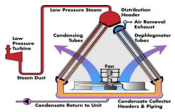
Air Cooled Condenser Users Group

ACCUG: Corrosion and Cycle Chemistry



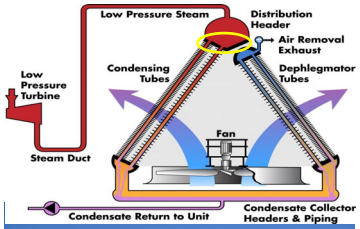
Fossil, Combined Cycle/HRSG and Industrial Plants
Review of History over Last 20 Years

Barry Dooley

ACCUG 2025
29th and 30th July 2025
Granbury, Texas

1

ACC Come in Many Sizes



But the two-phase FAC at the tube entries 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 has Serious Consequences

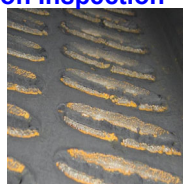
- **High concentrations of iron around the cycle**
  - **Boiler/HRSG deposits** (expensive chemical cleaning)
  - **Boiler/HRSG Tube Failures** (overheating and UDC / HD*)
  - **Steam Turbine Deposits** (including aluminum)
- **Need for Iron Removal Processes**
  - **Condensate Polishing and/or Filters** (5 µm absolute preferred)
- **Limitations around the cycle**
  - **Condensate polishing** (may have to change mode to AFO*)
- **Overall, an ACC "controls" the unit cycle chemistry**
  - **International Guidelines are freely available for ACC and two-phase flow** (IAPWS Volatile and FFS Guidance)

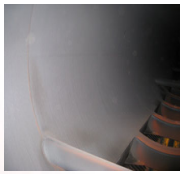
IAPWS

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

3

A Wide Variety of ACC Corrosion on Inspection





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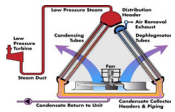
4

Discussion Items for ACCUG 2025



Reminder of ACC Damage & How it is Normally Addressed
DHACI provides uniformity for Inspections Worldwide
Monitoring Cycle Chemistry (total iron)
Introduction & Update of Film Forming Substances (FFS)
International Experiences & Missing Information

July 2025

5

There is an ACC Corrosion Index to Categorize Corrosion and Track Improvements

DHACI

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

6

DHACI for Tube Entries

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 included on slides

7

DHACI for Steam Transport 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.

Overall, an ACC maybe described as 4B

8

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

9

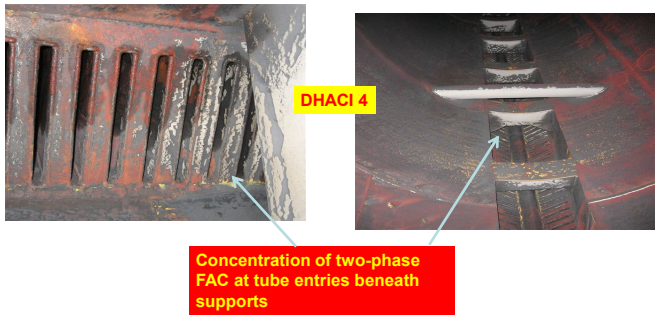
Inspections Worldwide show the same Features

Combined Cycle with ACC after ~ 15,000 hrs, pH 9.1.

10

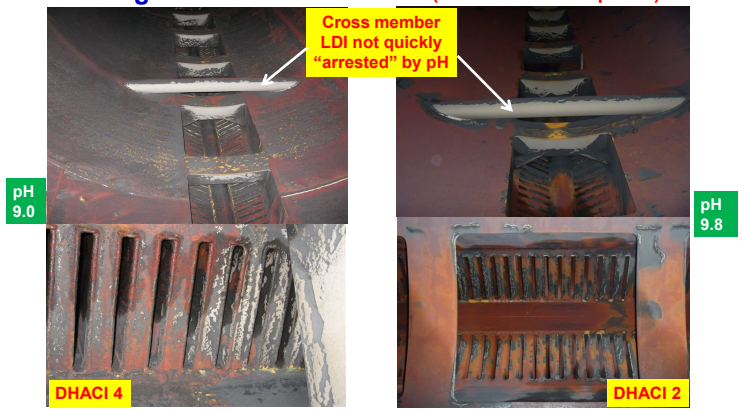
Inspections Worldwide show the same Features

750 MW Supercritical on OT at pH 9, ~4,000 hrs.



11

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



12

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

13

Damage takes time to arrest (2 Years with pH 9.8)

