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## Flow-Accelerated Corrosion

- Improving Plant Reliability Based on Inspection and Maintenance of Local Wall Thinning due to Flow-Accelerated Corrosion
- Deposition and Internal Oxide
   Growth in a Supercritical Boiler

## **Combined Cycles/HRSGs**

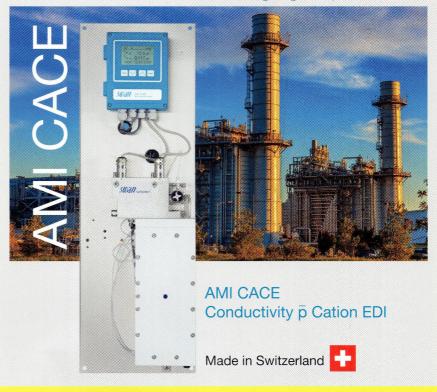
IAPWS TGD7-16 HRSG High Pressure Evaporator Sampling for Internal Deposit Identification and Determining the Need to Chemical Clean

## **Film Forming Amines**

IAPWS TGD8-16 Application of Film Forming Amines in Fossil and Combined Cycle Plants

# November/December 2016

Acid conductivity monitoring No more resin changing required



## Conferences

Report on the Power Cycle Chemistry Working Group Meeting in Dresden, Germany

### **Events**

# Report on the Power Cycle Chemistry Working Group Meeting in Dresden, Germany

Michael Rziha and Tapio Werder

#### **ABSTRACT**

This short report summarizes the work of the Power Cycle Chemistry (PCC) working group (WG) during the 2016 Annual Meeting of the International Association for the Properties of Water and Steam (IAPWS) in Dresden, Germany. Nearly 30 members of the PCC WG attended the meetings, joint workshops, and task group sessions during the week. Highlights of the week as well as an overview of all the activities within the working group are given in this report.

#### INTRODUCTION

This year's annual meeting of the International Association for the Properties of Water and Steam (IAPWS) was hosted by the German National Committee of IAPWS. The meeting was held September 11 16, 2016, at the Steigenberger Hotel de Saxe in Dresden, Germany.

IAPWS activities are based around the following five working groups:

- Thermophysical Properties of Water and Steam (TPWS)
- Sub-committee on Seawater
- Physical Chemistry of Aqueous Solutions (PCAS)
- Power Cycle Chemistry (PCC)
- Industrial Requirements and Solutions (IRS).

The highlights of the IAPWS working group sessions and other proceedings of the Executive Committee have been summarized in a press release, which was published in the last issue of this journal [1].

#### POWER CYCLE CHEMISTRY WORKING GROUP

The Power Cycle Chemistry (PCC) working group (WG) brings together scientists and engineers from academia and research organizations, power plant operators, equipment manufacturers, service providers, and other relevant interested parties from around the world with an interest in power plant chemistry.

During the annual meeting in Dresden nearly 30 members of the PCC WG met to review and to update all the mem-

bers on the work done since last year's meeting in Stockholm, Sweden [2].

The highlights of this year's PCC WG meeting are the following:

- Two new Technical Guidance Documents (TGDs) approved and released
- · One TGD in preparation
- Several white papers are in development.

In the following sections these highlights are presented in more detail.

#### **NEW TGDs APPROVED AND RELEASED**

These TGDs are both world firsts and are of course as always downloadable from the IAPWS website free of charge.

#### HRSG High Pressure Evaporator Sampling for Internal Deposit Identification and Determining the Need to Chemical Clean

IAPWS has previously published six TGDs applicable to fossil and combined cycle plants [3–8]. Through the use of these documents, optimum cycle chemistry guidance can be developed for combined cycle/heat recovery steam generator (HRSG) plants. The new TGD [9] includes guidance for the understanding of waterside deposits in the high pressure (HP) HRSG evaporators of combined cycle plants. The main objectives of this TGD are to provide guidance to operators of combined cycle/HRSG plants on:

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- Why HRSG HP evaporator deposits are very important in the overall reliability of HRSGs
- Where to sample HP evaporator tubing for analysis of internal deposits
- How to analyze HP evaporator internal deposits
- How to determine whether the internal deposits are satisfactory for continued operation without damage due to underdeposit corrosion or whether they need to be removed by chemical cleaning.

