geometrical layout seem to be susceptible to this. Operators

considering a change of treatment chemistry to a FFS-based concept should understand the possible impact of the FFS due to the adsorption on the boiling behavior on the surfaces under these critical operational conditions in order to evaluate any risk that might be related to the application of the FFS.

Waste Heat Boiler

Waste heat boilers in the industry frequently are of a simple design, like a tube heat exchanger, with limited maintenance access, e.g., for cleaning. They are susceptible to fouling, such as iron fouling. Boiler tube failures due to local overheating caused by deposits or under-deposit corrosion are common issues. Vertical quench coolers or transfer line exchangers are a special type of waste heat boiler used in crackers in the petrochemical industry and are characterized by high thermal load. Often steam systems in industrial applications consist of multiple waste heat boilers.

Treatment programs based upon FFS have the potential to reduce of corrosion and iron transport. However, in polluted systems special care has to be taken to avoid excessive iron transport, which might promote fouling of tubes.

Instantaneous Steam Generators

These boilers, also called quick-start boilers, are designed to produce steam in very short time after startup. They are operated at various pressures, often fed with softened water and characterized by frequent, even daily shutdowns. They are operated with a wide range of condensate return. During startup of the boiler, a substantial amount of cold water normally is injected and it may take some time until the hotwell reaches a stable and efficient level of operation. The heating coils are sensitive to corrosion and scaling. The inside in the furnace area should be properly wetted and cooled in order to avoid dryout, corrosion, and deposits. As the feedwater is evaporated without oxygen or carbon dioxide removal, there is significant potential for corrosion. Feedwater should be maintained at a high pH according to the specifications of the boiler manufacturer. To ensure proper steam quality, an efficient steam separator is important.

For a dry layup of the unit, it must be completely dry without any traces of water. In case of a wet layup, it should be kept completely wet and with appropriate water treatment. The heating coil has to be free from air or air pockets. FFS offer potential benefits for the protection of instantaneous steam generators, especially for preservation during standby periods (see Section 9.9).

Steam Transformers

Similar to waste heat boilers with a tube heat exchanger type design, these systems are utilized to transfer heat from one steam source to another without any physical contact between the different streams. An example of this is the transformation of directly extracted geothermal steam, containing contaminants such as hydrogen sulfide along with elevated levels of chlorides and silica and heavy metals, to produce higher purity saturated steam (at lower pressures and temperatures) via the boiling of boiler feedwater for use in industrial processes without these contaminants [81]. Treatment programs based upon FFS have the potential to reduce corrosion and iron transport of both the boiler water and the clean steam systems.

Boilers with Condensing or Sweetwater Condenser Attemperating Water Systems
These types of systems are present in some industrial boilers where the attemperating water is provided via the condensation of saturated steam from the boiler, which is then injected into the superheated steam for final steam temperature control. In these systems, compounds containing non-volatile components such as non-volatile FFS, polycarboxylates, sodium hydroxide, phosphate, or sodium sulfite can be dosed into the feedwater because this is not the source of attemperation water.

Auxiliary boilers
These boilers of small steam production capacity are normally operated only during startup or after shutdown of the plant, e.g., to provide gland steam. As a consequence, they are not continuously operated and thus need preservation during standby. FFS-based treatment chemistry has the potential of improved corrosion protection (Section 9.9). Operators considering the application of an FFS-based chemistry have to take into consideration that the auxiliary boilers are connected to the main steam system. For example, there might be a significant accumulation of gland steam in the condensate during longer standby periods of the main steam system, which could have a temporary impact on the steam quality after restart of the main steam system, e.g., by the decomposition of organic components.

9.11.1 Film Forming Amines and Film Forming Amine Products

There are a number of reports dealing with the application of FFA/FFAPs in steam systems with special boiler types. Steinbrecht *et al.* [53] studied the application of ODA and OLDA containing products under critical conditions (cold standby, warm standby, strong overdosage of FFAP) of large water space boilers. As a conclusion, FFA-containing cycle chemistry can be safely applied in these boilers, a result which was confirmed in later studies [50, 54]. Reference [18] describes an example of FFAP application.