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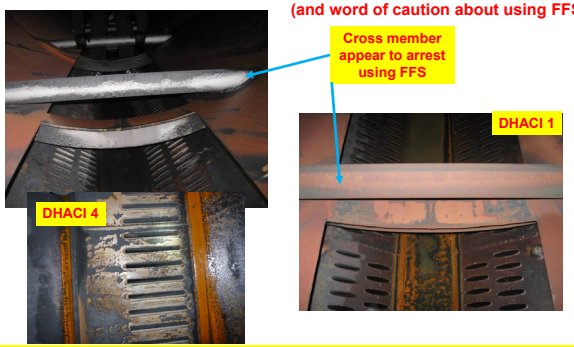
ACC Two-phase FAC can be "Arrested" with FFS

(Example of Significant Reduction in DHACI for FAC at Tube Entries in ACC. Accompanied by Significant Reduction of Total Iron in Condensate. But many cases where FFA and FFP have not "arrested" ACC FAC) (and word of caution about using FFS – see later)

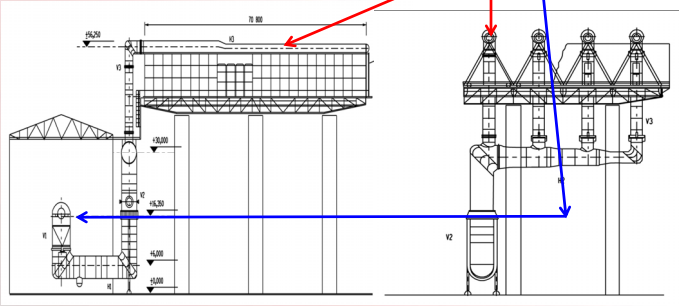


For ACC the FAC / Corrosion damage is the same worldwide with all chemistries and plant types (Based on assessment / inspection work conducted in Australia, Canada, Chile, China, Cote d'Ivoire, Dubai, India, Ireland, Mexico, Qatar, Abu Dhabi, UAE, South Africa, Trinidad, UK and US)

SLIDE 15

15

To Understand the FAC/Corrosion here we need to Understand the Environment in the PTZ



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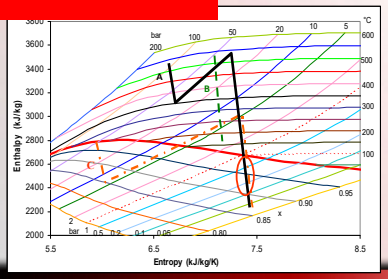
The PTZ Environment in the LP Steam Turbine is Completely Understood

Mollier Diagram
A.Fossil Reheat Turbine
B. Backpressure Turbine
C. Reheat Turbine in a nuclear LWR plant



Generation of the ACC Environment

Heterogeneous droplet Nucleation and Liquid Films on ST Blades

(Droplets and Liquid Films in the ACC vary from 0.1 – 50 microns and don't contain any oxygen until during shutdown)

Source: IAPWS Technical Guidance Document on Steam Purity

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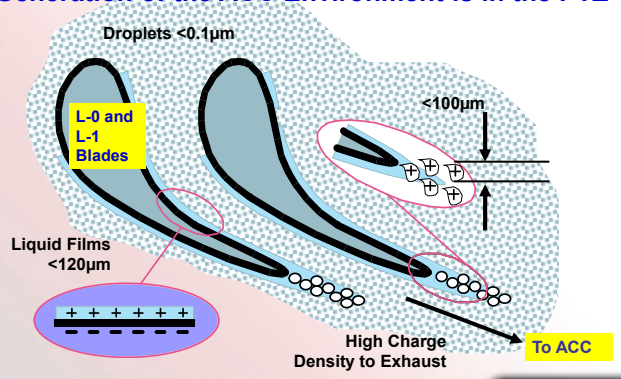
17

Generation of the ACC Environment is in the PTZ



Adapted from Dooley and Dooley and Rieger, 2001

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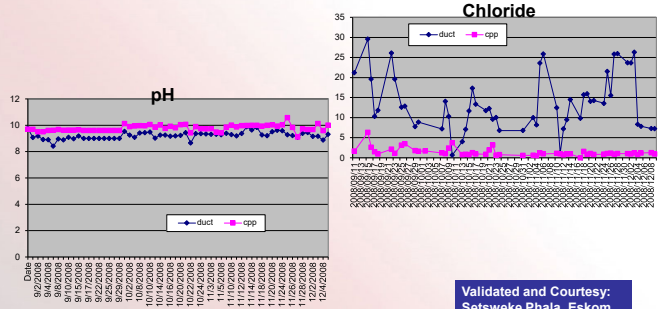
18

