International Association for the Properties of Water and Steam

IAPWS and IAPWS Cycle Chemistry Guidance Documents for Plants with ACC

International ACC Conference
Xian, China
13th – 16th October 2015

Barry Dooley
IAPWS Executive Secretary

The Members of IAPWS

are countries or neighbouring countries

- **Members**
  - BIAPWS [Britain and Ireland]
  - Canada
  - Czech Republic
  - Germany
  - Japan
  - Russia
  - USA
  - Scandinavia [Denmark, Finland, Norway, Sweden]
- **Associate Members**
  - Argentina and Brazil
  - France
  - Italy
  - Switzerland
  - Australia
  - New Zealand
  - Greece
  - (South Africa)

IAPWS Working Groups (WG)

(meet every year to conduct the IAPWS work & business with work continuing through the year by Task Groups)

- Thermophysical Properties of Water and Steam, TPWS
  - Established IAPWS area (1929) – Steam Tables
- Industrial Requirements and Solutions, IRS
  - Steam turbine manufacturers worldwide are members
- Subcommittee on Seawater, SCSW
  - Formed in 2008/2009 to address global seawater needs
- Physical Chemistry of Aqueous Solutions, PCAS
  - Formed in 1990 to support power plant chemistry
- Power Cycle Chemistry, PCC
  - Technical Guidance Documents for all Generating Sources

Details of each WG are on website (www.IAPWS.org)

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IAPWS Technical Guidance Documents for Fossil and Combined Cycle Plants

(with particular relevance for plants with ACC)

IAPWS Technical Guidance Documents (TGD) for Plants with ACC

- **Procedures for the Measurement of Carryover of Boiler Water and Steam (September 2008).** This document includes the procedures to measure carryover from drum boilers to assist in preventing steam turbine failure/damage.
- **Instrumentation for monitoring and control of cycle chemistry for the steam-water circuits of fossil-fired and combined-cycle power plants (September 2015)**. This document includes a table that can be used to determine the minimum key level of instrumentation required for any fossil or combined cycle/HRSG plant.
- **Volatile treatments for the steam-water circuits of fossil and combined cycle / HRSG power plants (July 2015).** This document includes the basis for AVT and OT for all plants with customization for plants with ACC and using ammonia and amines. Recently added guidance for fast start and frequently started HRSGs.

Freely available and downloadable on IAPWS website www.IAPWS.org

IAPWS Technical Guidance Documents (TGD) for Plants with ACC

- **Phosphate and NaOH treatments for the steam-water circuits of fossil and combined cycle / HRSG power plants (Oct 2015).** This document includes the basis for selecting the optimum boiler/HRSG evaporator water treatment for (phosphate and NaOH treatments) for all drum plants including customization for plants with ACC.
- **Steam Purity for Turbine Operation (Sept 2013).** This document covers guidance for a wide range of turbines (fossil, nuclear, industrial, geothermal, etc) and failure mechanisms. It includes customizations for plants using amines and with carbon dioxide.
- **Corrosion Product Sampling and Analysis (May 2014).** This document covers the optimum procedures and techniques for monitoring iron and copper. Includes a table of achievable iron levels for plants with ACC

Freely available and downloadable on IAPWS website www.IAPWS.org

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A few examples of IAPWS Guidance for Fossil and Combined Cycle Plants

(with particular relevance for plants with ACC)

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Technical Guidance Document

Monitoring and Analyzing Total Iron and Copper in Fossil and Combined Cycle Plants

Consensus of 21 Countries

Issued 1st May 2014

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Introduction and Rationale for Corrosion Product Sampling (CPS)

Significant problems with reliable and effective corrosion product sampling observed worldwide in fossil & combined cycle gas turbine (CCGT) plants.
Particularly needed in plants with ACC

Corrosion product levels critical to determining effectiveness or otherwise of cycle chemistry programs - Total Fe and Cu levels key aspects of IAPWS cycle chemistry Technical Guidance Documents (TGD)

