

# All-Volatile Treatment with Film Forming Amines – A First Suggestion for an Application Guidance

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## ABSTRACT

The positive properties of filming amines with respect to corrosion protection in water-steam cycles have been known for many decades. The application of film forming amines in industrial and utility steam-water cycles is constantly increasing. However, there are still no internationally accepted recommendations or guidelines covering the application of film forming and neutralizing amine blends. In this paper, the positive long-term field experience with film forming amines is summarized and an attempt is made to develop a first draft of a guidance for the use of alkalizing and film forming amines with all-volatile treatment. It is hoped that the proposed guidance will serve as a first blueprint for further discussions.

## INTRODUCTION

Hard to believe but true: the positive properties of filming amines with respect to corrosion protection in water-steam cycles have been known for many decades although the first applications of filming amines were reported not from the power industry but from the automotive industry (non-corrosive anti-freeze liquids for automobile heat exchange devices) and oil industry. The use of alkalizing amines for conditioning boiler, steam and condensate systems is also very old. You may find it interesting that the first patent application dealing with this topic was already filed in the first half of the 1930s [1]. The properties and the use of alkalizing amines have been very intensively studied in the last four decades. Their application in nuclear cycles with pressurized water reactors (see, e.g., [2]) and in fossil plant cycles (see, e.g., [3]) are in accordance with the current state of cycle chemistry technology. It has to be mentioned that the last (2015) revision of the IAPWS Technical Guidance Document: Volatile Treatments for the Steam-Water Circuits of Fossil and Combined Cycle/Heat Recovery Steam Generator (HRSG) Power Plants explicitly states that only volatile alkalizing agents should be added to the feedwater (commonly ammonia, but volatile amines may also be employed) [4]. In this way, the necessity of listing hundreds and hundreds of references related to alkalizing amines is dispensed with.

Sloan's patent applied for in 1939 [5] relates to the protection of ferrous metals against corrosion, and more particularly to the use of long-chain aliphatic amines as corrosion inhibitors for iron and steel surfaces, whether clean, rusty,

chemically treated or plated with a relatively less corrodible metal. As an example, the first two claims (out of eighteen specified in the patent application) are copied verbatim below:

1. The process for the protection from atmospheric corrosion of metallic surfaces susceptible to said corrosion which comprises applying to said surfaces a film of an acyclic aliphatic monoamine having an aliphatic group of a chain length of at least 8 carbon atoms, so as to provide a layer of amines having a thickness within the range corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.
2. The process for the protection of iron against oxidation which comprises coating the iron surface with a film of an acyclic aliphatic monoamine, the aliphatic group of said amine having a chain length of 10 to 24 carbon atoms so as to produce a layer of amines having a thickness within the range corresponding to a spread of 10,000 sq. ft. to 80,000 sq. ft./lb. of amines.

In the forties, a method of inhibiting corrosion was described which uses high molecular weight amines, amine salts and amine oxides. Extensive use commercially has been made of octadecylamine and octadecylamine acetate in carrying out this process [6]. Since octadecylamine is almost insoluble in water, many tasks were focused on the creation of adequate solutions or suspensions containing film forming aliphatic amines such as octadecylamine that would be well suited for dosing into water-steam cycles [7–10]. How to apply filming

amines for the control of steam and condensate return line corrosion is explained by Obrecht [11]. Instead of using octadecylamine acetate to accomplish dispersion or solution, it is recommended to use inhibitor emulsions of octadecylamine and other amines that can be easily dissolved in water.

The application of film forming amines for corrosion protection in steam/condensate systems in industrial steam generating has developed very rapidly. This is demonstrated by the fact that already in 1977, the Code of Federal Regulations (Title 21, § 173.310) addressed the impact of steam generation on food processing and stated limitations on the concentration of some substances (cyclohexylamine, diethylaminoethanol, hydrazine, morpholine, and octadecylamine) in the steam. For octadecylamine it says among other things: the concentration of octadecylamine is not to exceed  $3 \text{ mg} \cdot \text{kg}^{-1}$  in steam, and the use of such steam in contact with milk and milk products must be excluded. By the way, this data is still valid [12]. Figures 1 and 2 illustrate the feeding of amines in industrial generating units at the end of the sixties.

A new chapter in the use of filming amines for corrosion protection in fossil plant cycles was established by the

work of Moran and coworkers in the early eighties [15–17]. They introduced substances that belong to the oligo-alkylamino fatty amine family – often referred to as polyamines. The general chemical formula for these substances was given in [15] as



where

R is an unbranched alkyl chain with 12 to 22 carbon atoms,

m an integer of between 2 and 8 inclusive, and

n an integer of between 1 and 7 inclusive.

In [18] and [19], a very similar formula is presented, in which the numbers of carbon atoms are a bit more restricted than in [15] and the range of the integer n is defined in a way in which the formula represents not only polyamines but also alkyl monoamines.

In the last three decades, physical and chemical properties of polyamines as well as their behavior in plant cycles have been thoroughly investigated. A complete list of references would go beyond the scope of this contribution. Nevertheless, some of the most important scientific studies and publications focusing on polyamines are