The TGD was prepared over the last two years by the responsible task group (which was formed during the 2014 annual meeting in Moscow, Russia [10]) and reviewed by all National Committees and by the Editorial Committee (EC). The PCC WG approved the submission to the EC for approval in the Executive Meeting on Friday, September 16, where the TGD was finally authorized.

#### Application of Film Forming Amines in Fossil, Combined Cycle, and Biomass Power Plants

This new TGD [11] includes guidance for the application and use of film forming amines (FFAs) and film forming amine products (FFAPs). Recently FFAs have been introduced into the market and their use is continuing to increase. Unfortunately, because there are no international guidelines or limits for the successful application of these chemicals, there has been much misunderstanding and confusion for the operators about what exactly these chemicals can achieve when applied. In some cases, there has been damage to 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 FFA/FFAP cannot be clearly foreseen.

This IAPWS TGD is aimed at filling this gap and providing answers to the most common and most important questions asked by plant operators. The TGD includes not only some of the important scientific background but also the key guidance steps for applying FFAs in fossil, combined cycle, and biomass plants. The guidance is not applicable to nuclear plants. The TGD provides guidance for the user/operator on determining whether 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.

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#### **TGDs IN PREPARATION**

#### **Demineralized Water Integrity**

A TGD on demineralized make-up water integrity is seen as the appropriate next step in the existing suite of IAPWS TGDs. Having clear guidance steps to reduce the risk of contaminated demineralized water passing into the unit cycle is seen as a useful contribution. The scope of the TGD will involve:

- · Demineralized water quality limits
- Routine and non-routine demineralized water quality monitoring requirements
- Integrated demineralized water quality instrumentation at both the demineralization plant and make-up to the unit including operator alarms and corrective actions
- Hazard and operability study (HAZOP) type assessment of the demineralization plant to identify all of the contamination risks, including those from equipment failure, and demineralization plant isolation requirements
- · Staff training for contamination events
- · Contingency plans for contamination events
- · Summary case studies of contamination events.

The responsible task group is currently planning to finalize the TGD within the next year and to be able to present a final version for approval at the annual meeting in Kyoto, Japan, in 2017.

#### WHITE PAPERS TO BE DEVELOPED

#### **Use of Film Forming Amines in Nuclear Plants**

As mentioned above, the new TGD on the application of FFAs is not applicable to nuclear plants. The Nuclear Sub-committee discussed the possibility of a TGD for the application of FFAs in nuclear plants. There was consensus that there may be different effects compared to fossil plants. The first step will be to prepare a white paper comparing differences from fossil plants for the next annual meeting in Kyoto, Japan.

#### Iron Monitoring and Corrosion Product Sampling

Plants worldwide are required to follow flexible running regimes and therefore experience problems effectively controlling the cycle chemistry during large numbers of start-ups and during lay-up periods. Disturbances to the steam-water cycle during start-ups can limit the effective monitoring of cycle chemistry conditions and, in particular, the ability to detect contaminant ingress, whilst cycle chemistry during lay-up periods has a critical impact on

plant corrosion and chemical conditions at start-ups. Towards addressing these problems, the PCC working group agreed that a number of the existing TGDs should be updated to provide guidance on chemical sampling and monitoring instrumentation practices specifically for cycling plants. The white paper will include the findings from a sampling program which was carried out by the Scandinavian National Committee during the past year to close some of the knowledge gaps in this field.

#### **Geothermal Power Plant Chemistry and Corrosion**

Geothermal power plants have significant problems with corrosion and scaling that require fundamental research on the mechanisms involved and on solution chemistry in high-temperature environments, as well as guidance on steam purity. Consequently, IAPWS has established a task group on geothermal power plant chemistry with the aim of promoting work towards improving the knowledge of scaling and corrosion mechanisms in these types of power plants.

#### Air In-Leakage

The loss of efficiency and heat exchange performance due to air in-leakage is viewed as being poorly understood. Also guiding values for allowable air in-leakage rates are not commonly available. A new task group has been established to work on a white paper to provide more background information on this matter.

# PCAS / PCC JOINT WORKING GROUP MEETING AND WORKSHOP

During the Dresden meeting, the PCC WG proceedings included workshops in which the presentations listed below were given. A number of the presentations were used to introduce areas of potential future IAPWS interest.

# **Electrochemical Corrosion Potential Monitoring in Boiling Water Reactors**

Y. Wada, Hitachi, Ltd., R&D Group

An electrochemical corrosion potential (ECP) sensor is required to confirm the effectiveness of stress corrosion cracking (SCC) mitigation such as hydrogen water chemistry (HWC). ECP measurements in various types of reactors and with different sensor types at different locations were presented.