It is most important that the industrial plant operator checks with their boiler manufacturer on the use of FFAP as some do not recommend organic cycle chemistries.

A series of three papers [26, 74, 82] reports about the application of a FFAP in the steam system of a naphtha cracker equipped with transfer line exchangers of different layouts. A period of more than 10 years is covered. It was reported that boiler tube failures due to deposit formation could be eliminated and the overall system condition improved.

The application of FFA and FFAP in auxiliary boilers are reported for an industrial plant [71] and a Benson-type auxiliary boiler of a CCGT (combined cycle gas turbine) plant [83].

9.11.2 Film Forming Products

There is not the same detailed open literature and understanding for the effect of FFP for the application in steam systems with special boiler types. If a plant operator/owner is considering use of one of these FFP for any application, then it requires that plant personnel ask the critical questions regarding the application in systems with special boiler types.

9.12 Systems Using Poor Makeup Water Quality

There are several examples that epitomize the use of poor makeup water quality in industrial steam generation. These include OTSG (Once Through Steam Generators) in the oil sands industry and dilution steam generators in ethylene plants (Section 9.17). Industrial steam generators operating at relatively low pressure (< 6 MPa) are operated not only with DI water as makeup water but also with makeup water of low quality, e.g., water contaminated with organic matter and/or softened water. Poor quality makeup water leads to a reduction of the feed water quality. These steam generators may not deliver steam for a steam turbine, but the steam must be used only for applications which can accept a poor steam quality, e.g., drying and heating. Due to the conductivity limit of the boiler water, the condensate recovery is limited by the need to control the conductivity of the boiler water. FFS have a potential for improved corrosion protection due to their barrier formation. However, the use of poor water quality makeup cannot be recommended. DI water should be always used as makeup for the steam generator.

9.12.1 Film Forming Amines and Film Forming Amines Products

A successful application was described using a FFAP in a steam generator with three different types of boilers (one tube boiler being in standby), using softened water as make-up [22]. Oxygen corrosion in the condensate system was sharply reduced after changeover from a treatment with reducing agent (oxygen scavenger), phosphate, and ammonia to an FFAP product.

9.12.2 Film Forming Products

There is not the same detailed open or publicly available literature for the effect of FFP for steam generators using poor makeup quality. There is, however, application experience available from the chemical suppliers. If a plant operator/owner is considering use of one of these FFP for any application, then it requires that plant personnel ask the critical questions regarding application in these systems.

9.13 Systems with Sensitive Usage of Steam

Sensitive usage of steam is defined as applications where the process supply has contact with the following (non-exhaustive) list:

- food (e.g., cooking processes with steam, sugar industry), production of paper for food packaging, and application in sterilizers or pasteurizers. The treated steam may have direct contact (e.g., food cooking) or indirect contact (paper for food packages). The steam may contact food intentionally or unintentionally (due to leaks). Because of the contact with the treated steam, the components of the FFS may be incorporated into the food and as a consequence be consumed by human beings (or animals in the case of animal food production).
- in milk/dairy products processing, the use of chemicals in the steam system generally is very restricted. Often it is limited to those naturally present in milk, e.g., ammonia, and in a way that the naturally occurring concentrations are not exceeded.

- hospitals where steam is used for sterilization.
- humans (e.g., in laundries). In this case humans may be directly exposed to the treated steam via inhalation, skin contact, or swallowing.
- sensitive plant parts (e.g., catalyst). The exposure of plant parts to the treated steam may lead to adsorption of the FFS on the surface and as a consequence may impact their functionality.
- contact to manufactured goods (e.g., tire production, extrusion processes). The exposure of the manufactured good to the steam containing FFS may impact the properties of the goods.