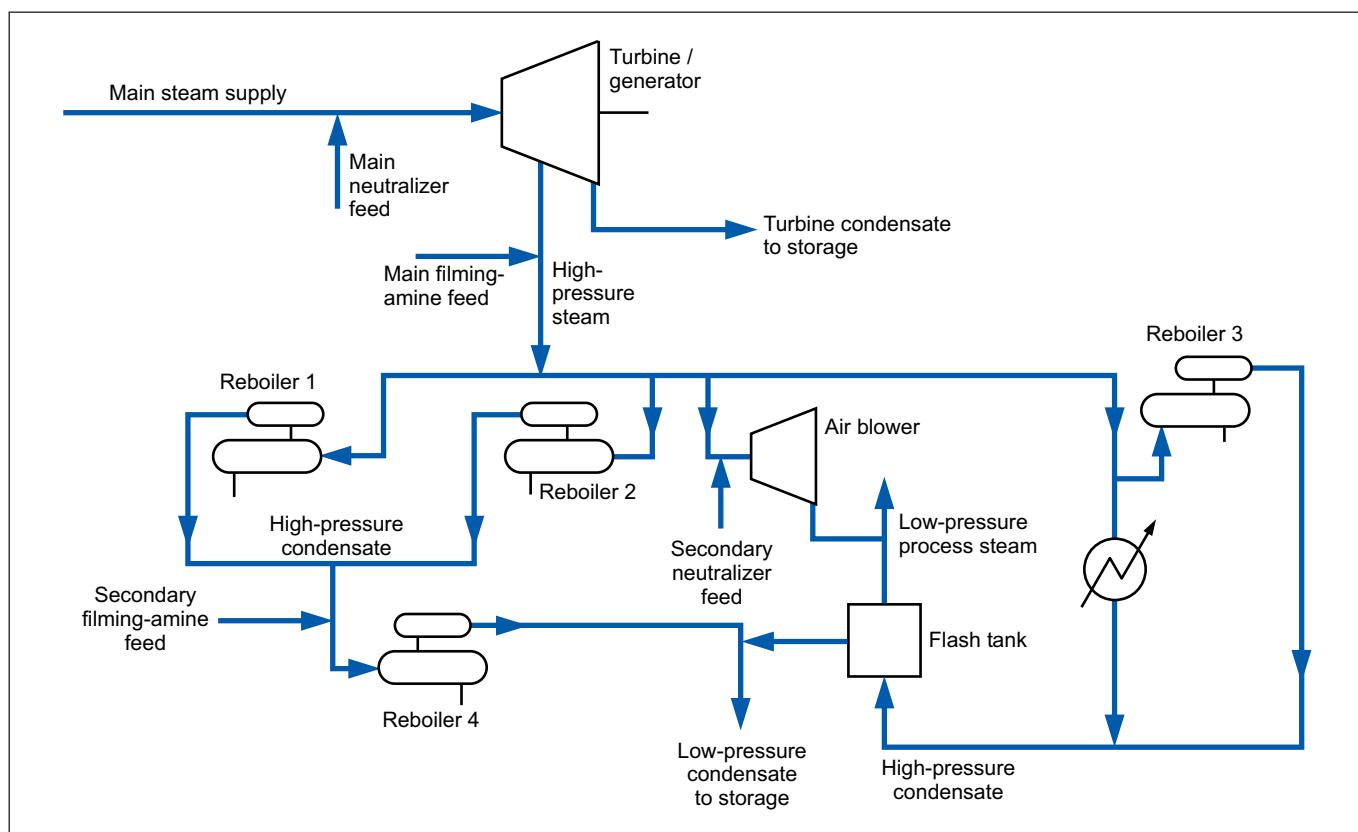


Figure 1:

Primary and secondary feed steam-generating systems for alkalinizing and filming amines in a steam/condensate system typifying complexity of industrial generating units [13].

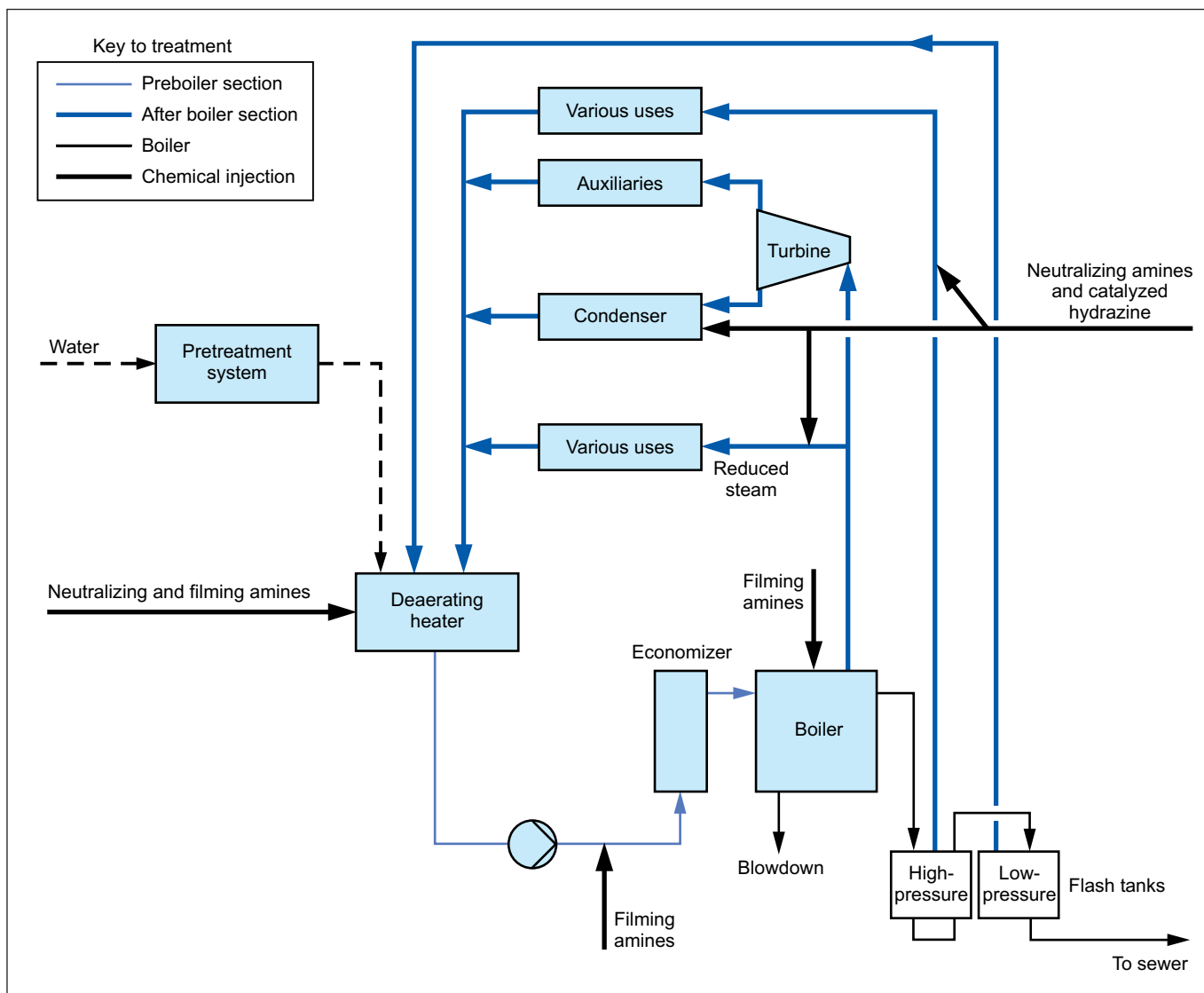


Figure 2:

Feed points for chemicals in steam-generating systems are selected to provide protection against corrosion in piping in equipment located both close to and far from the boiler [14].

worth noting. They deal with the basic chemistry of polyamines [15,19,20], their basicity and equivalent conductivity [21], adsorption and desorption behavior [22–24], and film characterization [25–32]. A large number of publications is devoted to polyamine application properties such as their impact on heat transfer and boiling behavior [33–34], on operational safety and on the magnetite layer [35–36], on flow resistance [37], on improvement of turbine efficiency [38,39], and on avoidance of early condensate corrosion [40].