# Modeling Actinide Solution Chemistry: Thermodynamic Fundamentals for the Nuclear Power Industry

P. Wang and A. Anderko, OLI Systems Inc.

A mixed-solvent electrolyte model was introduced that can predict the properties of electrolyte systems and the solubility of solids in multiphase and multicomponent systems. The model can be used in different applications, such as nuclear waste disposal, where it accurately predicts the dissolution of the nuclear waste matrix and migration of actinides.

#### IAPWS Geothermal Knowledge Gaps Project - Update

D. Addison, Thermal Chemistry Limited

This presentation was effectively the white paper for geothermal chemistry. The sub-task group is close to being able to produce a guideline. The intention is to update the geothermal section in the Steam Purity TGD and to write IAPWS Certified Research Needs (ICRNs) for missing knowledge.

#### **PCC WORKSHOP**

# The Journey to World Class Cycle Chemistry for a Conventional Fossil Plant via IAPWS TGDs

D. Addison, Thermal Chemistry Limited

This case study showed in detail how a cycle chemistry improvement project was outlined and implemented. The recommendations for improvement were based on IAPWS TGDs including all areas of cycle chemistry – from changing the chemical regime to training and mentoring for the chemical staff.

# Experiences with the Application of Film Forming Amines at Connah's Quay Combined Cycle Gas Turbine

P. McCann, Uniper UK Ltd

The operating regime of the Connah's Quay power plant varies considerably, between 1 and 4 units running with daily start-ups and shutdowns. Established preservation methods are difficult to implement without compromising start-up times. Therefore, the station evaluated a new treatment concept with film forming amines.

#### Studies on Two-Phase FAC: Modeling and Effects of Amine Breakdown Products

D. Lister, University of New Brunswick

This presentation gave an update on the work done by the University of Brunswick and the Technical University of Delft regarding two-phase flow-accelerated corrosion (FAC) and the effect of amine degradation products on two-phase FAC. The application of the methodology of single-phase FAC modeling to annular flows of liquid in two-phase systems is producing promising results.

#### Use of FFAP at HRSG Power Plant in Russia

F. Dyachenko, MPEI, Aminotek

The application of a film forming amine product (FFAP) in two different combined cycle power plants was shown. The two plant designs and their cycle chemistry limits were introduced and discussed.

#### Use of ODA at Russian Power Plants

T. Petrova, National Research University MPEI
The presentation discussed several points to be considered for the use of octadecylamine (ODA) at power plants.

# Behavior of Film Forming Amines in the Water/Steam Cycle of Power Generating Units

S. Vidojkovic, University of Belgrade

The chemical structures of octadecylamine (ODA), oleylamine (OLA), and oleyl propylenediamine (OLDA) as well as the influence of the structures on their behavior were shown in this presentation.

#### **SIAPWS Network**

K. Thomsen, COWI A/S

The Scandinavian National Committee (SIAPWS) presented its plans to establish a water chemistry network in Scandinavia through modern electronic media. The organizational structure, time frame for the set-up of the network, and open questions were presented to the PCC WG.

# Data from CPM Measurements – Results of a Preliminary Test of Sampling Uncertainty

K. Thomsen, COWI A/S

In order to revise the TGD on Corrosion Product Sampling and Analysis [9] a preliminary comparison test of sampling uncertainty was conducted in spring 2016. Even though the group of participating plants was small, first conclusions could be drawn, such as that a correlation between the log-normal distribution and particle size distribution of iron oxides seems likely.

# Water Chemistry Management Practices and Sampling Method of Japanese PWR Plants

N. Ishihara, Mitsubishi Heavy Industries, Ltd.

Radioactivity control, boric acid chemistry, and crevices are distinctive features of the chemistry in pressurized water reactor (PWR) plants compared with thermal power plants. Typical target substances for control parameters and diagnostic parameters in the primary and secondary water were presented as well as the challenges for sampling typically faced in nuclear power plants.

#### IAPWS – International Collaboration Project (Canada/ New Zealand) Electrochemical Corrosion Study

W. Cook, University of New Brunswick

The presentation summarized the status of the project, which was initiated at the last annual meeting in Stockholm, Sweden. The initial funding by IAPWS has been used for project scoping and design, test rig construction, and initial test work. The first tests are expected to start in January 2017.