The Liquid in ACC Upper Ducts

(Lower pH and higher chlorides)



Validated and Courtesy: Setsweke Phala, Eskom

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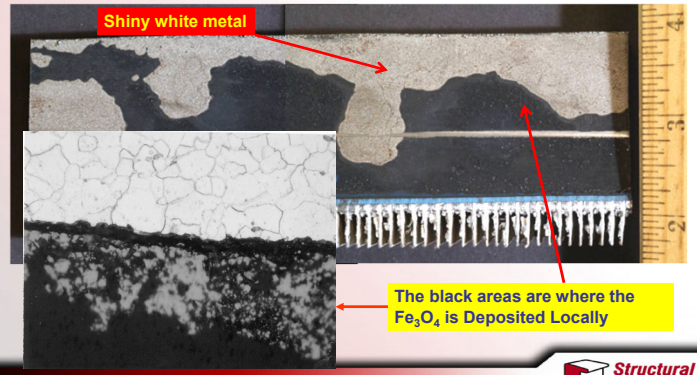
19

Inside diameter surface of an ACC Tube



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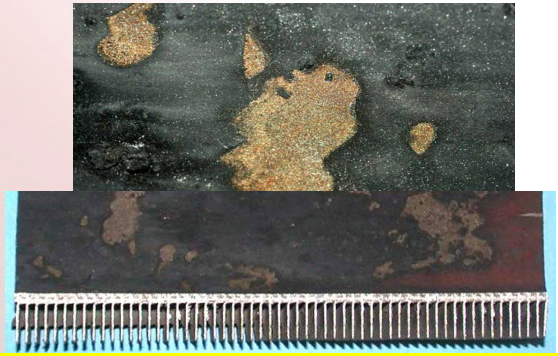
20

Another Tube Showed the Same Features



6 inch section of ACC tube and detail of the surface showing black deposits and white "bare" metal areas. Note some Fe_3O_4 has turned red

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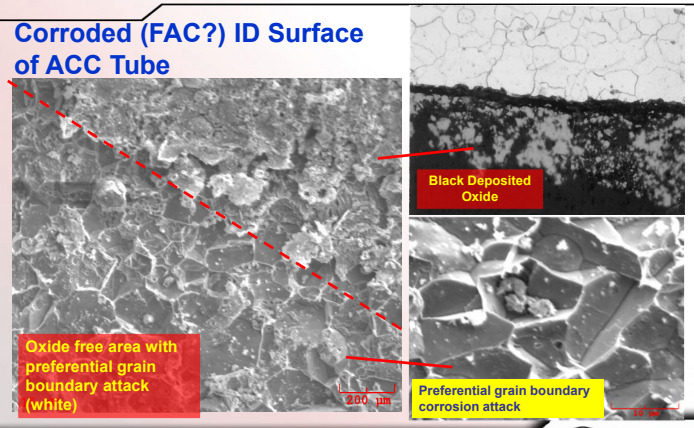
Corroded (FAC?) ID Surface of ACC Tube



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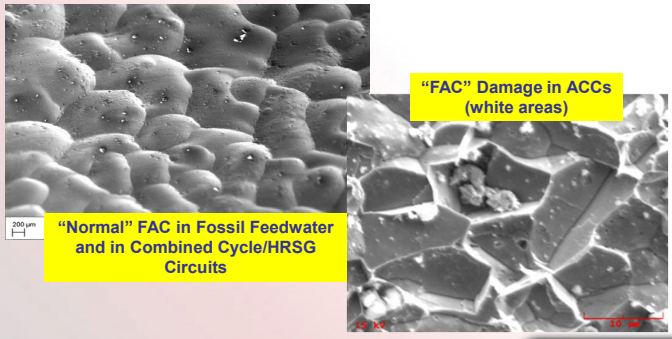
22

Typical Microscopic Appearance of FAC and ACC Corrosion



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Monitoring Condensate Iron to Categorize Corrosion and Track Improvements

ACC Users Group
Air Cooled Condenser Users Group

24

Sampling and Analysis of Corrosion Products

Something Old - IAPWS 2014 TGD + Something New – IAPWS 2025 White Paper

Suitable methods

- Sampling and locations
- 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)

IAPWS TGD 6-13, September 2014

25

Achievable Total Fe (& Cu) Levels Different Plant Types/Optimized Chemistry Steady/Base Loaded Plants