From the big group of polyamines three film forming amines are most commonly used:

- Octadecylamine
- Oleylamine
- Oleylpropylenediamine

Oleylpropylenediamine in particular has been the subject of recent studies.

Among the homologues of film forming amines (mono-, di-, tri-...), monoamines and diamines provide the best corrosion protection on steel. The diamines form thinner films than monoamines, which reduces the organic load in the water-steam cycle [23].

Since the first polyamine patent applications from Moran et al. [15] and Moran [17], the use of polyamine-containing proprietary mixtures for plant cycle treatment has been increasing rapidly. Following the first use in relatively low-pressure industrial steam generating cycles, polyamine-based treatment chemicals have been applied in many high-pressure cycles, not only at industrial steam generators but also in cogenerating and combined cycle plants

as well as in utility power plants. Although the vast majority of polyamine applications are reported from units with drum-type boilers or comparable steam-generating equipment in different industries, Schöntag presented a report about the successful implementation of a polyamine treatment in two cycles with once-through steam generators (steam parameter: 20 MPa, 540 °C) [41]. This information was later confirmed by [42].

## TREATMENT WITH FILM FORMING AMINE BASED PRODUCTS

Film forming amine based products are usually proprietary blends. The blends typically contain both film forming and alkalizing amines. For some specific applications, components of the mixture can be polycarboxylates and reducing agents. Especially when using monoamines as film forming amines (e.g., octadecylamine), other substances such as solubilizers or emulsifiers are often used.

This publication focuses on products exclusively based on film forming and alkalizing amines. Since both types of amines belong to the group of volatile substances, an attempt will be made to establish an operational guidance comparable to those for the three existing variants of all-volatile treatment: all-volatile treatment reducing and oxidizing, and oxygenated treatment.

This guidance is based on experience with the use of film forming amine blends gained in hundreds upon hundreds of industrial and utility water-steam cycles as well as in cogenerating and combined cycle plants operated in a wide range of operating pressures. Most users highlight the following benefits of this treatment:

- optimum pH control in both water and steam phases;
- very low concentrations of corrosion products in all plant cycle streams. Improvement in condensate and feedwater quality often makes a reduction in the boiler blowdown possible;
- much lower deposition in cycle components; surfaces in contact with water or steam are typically clean and smooth. Experience gained in systems with boilers originally operated on phosphate treatment confirms that after a conversion to treatment with the film forming amine blends turbines are cleaner and their efficiency increases;
- avoidance of boiler tube failures caused by under-deposit corrosion;
- corrosion protection under standby conditions (wet or dry standby);
- short startup times, increased unit availability;
- improved heat transfer;
- reduction or avoidance of flow-accelerated corrosion.

In order to be correct, three drawbacks of using blends with film forming and alkalizing amines have to be mentioned:

- due to partial decomposition of alkalizing amines, the cation conductivity of steam and condensate is a bit elevated. This fact causes difficulties in complying with turbine manufacturers' steam specifications although results of decades of operation with a slightly increased cation conductivity of the steam confirm that this small increase is not harmful;
- increased cation conductivity of condensate makes the condensate tightness surveillance more difficult – a possible small cooling water inleakage may be masked;
- the market with organic treatment chemicals is confusing. Unfortunately, there are some black sheep in the marketplace offering and supplying inadequate amine blends containing some undefined ingredients. For this reason, selection criteria are needed. These include, in particular, completeness of product documentation and compliance with regulations, service/troubleshooting capabilities, experience of the service staff, scientific background, and a certified quality management system.

It seems that the attitude towards alkalizing amines has changed in recent years. For example, Sadler et al. discussed a possible use of volatile amines in air-cooled fossil-fired boiler/turbine units to ensure that the pH in the early condensate droplets formed in air-cooled condensers is high enough to suppress any corrosion [43]. In the IAPWS Technical Guidance Document: Volatile Treatments for the Steam-Water Circuits of Fossil and Combined Cycle/HRSG Power Plants [4], all-volatile treatment is defined as a conditioning regime in which only volatile alkalizing agents are added to the feedwater (commonly ammonia, but volatile amines may also be employed). Unfortunately, the attitude towards film forming and alkalizing amines has not changed as yet, as demonstrated by the following statements in the VGB-Standard [44]:

- Plants using organic treatment chemicals should thoroughly reconsider the actual chemical regime and investigate whether the applied chemicals are really indispensable or if a reduction in the number of chemicals is feasible. Single substances should be preferred, rather than proprietary chemical blends.
- A redesign of systems may be a worthwhile challenge to reduce the number and dosing concentrations of organic treatment chemicals or even enable a chemical treatment according to Chapters 5.3.1 and 5.3.2 (*explanation: standard treatments without organic treatment chemicals*) and thus save operating costs.
- Plants with long-term good operational experience without any damage or upsets related to the use of organic treatment chemicals may continue with the proven chemical regime, but should take the above-mentioned statements into account.

It is interesting to mention that a VGB research project published in 2003 answered the question "Are amines an alternative to conventional agents for water-steam-cycles?" from the point of view of the heat transfer and new water conditioning agents with "yes" [35].

Dooley initially presented the Continuum of Treatments to help operators in selecting the boiler and feedwater treatments that match the equipment and the equipment capability (Figure 3). The width of the wedge or funnel in which the continuum of treatments is located is proportional to the level of possible contaminants in the cycle. So the point of the funnel represents a plant with a condensate polisher or a very tight condenser. The open end represents plants without polishing, using seawater or cooling water with a high content of dissolved solids, or with a cooling tower. The better the air-inleakage control, the nearer to the point of the wedge. Those treatments located in the continuum nearer to the open end are those which can better counteract contamination [45]. The continuum of treatments was later extended a bit as shown in Figure 4 [46].

Bursik discussed the application of film forming and alkalinizing amines in plant cycles in detail and pointed out that operators of steam generating systems in industry need a simple but reliable cycle treatment which requires only minimum surveillance and which can be applied almost without any special knowledge and staffing requirements on site. Adequately volatile organic chemical(s), adequately stable under pressure and temperature conditions within the cycle, could help to simplify the cycle chemistry control in many industrial cycles [47].

It cannot be excluded that such chemicals or chemical mixtures will find their way from steam generation in industry into steam generation in utilities, as demonstrated by utility applications in units operated in cycling or peaking modes of operation. Recently, an interesting report was presented at the VGB Conference "Chemistry in Power Plants 2015." Sylwestrzak et al. reported on operation experience gained with AVT(F) in five 125 MW units (main steam parameters: temperature 535 °C, pressure 12.7 MPa) [48].