# Water Chemistry Issues When Constructing a New Add-on Drum Boiler for an Existing Ultra-supercritical Boiler/Turbine

J. P. Jensen, DONG Energy

Due to the changing energy market in Europe a 300 MW biomass fired (wood chips) boiler is currently being added to an existing ultra-supercritical gas-fired unit. The water chemistry regime for the additional drum boiler as well as the changes in the steam-water cycle chemistry of the whole plant were explained in the presentation.

# Flue Gas Condensation – Possible Optimizations and Make-up Water Production

J. P. Jensen, DONG Energy

The presentation showed how to improve the energy efficiency by optimizing flue gas condensation and its impact on the make-up water production. Humidification of combustion air to reduce the flue gas temperature and heat recovery from the blowdown tank were explained in more detail.

# Overview of the Revision of JIS B 8223 "Water Conditioning for Boiler Feed Water and Boiler Water"

H. Hirano, retired senior research scientist of CRIEPI Much work has been done on revising the JIS B 8223 standard on steam-water chemistry for once-through boiler and combined cycle/HRSG power plants. The changes have been made in response to problems with powder scale formation in once-through boilers and FAC in HRSGs.

# High-AVT(LO) Water Treatment Application in a Combined Cycle Plant

S. Shinotsuka, Mitsubishi Hitachi Power Systems High-AVT(LO) has been established in the Japanese Industrial Standard with the purpose of restricting hydrazine use and taking preventive measures against FAC. It is an all-volatile treatment with a feedwater pH above 9.7 and dissolved oxygen levels less than 5 ppb. The presentation showed how the regime has been applied to the Himeji No. 2 combined cycle plant.

# Corrosion Product Sampling TGD Revision Project – Update for Flexible Operation Plants

D. Addison, Thermal Chemistry Limited

This presentation described the plans of the TGD sub-task group to develop current guidance and to address knowledge gaps regarding the planned revision of the TGD [8].

# Global Experience Optimizing Cooling Water Systems through Pulse-Chlorination

L. Daal

This presentation explained the pros and cons of existing options for biofouling control in cooling water systems. It

further showed a newly developed chlorination method which uses less chlorine and results in better plant reliability and performance than continuous or shock dosing.

#### PARTICIPATION IN IAPWS ACTIVITIES

IAPWS welcomes scientists and engineers with an interest in research, current developments, and operational experience in the field of power cycle chemistry. People interested in IAPWS power cycle chemistry activities should contact either the chair of their IAPWS National Committee (see the IAPWS website for contact details), the chair of the PCC working group, Michael Rziha, michael.rziha@siemens.com, or the IAPWS Executive Secretary, Dr. R. Barry Dooley, bdooley@structint.com. People do not need to be citizens or residents of member countries to participate in IAPWS working groups.

#### **IAPWS 2017 ANNUAL MEETING**

The next IAPWS meeting will be in Kyoto, Japan, August 27–September 1, 2017. Further information on meetings can be found at the IAPWS website (www.iapws.org) as it becomes available.

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#### **AUTHORS**

Michael Rziha is the key principal expert for plant chemistry at Siemens AG, where he is a consultant for the engineering departments with regard to all chemical operations and maintenance topics, as well as chemical cleaning, preservation, and steam cleaning concepts. From 1998 to 2013, Michael was leader of the department Plant Cleaning and Chemistry at Siemens Power Generation, which is responsible for the entire chemistry of power plants during erection and commissioning. Before that, he worked for 3 years in the design department of Siemens Power Generation (formerly KWU) as well as for 10 years as a chemical commissioning engineer in several projects (nuclear and fossil) worldwide. Michael is a member of several VGB committees concerned with chemistry and water processing and is the chair of the Power Cycle Chemistry working group of the International Association for the Properties of Water and Steam. He is also a member of the International Advisory Board of the PowerPlant Chemistry journal.



**Tapio Werder** is the current editor of the PowerPlant Chemistry journal. He started his work for the journal in 2014 as editorial assistant when Albert Bursik, founder and editor of the journal, retired and took a seat on the journal's International Advisory Board (IAB). In 2015 the responsibility for finding appropriate submissions and for the production of the journal as the editor was handed over to him completely. Since 2015 he has been the secretary of the Swiss Committee for the Properties of Water and Steam (SCPWS) – the Swiss National Committee of IAPWS.

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