Generally, two main groups of sensitive usages can be distinguished: first, applications which may impact health of human or animals and second, applications where crucial plant parts or the product may be deteriorated.

Operators who intend to apply FFS-based products in a steam generator where the steam has contact with food or humans should verify that there is full compliance with legislation. The legislation varies considerably with application and region. A comprehensive list cannot be given in this guidance document. Examples are FDA's boiler additive regulation, i.e., 21 CFR § 173.310, and BfR German Recommendation XXXVI for health-related evaluation of materials and objects for contact with food stuff. The supplier of the FFS-based product has to provide all information necessary to evaluate legal compliance of the chemical to be applied. Furthermore, changes in the relevant legislation and their impact on the applicability of the chemistry in use have to be taken into consideration during the usage of a chemical. The legal assessment of the compliance can be carried out by an independent certified expert organization.

Operators who intend to apply FFS-based products in steam generators where the steam has contact with sensitive plant parts or with the manufactured goods should clarify in advance the compatibility of the chemicals to be applied. The producer of the FFS-based product should provide all information necessary to assess compatibility with sensitive plant parts or with the manufactured goods. In the case where the manufactured goods which are exposed to the steam are used for food or food-related applications, e.g., paper for food packaging, the legal compliance also has to be evaluated accordingly.

9.13.1 Film Forming Amines and Film Forming Amine Products

Of the three FFA discussed in Section 3, ODA is listed in FDA's boiler additive regulation, i.e., 21 CFR § 173.310. The application of FFAP for food-related applications has been reported in sugar producing plants [84], which are operated generally in campaigns, i.e., periods of production alternating with long shutdown periods.

The application of FFAP in steam generating plants in a refinery [85] and in an ammonia producing plant [86] have been reported, where the steam treated with FFA has contact with a catalyst. No impact on the catalytic efficiency was observed. In the ammonia plant, the number of boiler tube failures was reduced after changeover from a phosphate, hydrazine, and ammonia-based treatment to an FFAP treatment due to the reduction of iron transport.

9.13.2 Film Forming Products

There is not the same detailed open or publicly available literature for the effect of FFP for sensitive applications of steam. If a plant operator/owner is considering use of one of these FFP for any application, then it requires that plant personnel ask the critical questions regarding the application in such systems.

9.14 Systems without a Steam Turbine

Many industrial power plants produce steam only for the processes and are not equipped with a steam turbine. In this case, the requirement for the steam quality according to the IAPWS TGD for Steam Purity for Turbine Operation [6] can be relaxed. It must be confirmed that the requirements of other binding or regulatory documents are adhered to. Steam purity requirements are process-specific and have to ensure that a deterioration of the process is avoided. For example, elevated iron concentrations can lead to material loss and quality problems in the process, such as discoloration of fabrics in laundries or blocking of nozzles.

Steam-volatile FFS can protect the complete steam/condensate system against oxygen corrosion, as in industrial steam generators there is often oxygen ingress into the system, especially in complex and branched systems.

9.15 Systems with Foreign Steam Usage and Foreign Steam Supply

Foreign steam usage is commonly applied in industrial plants. Steam is exported to a consumer at a different plant, which may belong to the same company or not. Steam and condensate piping may be many kilometers in length. In case of an intended change of cycle chemistry to a FFS-based treatment program, the operator has to consider how the foreign steam is used and for what process. Therefore, the operator should take into consideration the recommendations of the customization sections, especially in case of sensitive usage of the steam (Section 9.13). The requirements for the foreign steam may be markedly different from the ones of the main steam system. This applies not only to FFS-based treatment programs, but to all cycle chemistries.