By the way, the number of cycles with high pressure boilers operated on amine treatment was already steadily increasing in 2002. For the first time, a modified version of the continuum of treatments including amine treatment (use of film forming and alkalinizing amines) – Figure 5 – was presented [47].

Though the organic cycle treatment chemicals have already been used for decades, there are no internationally accepted recommendations or guidelines covering the application of film forming and neutralizing amine blends. The treatment with film forming and neutralizing amines does not require the addition of reducing agents or oxygen injection. For this reason, the oxidizing all-volatile treatment, AVT(O), can be taken as the basis for establishing cycle chemistry limits for all-volatile treatment based on the application of film forming and alkalinizing amines.

Feedwater chemistry is critical to the overall reliability of fossil and HRSG plants. Corrosion takes place in the feedwater system (heaters and interconnecting pipework), and the associated corrosion products flow into the boiler/HRSG, where they may deposit in various areas. These

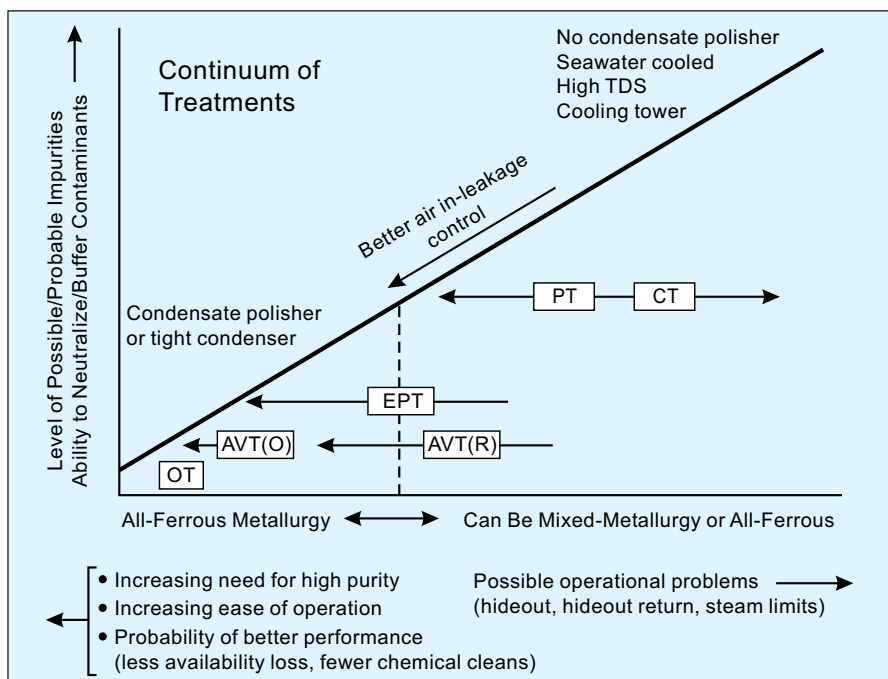


Figure 3: Summary of possible boiler water and feedwater for fossil plants as a function of equipment and equipment capability [45].  
 PT phosphate treatment  
 CT caustic treatment  
 EPT equilibrium phosphate treatment  
 AVT(O) all-volatile treatment oxidizing  
 AVT(R) all-volatile treatment reducing  
 OT oxygenated treatment

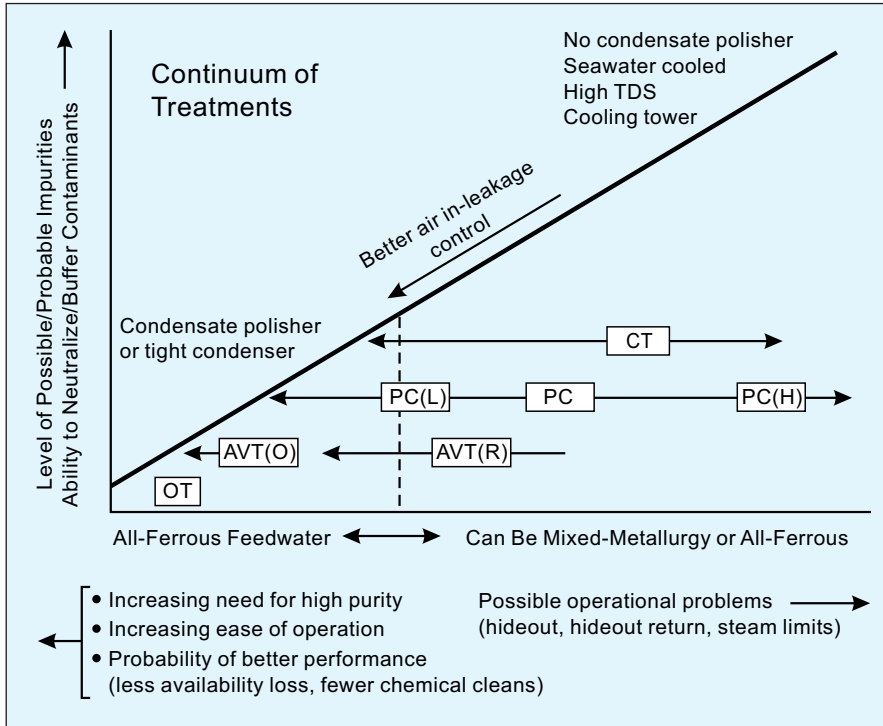


Figure 4:

Extended version of the continuum of treatment as presented by Dooley and Shields [46].

- PC phosphate continuum treatment
- PC(L) low-level phosphate treatment
- PC(H) high-level phosphate treatment