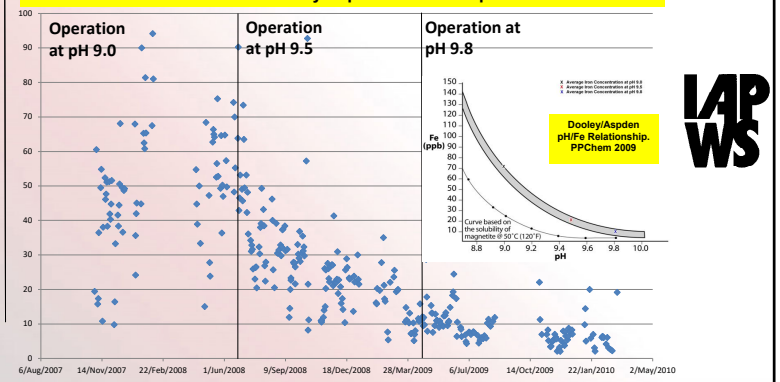
Feedwater		
OT:	Total Fe =	< 1 µg/kg
AVT:	Total Fe =	< 2 µg/kg
AVT (Mixed):	Total Fe & Cu =	< 2 µg/kg
HP/LP Heater Drains:	Total Fe & Cu =	< 1 µg/kg
HRSG Evaporators/Drums		
AVT/PT/CT:	Total Fe =	< 5 µg/kg
Units with Air-Cooled Condenser (ACC)		
ACC Outlet:	Total Fe =	< 10 µg/kg
Post Condensate Filter: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

IAPWS TGD 6-13, September 2014

Higher than these values indicates an RCCS (A cycle chemistry deficiency)

26

Plant Improvements in ACCs (reduction of total iron) are Directly in Agreement with the Dooley/Aspden relationship



Source: Richardson and Joy, Data from 650 MW Unit with ACC

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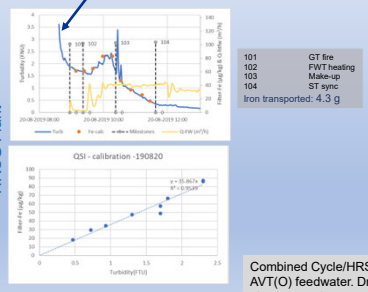
27

New IAPWS Procedure to Quantify CP Transport During Startup

For Fast Start or Frequently Started Plants the important Corrosion Product Indicator is how quickly the Fe decay takes place from the high shutdown level during startup. This can be monitored by using Proxy Analysis for Total Iron (turbidity) and overlaying the decay profile on IAPWS Decay Map

- Summary of procedure
  - Flush feedwater sample point as soon as pressure is available
  - Measure and register oxide levels in feedwater by proxy methods during startup
  - Take samples for filtered iron intermittently to establish correlation to proxy results
  - Note times for milestones: First fire, by-pass, turbine roll-up, synchronisation etc.
  - Plot iron levels versus time after First fire, mark milestones
  - Integrate (iron level * feedwater flow) from First fire to steady-state level → iron transported to boiler during startup

Example: Startup of a Well Operated HRSG Plant



Combined Cycle/HRSG. AVT(O) feedwater. Dry air preservation.

IAPWS White Paper, January 2025

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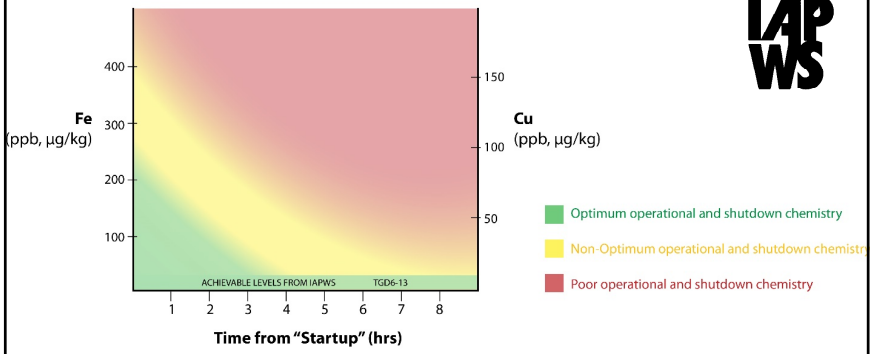
IAPWS CORROSION PRODUCT DECAY MAP



Guidance is provided in Section 7 of White Paper. The goals for each plant should be for the profile to be in the Green Area with short times to reach achievable levels. Zero time can be start of BFP, first fires, synchronization, pressure changes or other.