Import of foreign steam or supply of steam or condensate return from a foreign plant is a common practice of water saving. The operator should consider the quality of the foreign steam/condensate and possible interaction of chemical substances added intentionally or from leakages into the steam/condensate at the foreign plant before changing to a FFS-based treatment program in order to avoid deterioration of the steam or general water quality and resultant problems. The operator should consider precautionary measures, such as condensate polishing in this case. This applies not only to FFS-based treatment programs, but to all cycle chemistries.

9.15.1 Film Forming Amines and Film Forming Amine Products

The application of FFA/FFAP in steam generating plants with foreign steam usages and/or foreign steam/condensate supply has been described for many different industrial power plants. Examples can be found in [48, 49, 71, 74, 86].

9.15.2 Film Forming Products

There is not the same detailed open or publicly available literature for the effect of FFP for systems that provide steam and have return condensate. If a plant operator/owner is considering use of one of these FFP for any application, then it requires that plant personnel ask the critical questions regarding the application in systems with foreign steam usage and foreign steam supply.

9.16 Systems Connected to District Heating Units

District heating systems are pressurized hot water systems which provide heat to industrial and/or residential areas. They are characterized by high system volume and by long and branched piping systems, frequently with air leakages into the system. FFS have a potential for improved corrosion protection of the network against oxygen corrosion due to air leakage. In old and polluted systems, the dosage must be carefully controlled and the system well monitored to avoid a detrimental remobilization of metal oxides/hydroxides or other pollutants.

District heating systems are normally operated at an operational pressure below that of the water systems to be heated, in order to avoid leakage of district heating water into the secondary systems, e.g., hot water systems in households. If the secondary systems use drinking water, heating is typically carried out in double-walled heat exchangers. The most common material is carbon steel, but yellow metals can also often be found.

Two main types of steam generation are common to provide heat to the district heating systems: systems directly connected to the heating system, or systems with heating condensers. In the latter case, the chemical treatment of the district heating is not subject of this guideline, since it can better be characterized as a closed heating/cooling system. Special care has to be taken for heating condensers, as they are normally operated only during the heating period and are not operational during longer periods.

9.17 Dilution Steam Systems

A dilution steam system is a unit designed to produce dilution steam of about 8 bar in a steam cracker. The dilution steam is then used to dilute the feedstock and minimize coke formation in the furnaces where the cracking reactions occur. The dilution steam system is generally fed with water that does not have normal boiler feedwater quality. It has a pH of 8-9 and a conductivity of about 100 to 1000 μS/cm. The process water is often buffered at high pH because of the presence of ammonia which is inherent to the cracking process or because of the addition of an alkalizing amine.

Classic dilution steam system configurations contain a process water stripper (PWS) aimed at stripping organics that are present in the feed water and that can contribute to organic fouling downstream of the stripper. A process water stripper normally operates at 120 °C and about 2 bar. If no alkalizing agents are dosed in the feed of the column, acid corrosion might occur at the bottom of the column, as the ammonia will be partially stripped out of the stream at those conditions. A few preheaters are generally installed between the PWS and the Dilution Steam Generator (DSG) in order to preheat the feed. They generally have a high fouling tendency but a low corrosion potential. Corrosion issues mainly occur in the dilution steam generators where high temperature and high pressure are present. Feed of the DSG typically is about 150-200 t/h, whereas its blowdown is about 10% of the feed. This leads to concentration of potentially corrosive species (such as chloride) in the bottom of the vessel and increases the risk of pitting corrosion.

A FFAP can be dosed to the feed of the PWS in order to protect both the bottom and the top of the column. However, attention needs to be paid to the foaming properties of the amine in order to avoid disturbance in the column. Part of the FFAP will then adsorb on the preheater and the DSG to protect them against corrosion. Residuals of FFA should be measured in the blowdown of the DSG and should always be in the desired range. Biodegradation of the FFAP that is used is also to be considered as some plants send their blowdown to a biological waste water plant. FFA/FFAP can reduce the amount of pitting and under-deposit corrosion in the dilution steam generators. Before using an FFA/FFAP in a dilution steam system, the chemicals to be applied should be evaluated with regard to risk of forming explosive compounds such as nitro compounds in steam crackers (blue gums).