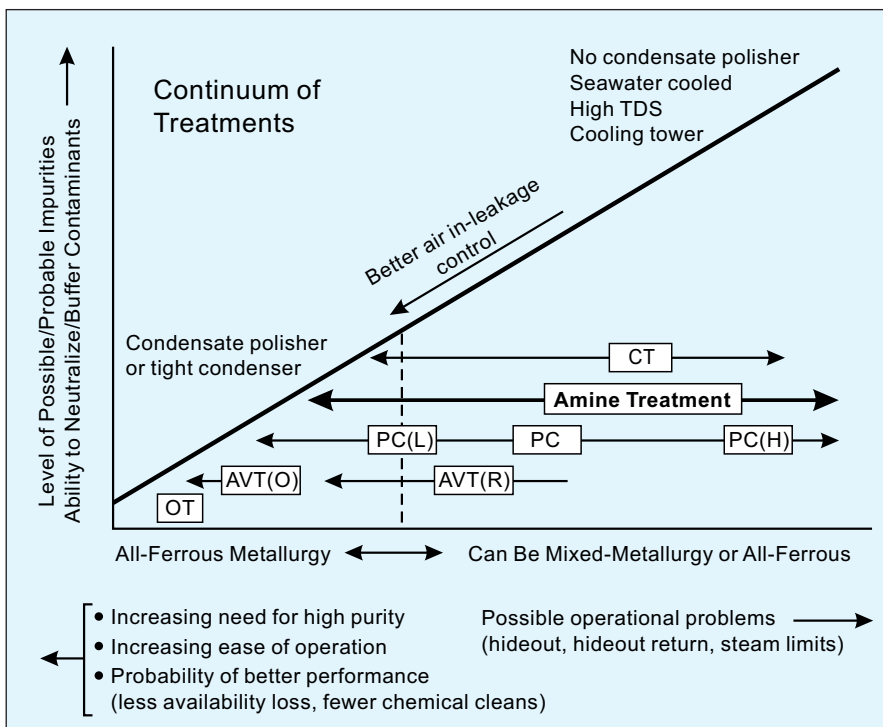


Figure 5:

Modified version of the continuum of treatments also containing film forming and alkalinizing treatment as presented in [47] and [49].

deposits can act in the boiler/HRSG evaporator as initiating centers for many of the tube failure mechanisms, and in the steam turbine as a source of either efficiency losses or blade/disk failures. The choice of feedwater chemistry depends primarily on the materials of construction and secondly on the feasibility of maintaining purity around the water-steam cycle [4].

Three distinct treatments are covered in [4]:

- AVT(R) – All-Volatile Treatment (Reducing)  
This treatment involves the addition of ammonia (or an amine or blend of amines of lower volatility than ammonia) and a reducing agent (usually hydrazine or one of the acceptable substitutes)



- AVT(O) – All-Volatile Treatment (Oxidizing)  
This all-volatile treatment has emerged as the much preferred treatment over the last 20 years for feedwater systems which only contain all-ferrous materials (copper alloys can nevertheless be present in the condenser). This treatment involves the addition of ammonia (or an amine or blend of amines of lower volatility than ammonia). A reducing agent should not be used during any operating or shutdown period.
- OT – Oxygenated Treatment  
For conventional fossil plants, OT involves oxygen and ammonia injection at the condensate polisher outlet and operation with the vents on the feedwater heaters and deaerator closed.

A further AVT option, based on the usage of alkalizing and film forming amines, is being applied frequently. Unfortunately, this treatment, called AVT(F), is not covered in any major plant cycle chemistry guidelines. In this paper, an attempt is made to develop a first draft of an AVT(F) guidance that should be used as the basis for further discussions.

### ALL-VOLATILE TREATMENT WITH ALKALIZING AND FILM FORMING AMINES – AVT(F)

Based on experience from many units operated on AVT(F), [Table 1](#) shows a comparison of normal or target AVT(F) values and normal or target values as specified in the IAPWS Technical Guidance Document for AVT(O) [4]. It should be clear that the presented AVT(F) values are a first attempt to summarize and reflect on the positive long-term field experience, and that the data presented are intended to serve as a first blueprint for further discussions.

In the IAPWS document it is explicitly stated that industrial steam raising plants are not covered in the Guidance Document [4]. In contrast, the AVT(F) data is applicable to all industrial steam generating installations, to water-steam cycles in utilities, and also to multi-pressure combined cycle/heat recovery steam generator drum units.

As already mentioned, increased cation conductivity of condensate makes the condensate tightness surveillance more difficult – a possible small cooling water inleakage may be masked. For this reason, compliance with appropriate recommendations specified in detail in the IAPWS Technical Guidance Document: Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-Water Circuits of Fossil-Fired and Combined Cycle Power Plants [50] is strongly advised. According to [50], the on-line measurement of sodium ion provides a very sensitive indication of the ingress of contaminants into condensate.

As with all other guidelines or recommendations dealing with plant cycle chemistry, the master data in the AVT(F) column in [Table 1](#) necessarily require careful customization. During the customization process, development of action and shutdown levels as well as consideration of all system conditions, such as cycle design, operating pressure, mode of operation, materials in contact with water and steam, cooling media characteristics and type of cooling, are essential. Due to lack of space, complete instructions on how to customize the AVT(F) normal/target values cannot be given in this publication. Bear in mind that in the IAPWS Technical Guidance Document: Volatile Treatments for the Steam-Water Circuits of Fossil and Combined Cycle/HRSG Power Plants [4], the section dealing with customization consists of 12 pages, and in the IAPWS Technical Guidance Document: Phosphate and NaOH Treatments for the Steam-Water Circuits of Drum Boilers of Fossil and Combined Cycle/HRSG Power Plants [51], the figure is still 11 pages. For this reason, only some of the more important points follow.

A large number of industrial steam generating plants operate at operating pressures  $\leq 6$  MPa, and many of them do not have steam turbines. For such plants a significant relaxation of the boiler water cation conductivity normal/target value of  $\leq 5 \mu\text{S} \cdot \text{cm}^{-1}$  is possible. For example, the admissible cation conductivity of boiler water of a boiler operated at 6 MPa can be increased to  $\leq 25 \mu\text{S} \cdot \text{cm}^{-1}$ .

A major benefit of the AVT(F) is the fact that the protective film developing throughout the entire facility protects not only surfaces made of steel but also copper-containing materials. Recent studies and experiments with closed cooling systems also provide encouraging results with respect to the protection of aluminum [52].

When applied correctly, alkalizing and film forming amines provide excellent protection against single-phase flow-accelerated corrosion. Scientific research by Lister et al. [53] confirms that under AVT(F) single-phase flow-accelerated corrosion can be substantially reduced or even avoided. Initial experience in the operation of air-cooled condensers on AVT(F) shows promising results with respect to significant reduction or avoidance of two-phase flow-accelerated corrosion [54,55].