Critical activity either not done at all or conducted incorrectly

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Achievable Total Fe & Cu Levels – Different Plant Types/Optimized Chemistry

Feedwater		
OT:	Total Fe =	< 1 µg/kg
AVT:	Total Fe =	< 2 µg/kg
AVT (Mixed):	Total Fe & Cu =	< 2 µg/kg
HP/LP Heater Drains:	Total Fe & Cu =	< 10 µg/kg
HRSG Evaporators/Drums		
AVT/PT/CT:	Total Fe =	< 5 µg/kg
Air - cooled Condenser (ACC)		
ACC Outlet:	Total Fe =	< 10 µg/kg
Post Condensate Filter:	Total Fe =	< 5 µg/kg
Cogeneration Plants		
Condensate Return:	Total Fe =	< 10 µg/kg*

**Depends on cogen plant design and function*

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Analytical Methods for Total Iron

Suitable methods

- Post sample digestion UV-Vis (Ferrozine) with a 5 cm cell - Fe only
- Graphite Furnace Atomic Absorption spectrometry (GF-AA) post sample digestion
- Inductively coupled plasma mass spectrometry (ICP-MS) post sample digestion

Key points are:

1. Full digestion for all samples required
2. Detection limit of < 2 µg/kg required (lower the DL the better)

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Key Highlights of CPS TGD

1. Sampling system design critical for CPS – turbulent flow in all aspects of system most important aspect
2. CPS of steam not required
3. CPS is a periodic activity
4. CPS should be undertaken during constant unit operating conditions rather than at a convenient time of the day
5. Most common CPS problems are a lack of sample digestion and analytical method with high DL

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Technical Guidance Document
Steam Purity for Turbine Operation

Consensus of 21 Countries

Issued September 2013

Customization for Turbine Types and Chemistries

Steam Turbine Systems and Operations

1. Cycling or Peaking Operation
2. Extended Periods of Shutdown
3. Backpressure Turbines
4. Industry and Process Supply
5. Solar and Biomass Steam Generating Systems
6. Geothermal Steam
7. Nuclear Power Plants
8. Ultrasupercritical Turbines (>600 °C)

Chemistry Parameters

9. Boilers using Phosphate Treatment
10. Elevated Levels of Carbon Dioxide
11. Organic Decomposition Products
12. Elevated Levels of Silica
13. Major Components with Copper or Aluminum

Customization for Turbine Types:
Example for Organic Decomposition Products

Natural organic matter:
Will partly decompose to organic acids
☞ No allowance to "standard case" CACE limits

Amines for feedwater treatment:
Will partly decompose to organic acids; depending on temperature, some amine may pass into the steam and neutralize or over-compensate the effect of the acid
☞ Allowance on CACE is possible, but only under conditions:

- The exact composition of the product must be known
- The species of decomposition products must be known
- The decomposition products will not decrease pH in the liquid films in the turbine
- Regular ion chromatography analysis
- Always use on-line monitoring of Na

Customization for Turbine Types:
Example for Boilers using Phosphate Treatment

With drum boilers that use solid alkalizing agents it may be difficult to meet the "standard case" Na limits in steam because of carryover of boiler water.

Tri-sodium phosphate (TSP) is not known to be corrosive to turbine materials. Relaxed Na limit in steam is possible.

Customized Na limit will depend on turbine inspection results indicating which quantities lead to excessive turbine deposits.

Maximum allowance is up to a Na limit of < 5 µg/kg

But no allowance is possible if other products than TSP are used (Phosphate blends, NaOH, proprietary chemicals of undisclosed composition)

Customization for Turbine Types:
Example for Elevated Levels of Carbon Dioxide

Moderate concentrations of carbon dioxide do not significantly influence turbine chemistry in alkalized steam.