9.18 Examples of Systems in Production

In industrial power plants, steam is used not only as the heating source to drive a steam turbine for power generation but also as a process raw material in a manufacturing process. In this section, steam systems in selected industrial production plants are discussed. These examples are illustrative and are not meant to be exhaustive.

9.18.1 Systems in Ethylene Production

There is considerable published experience with the application of FFAP in the high pressure (125 bar) steam system of a naphtha cracker [26, 74, 82]. It must be understood, however, that ethylene plants also have a “dirty” lower pressure water/steam cycle referred to as process steam system or dilution steam system.

In ethylene plants, pyrolysis furnace effluent is cooled in a quench water tower. This results in condensation of an organic phase and of the process steam used as a diluent in pyrolysis. Pyrolysis gasoline, heavy tars, and water are subsequently separated by gravity in a drum. The organics-laden water then proceeds to a steam stripper designed to remove dissolved hydrocarbons, notably styrene, before it becomes the feedwater to the dilution steam generators. The process steam produced is returned to the cracking furnaces.

The hydrocarbon/water separation, which is at the heart of the plant, poses challenges in terms of pH and interface control. Moreover, the operating temperature of the stripper (> 120 °C) promotes polymerization of olefinic species such as styrene. Indeed, polystyrenic and pytar fouling of dilution steam generators is a major issue in ethylene manufacturing.

FFS may be incompatible with the nature of the organic fouling or simply “overwhelmed” by its quantity. The deportment of film-forming molecules during cracking and decoking must be regarded. They (or their breakdown products) should not interfere with the quality of the phase separation in, or (given the surface active properties of FFS) interact with emulsion breakers added to, the quench water tower.

9.18.2 Systems in Ammonia Production

In most ammonia plants, the hydrogen needed to react with nitrogen from the air in the synthesis section is produced through steam reforming of natural gas, followed by a water gas shift. Both of these unit operations involve the use of catalysts. Compatibility of the catalysts with FFS is of paramount importance and should be established in cooperation with the catalyst supplier.

Non-reacted steam from reforming is condensed in the process. The process condensate contains ammonia, carbon dioxide, alcohols (methanol, ethanol), and short-chain carboxylic acids (formic, acetic) as main impurities. It first proceeds to a steam stripper. After that, there are several treatment options. For all practical purposes, it is mentioned here that residual methanol and ethanol after stripping do not adsorb onto ion exchange resin in any significant way, and that it is common for steam systems in ammonia plants to contain from several to tens of ppm of methanol in boiler water [87].

Raeymaekers has described the experience with an FFAP in a 125 bar steam system of an ammonia plant [86].

9.18.3 Systems in Paper Production

In pulp and paper mill factories, boilers are installed for in-house power generation and for heat sources of digester and paper-making dryers. Approximately 40% of all steam in paper mills is used for drying sections.

As the steam may have contact with paper used for food packaging, the operator intending to apply a FFS-based product should verify that there is full compliance with legislation (see Section 9.13).

Film Forming Amines and Film Forming Amine Products
The application of FFAP in power plants of paper mills has been published [39, 40, 78]. Mori [88] reports of the application of a FFAP containing only FFA in the drying cylinders of paper mills. Hydrophobicity of the surfaces due to FFAP decreased the thickness of the water film in the dryers. The liquid film layer of condensed water on metal was reduced by the FFA, so that heat transfer resistance decreased accordingly.

Plant results indicate that the FFAP typically reduces the steam consumption of the dryers by 5% to 10%.

Film Forming Products
There is not the same detailed open or publicly available literature for the effect of FFP for systems in industrial paper plants. If a plant operator/owner is considering use of one of these FFP for any application, then it requires that plant personnel ask the critical questions regarding the application in these systems for paper production.

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