AVT(F) offers two distinctive advantages:

- This treatment is applicable to very different systems without any major changes. The system configuration (small low-pressure steam producing plant, large utility unit, industrial steam generator with or without steam sendout, combined cycle HRSG plant) makes no significant difference in the practical application of AVT(F).
- Units operated on AVT(F) are very insensitive to load transients, frequent startups/stops, and prolonged shut-

Locations/Parameters	Normal/Target Values	
	AVT(F)	IAPWS AVT(O)
<b>Condensate Pump Discharge</b>		
Conductivity after cation exchange [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	$\leq 0.6^{(1)}$	< 0.3
Dissolved oxygen [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 20	< 10
Sodium [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 3	< 3
pH	8.8–9.5 <sup>(2)</sup>	
Silica [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 20	
Film forming amine [ $\text{mg} \cdot \text{kg}^{-1}$ ]	qualitative proof –0.3	
<b>Condensate Polisher Outlet</b>		
Conductivity [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	<sup>(3)</sup>	< 0.2
Sodium [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	<sup>(3)</sup>	< 2
<b>Economizer Inlet, Preheater Inlet or Feed Pump Discharge</b>		
Conductivity [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	consistent with pH	consistent with pH
Conductivity after cation exchange [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	$\leq 0.6^{(1)}$	< 0.2
pH	8.8–9.5 <sup>(2)</sup>	9.2–9.8
Dissolved oxygen [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	5–20	5–10
<b>Boiler Drum/Blowdown/Downcomer</b>		
Conductivity [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	consistent with pH	consistent with pH
Conductivity after cation exchange [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	$\leq 5$	< 1.5
pH	8.8–10	9–9.6
<b>Saturated Steam</b>		
Conductivity after cation exchange [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	$\leq 0.6^{(1)}$	< 0.2
Sodium [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 2	< 2
pH	8.8–9.5 <sup>(2)</sup>	
SiO <sub>2</sub> [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 20	
<b>Main Steam/Reheat Steam</b>		
Conductivity after cation exchange [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	$\leq 0.6^{(1)}$	< 0.2
Sodium [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 2	< 2
pH	8.8–9.5 <sup>(2)</sup>	
SiO <sub>2</sub> [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 20	
<b>Makeup</b>		
Conductivity [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	< 0.1	< 0.1
Conductivity after cation exchange [ $\mu\text{S} \cdot \text{cm}^{-1}$ ]	< 0.1	< 0.1
SiO <sub>2</sub> [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	< 10	< 10

Table 1:

Guidance for AVT(F) compared to the IAPWS Guidance for AVT(O).

The guidance for AVT(F) is applicable to fossil plants with drum units, with drum pressures ~13 MPa (at higher pressures only limited experience is available), all-ferrous and mixed metallurgy systems, no reducing agent, copper and non-copper tubed condensers, without condensate polishers, and not cooled by high total dissolved solids cooling water.

(1) the conductivity after cation exchange is plant specific

(2) for systems containing copper and copper alloys: pH 8.8–9.3

(3) the large majority of systems operated on AVT(F) do not have condensate polishers

The IAPWS Guidance for AVT(O) is applicable to fossil plants with drum units, with drum pressures ~17 MPa, all-ferrous systems, no reducing agent, non-copper tubed condensers, with a condensate polisher, and not cooled by seawater or brackish water [4].



downs. The corrosion product level during startup of the unit is typically very low. Layup procedures (dry or wet layup) based on the application of alkalizing and film forming amines are compatible with operation on AVT(F).

## FREQUENTLY ASKED QUESTIONS (FAQs)

For lack of space, this publication cannot deal with all aspects of AVT(F) in detail. Nevertheless, brief comments on or answers to some FAQs follow.

### – Can AVT(F) be utilized in steam-water cycles with shell boilers?

Yes, there is enough practical experience with AVT(F) in such cycles. The interested parties may find useful information in [56] and [57].

### – Is there any positive experience with film forming amines in terms of dry or wet layup of steam generators or entire steam-water cycles?

The application of film forming amines for the layup of steam generators and entire steam-water cycles has been carried out for several decades. It is however advisable to carefully read the recent work and reports in the literature. You will find some interesting publications listed in the references under [23] and [58–61].

### – What about the corrosion product levels in steam-water cycles operated on AVT(F)?

According to the major plant cycle chemistry guidelines and IAPWS Technical Guidance Documents, satisfying the "rule of 2 and 5" (first defined by Dooley [62]), whereby the iron level is consistently less than  $2 \mu\text{g} \cdot \text{kg}^{-1}$  in the feedwater and less than  $5 \mu\text{g} \cdot \text{kg}^{-1}$  in the boiler water, provides an indication that flow-accelerated corrosion is not active, but also prevents excessive deposition of corrosion products in the boiler/evaporator tubing [63]. In systems operated on AVT(F), the "rule of 2 and 5" is generally complied with. In units operated in peaking or cycling mode, reaching the "rule of 2 and 5" limits occurs much faster with AVT(F) treatment than with AVT(O) treatment.

### – Can AVT(F) be applied in steam-water cycles with main steam temperatures higher than 450 °C?

There are many units with main steam temperatures > 450 °C operated on AVT(F). These are only some examples:

- co-generation units with once-through steam generators, main steam temperature 540 °C [41] (decommissioned);
- a combined heat and power plant with drum boilers, main steam temperature 525 °C [18];
- a lignite-fired power plant with drum boilers, main steam temperature 535 °C [48];
- a high-pressure steam system of a naphtha cracker, main steam temperature 520 °C [54];

- two combined cycle plants, main steam temperature 565 °C [64].

## SUMMARY

The application of film forming amines in industrial and utility steam-water cycles is constantly increasing. Though these organic cycle treatment chemicals have already been used for decades, there are no internationally accepted recommendations or guidelines covering the application of film forming and neutralizing amine blends. This paper represents a first attempt to summarize and reflect on the positive long-term field experience with film forming amines and is intended to serve as a first blueprint for further discussions. The authors greatly appreciate the IAPWS activities (see remark below) devoted to the development of an internationally accepted Technical Guidance Document on the use of film forming amines in steam-water cycles.

Fourteen years ago, the paper "Carbon Is Not Equal to Carbon" was presented [65]. In this paper (already in 2001) it was confirmed that organic plant cycle treatment chemicals are increasingly being applied in fossil power generation. Roothoof et al. investigated the thermal stability of alkalizing amines and of a long-chain diamine with surprising results – the decomposition products do not endanger plant cycle components [66]. The  $0.2 \mu\text{S} \cdot \text{cm}^{-1}$  problem was also raised. Unfortunately, the current situation does not markedly differ from that in 2001. But not only from the situation in 2001 – the first report about a successful application of film forming amines in a large utility power plant (8 x 200 MW, steam parameters: 13.7 MPa, 540 °C) was already published in 1992 [67]. How time flies!

We hope that this publication will help to get things moving, and we are very curious about the new IAPWS Technical Guidance Document on the use of film forming amines in steam-water cycles to be presented next year.

