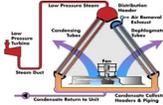




ACCUG
Corrosion and
Cycle Chemistry
Section

Fossil, Combined Cycle/HRSG and Industrial Plants
Background and Updates on Film Forming Substances (FFS)

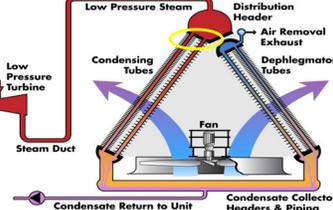


Barry Dooley
Presented by Andy Howell
ACCUG 2022
12th – 15th September 2022
Bramford, Connecticut, USA




1

ACC Come in Many Sizes





But the FAC / Corrosion damage is the same worldwide with all chemistries
and plant types (Based on assessment/inspection work conducted in Australia, Canada, Chile,
China, Cote d'Ivoire, Dubai, India, Ireland, Mexico, Qatar, Abu Dhabi, South Africa, Trinidad, UK and US)

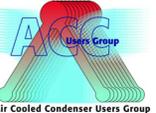
2

Corrosion/FAC in ACC and The Consequences

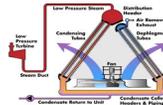
- High concentrations of iron around the cycle
 - Boiler/HRSG deposits (expensive chemical cleaning)
 - Boiler/HRSG Tube Failures (overheating and UDC / HD*)
 - Steam Turbine Deposits (including aluminum)
- Need for Iron Removal Processes
 - Condensate Polishing and/or Filters
- Limitations around the cycle
 - Condensate polishing (may have to change mode to AFO*)
- Overall an ACC “controls” the unit cycle chemistry
 - International Guidelines now available for ACC and two-phase flow (IAPWS Volatile and FFS Guidance)

* UDC / HD – Under-deposit corrosion / hydrogen damage.
* AFO – Ammonium form operation

3



Discussion Item for ACCUG 2022



Reminder of ACC Damage & How Normally Addressed
DHACI is an appendix if required
The Recent Introduction of Film Forming Substances (FFS)
International Experience & Missing Information



September 2022



4

Inspections Worldwide show the same Features
 Combined Cycle with ACC after ~ 15,000 hrs, pH 9.1.



5

Inspections Worldwide show the same Features
 750 MW Supercritical on OT at pH 9, ~4,000 hrs.



6

Damage takes time to Arrest (after 2 Years with pH 9.8)



7

Damage takes time to arrest (15 Months with pH 9.8)



8

ACC Two-phase FAC can also be "Arrested" with FFS
 (Reduction in DHACI for FAC at Tube Entries in ACC
 Accompanied by Significant Reduction in Total Iron in Condensate)

DHACI 4

DHACI 1

Cross member appear to arrest using FFS

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IAPWS

International Nomenclature

There was lots of confusion worldwide on amine (FFA/FFAP) and non-amine (FFP) based substances. IAPWS introduced the nomenclature for the FFS in the initial Guidance Document

Film Forming Substances (FFS)

```

  graph TD
    FFS[Film Forming Substances (FFS)] --> FFA[FFA/FFAP]
    FFS --> FFP[FFP]
  
```

Film Forming Amines (FFA)
 Octadecylamine – ODA
 Oleyamine – OLA
 Oleyl Propylenediamine – OLDA

Film Forming Products (FFP)
 Proprietary

IAPWS Technical Guidance Documents for FFS
 Freely available and downloadable on the IAPWS website www.IAPWS.org

10

A little background on FFA Chemical Structure

Hydrophobic end (Repels water)

Hydrophilic end (Attaches to metal / metal oxide surfaces)

Hydrophilic head

Metal Surface or Oxide

Metal

Hydrophobic film "protects" the steel by decreasing contact between water/metal

1. Adsorption
2. Ionic Interaction
3. Vander Waals forces

Hydrophobic Bond

11

Film Forming Substances (FFS)
A little background - hydrophobicity

Hydrophilic Surface

Hydrophobic Surface

Source: www.sciencebrainwaves.com

12

Film Forming Substances Wide Range of Products and Mixtures

Product Type	Film Forming Products (Non Amine)	Film Forming Amines – pH or surfactant stabilized	Film Forming Amines – Homogenization / Emulsions	Film Forming Amines – pH stabilized and blended with dispersants
Application	Fossil/Industrial	Fossil/Industrial	Fossil/Industrial/ Nuclear (ODA)	Fossil/Industrial
Description	Proprietary, Likely to be Carboxylic acids	ODA/OLA/OLDA with neutralizing amines	ODA/OLDA	ODA/OLA/OLDA With neutralizing amines & Polycarboxylate dispersants
Concentration (Active)	<1%	<1-5% mostly Some up to 80%	<1-5%	<1-5%
Chemical & Thermophysical Properties Understood	Limited Understanding	Limited Understanding Except for ODA		