A limited allowance to CACE (max 2 µS/cm) can be applied in systems with feedwater pH>8.5, and the absence of corrosive anions like Cl and SO_4 can be reasonably excluded:

- **Use of degassed CACE**
- **Regular ion chromatography analysis**
- **Always use on-line monitoring of Na**

New IAPWS TGD for 2015 / 2016

- **Amendment of IAPWS TGD for Fast Start HRSGs. 2015**
  - **Instrumentation**
  - **Volatile Treatments (AVT and OT)**
  - **PT and CT**
- **New IAPWS TGD on "HRSG HP Evaporator Sampling for Internal Deposit Determination". 2016**
- **New IAPWS TGD on "Ensuring the Integrity and Reliability of Demineralized Make-up Water Supply to the Unit Cycle". 2016**
- **New series of Guidelines on Amines**
  - **Neutralizing Amines (2016)**
  - **Film Forming Amines (FFA) (2016)**

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Technical Guidance Documents

HRSG HP Evaporator Sampling for Internal Deposit Determination

Currently in development with input from 21 countries including most of the HRSG Manufacturers worldwide

For Publication 2016

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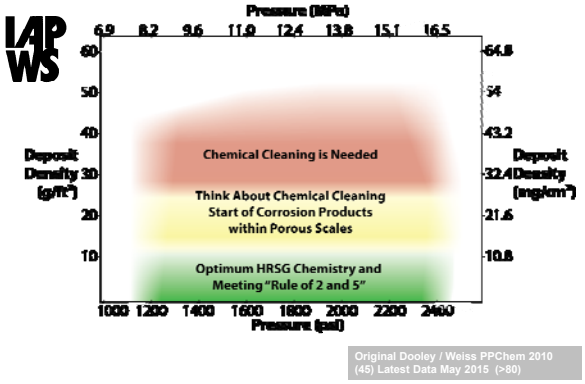
IAPWS Deposition Map for HP Evaporators



Original Dooley / Weiss PPChem 2010 (45) Latest Data May 2015 (>80)

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Technical Guidance Documents

Film Forming Amines

Currently in development by IAPWS Task Group which includes many of the chemical supply companies. Also with input from 21 countries including most of the HRSG Manufacturers

For publication in 2016

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PCC Technical Guidance Documents
Film Forming Amine TGD

Task Group Members

Chemical Supply Companies
- Kurita
- GE Water
- Anodamine
- Helamin
- Nalco
- Reicon

Manufacturers
- HRSG
- Steam Turbine
- Instruments

IAPWS Members Worldwide from 21 Countries

IAPWS TGD will be non-commercial and contain no proprietary items

PCC Technical Guidance Documents
Film Forming Amine TGD

Some Initial Questions that Fossil and Combined Cycle Plants Need Answering and the IAPWS TGD will Address

- Information on what FFA are and what they can do. Operationally and for shutdown and/or layup?
- How to determine which to use for which application and how to determine the amount to use and optimize?
- Are they applicable to different metallurgies (all-ferrous, mixed metallurgy and aluminium containing systems)?
- How to analyze and confirm content? What instrumentation is needed? Is there a need for additional instruments than included in IAPWS TGD?
- How to determine if successful? Monitoring of Total Iron / Copper? Is there a need for additions to the IAPWS TGD?
- How to use in Boilers, Feedwater, Steam Turbines, ACC?

IAPWS TGD will be non-commercial and contain no proprietary items

PCC Technical Guidance Documents
Film Forming Amine TGD

Base Case

1. Operation. All-ferrous fossil, combined cycle and biomass plants
   - Which FFA to use
   - "Monitoring #1" baseline before use
   - How much to dose and where
   - How to analyze content of FFA in cycle
   - How to determine optimum use (Monitoring #2)
2. Shutdown/Layup

Customizations

3. Different FFAs and Combinative Mixtures
4. Major Components with Copper or Aluminum
5. Different Temperature/Pressures
6. Systems with ACC and Condensate Polishers
7. Seawater Cooling
8. Industrial Plants

IAPWS TGD will be non-commercial and contain no proprietary items

The Premier International Resource for all areas of water and steam

- Freely available and downloadable on IAPWS website
  - www.IAPWS.org
- Please give full attribution to IAPWS
- New areas of interest and involvement from China?