## REMARK

According to the Press Release about the 2015 Annual Meeting of the International Association for the Properties of Water and Steam in Stockholm, Sweden, in the meetings of the Power Cycle Chemistry Group three new Technical Guidance Documents are currently being prepared for release at the 2016 meeting. These include guidance on the use of film forming amines in water-steam cycles [68]. Persons interested in active involvement may contact either the IAPWS executive secretary Barry Dooley ([bdooley@structint.com](mailto:bdooley@structint.com)) or Technical Guidance Document Task Group members Wolfgang Hater ([wolfgang.hater@kurita.eu](mailto:wolfgang.hater@kurita.eu)) and Marco Lendi ([marco.lendi@swan.ch](mailto:marco.lendi@swan.ch)).

## REFERENCES

- [1] Dreyfus, M. E., *Compound and Method for Conditioning Boiler, Steam and Condensate Systems*, **1934**. United States Patent and Trademark Office, US 2053024 A.
- [2] *PWR Advanced Amine Application Guidelines, Revision 2*, **1997**. Electric Power Research Institute, Palo Alto, CA, U.S.A., TR-102952-R2. The document is downloadable at [www.epri.com](http://www.epri.com).
- [3] *Assessment of Amines for Fossil Plant Applications*, **2010**. Electric Power Research Institute, Palo Alto, CA, U.S.A., 1017475.
- [4] *IAPWS Technical Guidance Document – 2015 Revision: Volatile Treatments for the Steam-Water Circuits of Fossil and Combined Cycle/HRSG Power Plants*, **2015**. The document is downloadable at [www.iapws.org](http://www.iapws.org).
- [5] Sloan, C. S., *Protection of Ferrous Metals against Corrosion*, **1939**. United States Patent and Trademark Office, US 2333206 A.
- [6] Kahler, H. L., *Method of Protecting Systems for Transporting Media Corrosive to Metal*, **1946**. United States Patent and Trademark Office, US 2460259 A.
- [7] Cross, J. M., *Water-Soluble Compositions Containing Water-Insoluble Organic Amines*, **1950**. United States Patent and Trademark Office, US 2779741 A.
- [8] Maguire, J. J., *Octadecylamine Materials and Process*, **1954**. United States Patent and Trademark Office, US 2712531 A.
- [9] Denman, W. L., *Corrosion Inhibiting Composition and Method*, **1956**. United States Patent and Trademark Office, US 2882171 A.
- [10] Walker, J. L., Cornelius, T. E., *Filming Amine Emulsions*, **1973**. United States Patent and Trademark Office, US 3860430 A.
- [11] Obrecht, M. V., *Heating, Piping & Air Conditioning* **1964**, October, 116.
- [12] *The Code of Federal Regulations, 21 CFR 173.310 – Boiler Water Additives*, **2011**. U.S. Government Publishing Office, Washington, DC, U.S.A.
- [13] Tatura, G., *Power* **1979**, September, 106.
- [14] Beecher, J., *Power* **1981**, July, 74.
- [15] Moran, F., Rocher, S., Duprat, M., *Corrosion Inhibiting Composition, Process for Its Preparation and Its Use in the Field of Metal Surface Protection*, **1981**. European Patent Office, EP 0065609 A1.
- [16] Duprat, M., Dabosi, F., Moran, F., Rocher, S., *Proc., 8th International Congress on Metallic Corrosion*, **1981** (Mainz, Germany), Volume II, 1218.
- [17] Moran, F., *Corrosion Inhibiting Composition for Protecting the Metallic Surfaces of Plants Using Water as a Thermal or Energetic Fluid, and Process for Protecting These Surfaces*, **1983**. European Patent Office, EP 0134365 A1.
- [18] Hater, W., Rudschützky, N., Olivet, D., *PowerPlant Chemistry* **2009**, 11(2), 90.
- [19] Hater, W., de Bache, A., *ipw* **2010**, 10–11, 12.
- [20] Moran, F., *Scale and Corrosion Inhibiting Composition for Protecting Surfaces in Contact with Water and Method for the Preparation of Said Composition*, **1954**. European Patent Office, EP 0774017 B1.
- [21] Hater, W., de Bache, A., *PowerPlant Chemistry* **2013**, 15(4), 289.
- [22] Bohnsack, G., *Proc., VGB Expert Conference Industrial, Cogeneration and Combined Heat and Power Plants*, **1996** (Münster, Germany). VGB Technische Vereinigung der Grosskraftwerksbetreiber, Essen, Germany [in German]. Paper also published as Bohnsack, G., *VGB Kraftwerkstechnik* **1997**, 77(10), 841 [in German].
- [23] Hater, W., de Bache, A., Petrick, T., *PowerPlant Chemistry* **2014**, 16(5), 284.
- [24] Hater, W., de Bache, A., Petrick, T., *European HRSG Forum*, **2014** (Heidelberg, Germany). The paper is downloadable at [www.europeanhrsgforum.de](http://www.europeanhrsgforum.de).
- [25] Allard, B., Chakraborti, S., Kannappan, A., *Kemist Tidskrift* **1982**, 9, 107 [in Swedish].
- [26] Allard, B., Chakraborti, S., *Svensk Papperstidning* **1983**, 86(18), R 186.
- [27] Duprat, M., Lafont, M.-C., Dabosi, F., Moran, F., *Electrochimica Acta* **1985**, 30(3), 353.
- [28] Ochoa, N., Moran, F., Pébère, N., *Journal of Applied Electrochemistry* **2004**, 34(5), 487.
- [29] Ochoa, N., Moran, F., Pébère, N., Tribellet, B., *Corrosion Science* **2005**, 47(3), 593.
- [30] Frahne, D., Blum, T., *PowerPlant Chemistry* **2006**, 8(1), 21.
- [31] Foret, C., Stoianovici, G., Chaussec, G., de Bache, A., zum Kolk, C., Hater, W., *Proc., EUROCORR 2008 (on CD)*, **2008** (Edinburgh, United Kingdom, September 7–11, 2008).
- [32] Öztürk, I., Sezer, E., *Proc., EUROCORR 2011 (on CD)*, **2011** (Stockholm, Sweden, September 4–8, 2011).
- [33] Topp, H., Steinbrecht, D., Hater, W., de Bache, A., *PowerPlant Chemistry* **2010**, 12(7), 388.
- [34] Gasnier, C., Lister, H. D., *Proc., International Conference on Heat Exchanger Fouling and Cleaning*, **2013** (Budapest, Hungary), 85.