This Wide Range of FFS Makes Application, Research and Common Solutions Difficult

13

Film Forming Substances Wide Range of Vendors Globally

Non-Exclusive Vendor Examples (from IAPWS FFS International Conferences)

Film Forming Products (Non Amine)	Nalco, Anodamine, Cortec
Film Forming Amines – pH or surfactant stabilized	Nalco, Suez, Chemtreat, Helamin, Fineamin, Solenis
Film Forming Amines – Homogenization stabilized	Reicon, Kurita, Suez
Film Forming Amines – pH stabilized and blended with dispersants	Helamin, Fineamin

This Wide Range of FFS Makes Application, Research and Common Solutions Difficult

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Key Highlights of FFS Applications in Fossil, Combined Cycle/HRSG and Industrial Plants

IAPWS has organized five FFS Conferences (2017, 2018, 2019, 2021 & 2022) From these and the publication of two IAPWS TGD, the following provides an outline of major results:

- Basic understanding has improved worldwide since 2014
- Universal reductions in feedwater Fe and Cu transport but no equivalent understanding of the mechanisms of oxide growth “formation/reductions” in condensate (ACC), feedwater, boiler water and steam
- General observations of hydrophobic films on water-touched surfaces, but it is underlined that hydrophobicity (contact angle) does not prove presence of film or protection
- Film formation and adsorption remains very questionable on superheated steam-touched surfaces
- Still problems occurring in plants worldwide (but not openly published): internal deposits, tube failures especially UDC, formation of “gunk” (gel-like) deposits in drums and on heat transfer surfaces, in steam turbines, and strainers/filters

A couple of examples →

SLIDE 15

15

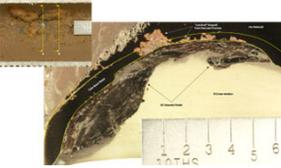
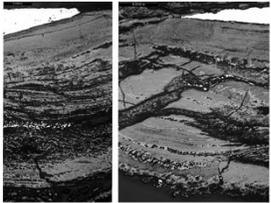
HP Evaporator Heavy Deposits and Failure

Double Pressure HRSG (9 and 0.5 MPa). HTF after FFAP Application with no IAPWS Section 8 Review



Structural Integrity Associates, Inc.

Severe Under-deposit Corrosion in typical multi-laminated morphology

SLIDE 16

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Beware of Increasing HP Evaporator Deposits after FFS Application (without detailed prior review)

2018 Assessment
2003 - 2015 AVT(R) and PT
2015 - 2018 AVT(O) and PT
Total Loading 18 - 22 g/ft²

2022 Assessment
2015 - 2020 AVT(O) and PT
2020 - 2022 AVT(O) + FFP
Total Loading 44 - 67 g/ft²

Structural Integrity Associates, Inc.

17

LP Drum Deposits

Triple Pressure HRSG. Gunk formation in LP Drum with no prior IAPWS Section 8 Review Before Application

FTIR of gunk deposits indicated the presence of hydrocarbon and functional groups of carbonyl or carboxylic acid.

SLIDE 11

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Film Forming Substances

IAPWS has organized five FFS Conferences (2017, 2018, 2019, 2021 & 2022)
From these and the publication of two IAPWS TGD, the following provides an outline of major topics addressed and researched

- Plant applications: fossil, combined cycle / HRSG and industrial plants w and w/o ACC, and nuclear, ammonia, fertilizer, geothermal and closed cooling.
- Lots of examples of operation, shutdown & preservation, but success results from following Section 8 in IAPWS TGDs
- Thermal decomposition / thermolysis, stability - effect of residence time, temperature, for ODA and OLDA (what about FFP?)
- Film formation - detection visually (multiple plants), Laboratory - X-ray Photoelectron Spectroscopy (XPS), Electrochemical Impedance Spectroscopy (EIS)
- Adsorption on surfaces. Laboratory work on metal surfaces for mainly ODA (what about oxides, other FFA and FFP)
- In-situ film formation, thickness and porosity - effectiveness of nm film with ODA is good at 80°C and 120°C (other FFA and FFP?)
- Flow-accelerated Corrosion (FAC) and FFS in the laboratory- good representation for single-phase but still some disconnect with some two-phase results from plants

Sources at IAPWS FFS Confs: Xue, De Mayer & Vidokjovic (Ghent), Roy (CEA), Hater (Kurita), Pabare (U of Toulouse), Lister (UNB)

SLIDE 13

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Some Final Thoughts on “corrosion” in ACC