- [35] Steinbrecht, D., *Proc., VGB Expert Conference Industrial, Cogeneration and Combined Heat and Power Plants*, **2002** (Rostock, Germany). VGB Technische Vereinigung der Grosskraftwerksbetreiber, Essen, Germany [in German]. Paper also published as Steinbrecht, D., *VGB PowerTech* **2003**, 83(9), 120 [in German].
- [36] Topp, H., Hater, W., de Bache, A., zum Kolk, C., *PowerPlant Chemistry* **2012**, 14(1), 38.
- [37] Ryzhenkov, V. A., Petrova, T. I., Ryzhenkov, A. V., *PowerPlant Chemistry* **2012**, 14(7), 449.
- [38] Duisters, H., Savelkoul, J., *Proc., AIChE Safety in Ammonia Plants and Related Facilities Symposium*, **2005** (Toronto, ON, Canada). American Institute of Chemical Engineers, New York, NY, U.S.A., 46, 93.
- [39] Savelkoul, J., van Lier, R., *PowerPlant Chemistry* **2005**, 7(12), 733.
- [40] Savelkoul, J., Janssen, P., Verhoef, H., *PowerPlant Chemistry* **2001**, 3(6), 326.
- [41] Schöntag, W., *Proc., PowerPlant Chemistry Seminar "Feedwater and Boiler Water Treatment in Industrial, Co-Generation, and Refuse Incineration Plants and in Units with Heat Recovery Steam Generators"*, **2000** (Mannheim, Germany). PowerPlant Chemistry GmbH, Neulussheim, Germany, paper #4.
- [42] Bursik, L., *PowerPlant Chemistry* **2002**, 4(2), 81.
- [43] Sadler, M. A., Aspden, D., Cutler, F. M., Mathews, J. A., *PowerPlant Chemistry* **2009**, 11(1), 36.
- [44] *VGB-Standard Feed Water, Boiler Water and Steam Quality for Power Plants/Industrial Plants*, **2011**. VGB PowerTech Essen, Germany, VGB-S-010-T-00;2011-12.EN.
- [45] Dooley, B., *PowerPlant Chemistry* **2002**, 4(6), 320.
- [46] Dooley, B., Shields, K., *Proc., Seventh International Conference on Cycle Chemistry in Fossil Plants 2003*, **2004** (Houston, TX, U.S.A.). Electric Power Research Institute, Palo Alto, CA, U.S.A., 1009194, 3.
- [47] Bursik, A., *PowerPlant Chemistry* **2002**, 4(12), 743.
- [48] Sylwestrzak, E., Moszczynski, W., Hater, W., Dembowski, T., de Bache, A., *VGB Conference "Chemistry in Power Plants 2015"*, **2015** (Berlin, Germany). VGB Powertech, Essen, Germany, Paper #V16.
- [49] Bursik, A., Bezzoli, P., Graf, A., *Proc., Seventh International Conference on Cycle Chemistry in Fossil Plants 2003*, **2004** (Houston, TX, U.S.A.). Electric Power Research Institute, Palo Alto, CA, U.S.A., 1009194, 615. Paper also published as Bursik, A., Bezzoli, P., Graf, A., *PowerPlant Chemistry* **2003**, 5(6), 373.
- [50] *IAPWS Technical Guidance Document – 2015 Revision: Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-Water Circuits of Fossil-Fired and Combined Cycle Power Plants*, **2015**. The document is downloadable at [www.iapws.org](http://www.iapws.org).
- [51] *IAPWS Technical Guidance Document – 2015 Revision: Phosphate and NaOH Treatments for the Steam-Water Circuits of Drum Boilers of Fossil and Combined Cycle/HRSG Power Plants*, **2015**. The document is downloadable at [www.iapws.org](http://www.iapws.org).
- [52] Forêt, C., Stoianovici, G., Blériot, P., Hater, W., Matheis, J., *PowerPlant Chemistry* **2014**, 16(6), 361.
- [53] Lister, D. H., Weerakul, S., Caravaggio, M., *Laboratory Tests on the Effects of Amines on FAC in Single-Phase and Two-Phase Flows*, **2015**. Paper presented at the IAPWS Annual Meeting (Power Cycle Chemistry Group), Stockholm, Sweden, June 28–July 3, 2015.
- [54] van Lier, R., Janssen, G., Savelkoul, J., *PowerPlant Chemistry* **2008**, 10(12), 696.
- [55] Kolander, B., de Bache, A., Hater, W., *PowerPlant Chemistry* **2013**, 15(2), 137.
- [56] Topp, H., Steinbrecht, D., Hater, W., de Bache, A., *PowerPlant Chemistry* **2010**, 12(7), 388.
- [57] Topp, H., Hater, W., de Bache, A., zum Kolk, C., *PowerPlant Chemistry* **2012**, 14(1), 38.
- [58] Dooley, R. B., Shields, K. J., *PowerPlant Chemistry* **2013**, 15(3), 168.
- [59] Hater, W., Digiario, C., Frayne, C., *Proc., 73rd International Water Conference*, **2012** (San Antonio, TX, U.S.A.). Engineers' Society of Western Pennsylvania, Pittsburgh, PA, U.S.A., Paper IWC-12-20.
- [60] Wagner, R., Czempik, E., *VGB Powertech* **2014**, 94(3), 48.
- [61] Hater, W., *Dry Layup of Steam Generators with Film Forming Amines Studies and Field Experiences*, **2015**. Paper presented at the Eleventh International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators, 2015 (St. Louis, MO, U.S.A.). Electric Power Research Institute, Palo Alto, CA, U.S.A.
- [62] Dooley, R. B., *PowerPlant Chemistry* **2008**, 10(2), 68.
- [63] *IAPWS Technical Guidance Document: Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants*, **2013**. The document is downloadable at [www.iapws.org](http://www.iapws.org).

- [64] Rossi, T., Dale, T., *Polyamine Technology for Fossil and Combined Cycle Power Plant Corrosion Protection*, **2015**. Paper presented at the Eleventh International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators, 2015 (St. Louis, MO, U.S.A.). Electric Power Research Institute, Palo Alto, CA, U.S.A.
- [65] Bursik, A., Staudt, U. W., *PowerPlant Chemistry* **2001**, 3(3), 136.
- [66] Roothoof, R., Bohnsack, G., de Caluwe, R., *Proc., Fifth International Conference on Cycle Chemistry in Fossil Plants*, **1997** (Charlotte, NC, U.S.A.). Electric Power Research Institute, Palo Alto, CA, U.S.A., TR-108459, 4-13.
- [67] Moran, F., Rosenbluth, G., *Proc., Journées Information Eaux*, **1992** (Poitiers, France), Paper Number 47 [in French].
- [68] Press Release – International Association for the Properties of Water and Steam, 2015 Annual Meeting, Stockholm, Sweden, *PowerPlant Chemistry* **2015**, 17(4), 237.

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