(Based on work conducted in Australia, Canada, Chile, China, Cote d'Ivoire, Dubai, India, Ireland, Mexico, Qatar, Abu Dhabi, South Africa, Trinidad, UK and US)

- Increasing condensate pH to 9.8 will gradually eliminate the FAC damage at the tube entries and iron levels will reduce to international suggested levels (5 - 10 ppb). Documented by reducing the DHACI. FFS also work but not sufficient detailed documentation before and after application and currently no understanding of/for improvement using the wide range of FFS.
- Damage on cross members is not “arrested” as quickly by increasing pH. Is this LDI caused by the larger droplets leaving the PTZ of the LP Steam Turbine?
- FFS appears to arrest FAC/Corrosion in the two-phase environments of an ACC.
- Much care is required when using FFS for possible problems in remainder of plant (boiler/HRSG tube failures, deposits, drums, valves, etc). Problems observed in the wide range of FFS supplied.

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The ACC Corrosion Index to Compare and Categorize Corrosion and Track Improvements

DHACI

(Dooley, Howell, Air-cooled Condenser, Corrosion Index)

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DHACI for Tube Inlets

1. Tube entries in relatively good shape (maybe some dark deposited areas)
2. Various black/grey deposits on tube entries as well as flash rust areas, but no white bare metal areas
3. Few white bare metal areas on a number of tube entries. Some black areas of deposit
4. Serious white bare metal areas on/at numerous tube entries. Lots of black areas of deposition adjacent to white areas
5. Most serious. Holes in the tubing or welding. Obvious corrosion on many tube entries

Examples were included on slides

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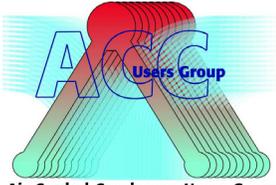
DHACI for Lower Ducts

- A. Ducting shows no general signs of two-phase damage
- B. Minor white areas on generally grey ducting. Maybe some tiger striping with darker grey/black areas of two-phase damage
- C. Serious white bare metal areas in the hot box and at numerous changes of direction (eg. at intersections of exhaust ducting to vertical riser). White areas are obvious regions of lost metal.

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What Guidance is Currently Available?

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Air Cooled Condenser Users Group
<http://acc-usersgroup.org/>
ACC.01
 Original Issue: May 12, 2015
 Revision due: May 12, 2018

Guideline for Internal Inspection of Air-Cooled Condensers

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International Association for the Properties of Water and Steam

IAPWS
Technical Guidance Documents
for
Fossil and Combined Cycle Plants
 (with particular relevance for plants with ACC)

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IAPWS Technical Guidance Documents for Combined Cycle 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. **TGD1-08**
- **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. Also addresses fast and/or frequently started units. **TGD2-09(2015)**
- **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 and/or frequently start. **TGD3-10(2015)**

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

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IAPWS Technical Guidance Documents Combined Cycle 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 plants with **TGD4-11(2015)**
- **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. **TGD5-13**
- **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 including those with ACC. **TGD6-13(2014)**

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

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IAPWS Technical Guidance Documents Combined Cycle Plants & with ACC

- **HRSG HP Evaporator Sampling for Internal Deposit Identification (Sept 2016).** This document includes the locations where to take samples from HGP and VGP HRSGs, how to analyze the samples, and an IAPWS map to assist in determining whether the HRSG HP evaporator needs to be chemically cleaned. **TGD7-16**
- **Application of FFS in Fossil, Combined Cycle and Biomass Plants (Revision October 2019).** This document covers optimum application guidance for FFA / FFAP / FFP in all-ferrous plants. It also includes customizations for shutdown / layup, multiple pressures, mixed-metallurgy feedwater systems, condensate polishing, and units with ACC. **TGD8-16(2019)**
- **Air In-leakage (Sept 2018).** This document covers guidance for the monitoring and control of AIL for a wide range of fossil, biomass, nuclear, and industrial plants including those with ACC. The major performance and cycle chemistry aspects are included. **TGD9-18**

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

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IAPWS Technical Guidance Documents Combined Cycle Plants & with ACC

- **Application of FFS in Industrial Steam Generators (October 2019).** This document covers optimum application guidance for FFA / FFAP / FFP in industrial plants. It also includes customizations for shutdown / layup, multiple pressures, mixed-metallurgy and aluminum feedwater systems, condensate polishing, units with ACC, special boiler types and with **TGD11-19**akeup.
- **Chemistry Management in Generator Water Cooling (October 2019).** This document covers guidance for all generators with water-cooled windings. The high - and low - oxygen chemistries for operation and shutdown are included. **TGD10-19**

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

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Resources for all areas of water and steam

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- www.IAPWS.org

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