IAPWS White Paper, January 2025

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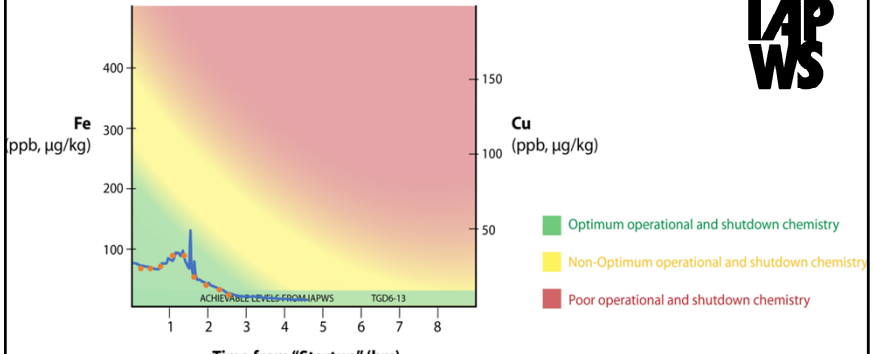
IAPWS CORROSION PRODUCT DECAY MAP



Decay Profile for well operated combined cycle/HRSG plant is superimposed. AVT(O). Dry air preservation of boiler

IAPWS White Paper, January 2025

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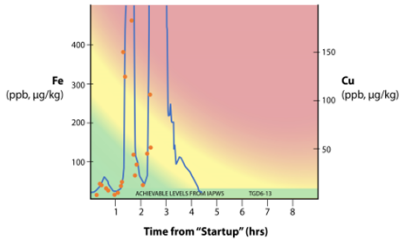
30

Examples from Plants that need to improve Operation and/or Shutdown Chemistries

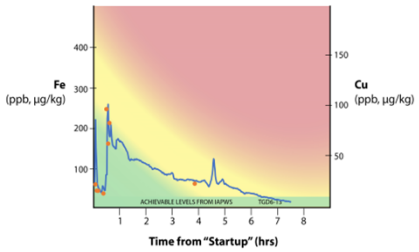
(can easily be seen by superimposing on IAPWS Decay Map)

IAPWS CORROSION PRODUCT DECAY MAP



All-ferrous feedwater. Cu condenser. AVT(O). Daily load cycling. Startup in 60MW increments

IAPWS CORROSION PRODUCT DECAY MAP



All-ferrous feedwater. AVT(O). Summer shutdown with no protection.

IAPWS White Paper, January 2025

Decay Profiles in the Red/Yellow indicate an RCCS

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Possible Major Uses for the Decay Map and Concept

A. Fine tuning the cycle chemistry /shutdown procedures of a unit and/or arresting FAC. Minimize Fe with decay profile moving towards the green.
B. Fine tuning the cycle chemistry for a unit with an ACC. Fe measured in the condensate. Improvement in chemistry indicated by the decay profile moving towards the green and reduced DHACI.
C. Verifying "benefits" of application of an FFS. Fe levels at the economizer inlet and drums before and after.
D. White Paper Guidance Section 10 provides indicators for supercritical, drum units (all-ferrous and mixed-metallurgy), and combined cycle/HRSGs – optimum and non-optimum chemistries.
E. Before and after fireside cleaning of HRSG tubing. Fe levels at the economizer inlet/BFP.

IAPWS White Paper January 2025

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Update on the use of an FFS

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

Please ensure you use Section 8 in the IAPWS Guidance: Corrosion Products and Internal WW and HP Evaporator Deposits

IAPWS TGD: Application of FFS in Fossil, Combined Cycle and Biomass Plants (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)

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 poor makeup. TGD11-19

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

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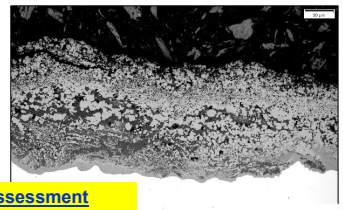
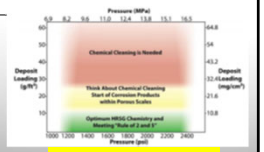
Please do not add FFS if your HP Evaporator looks like this and/or has corrosion reaction products

(use the IAPWS Deposit Map to make an assessment)



2023 Assessment
Total Loading ~65 mg/cm²



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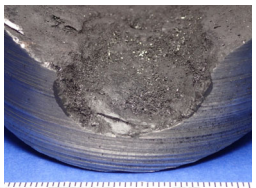
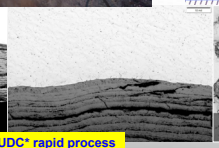
IAPWS Deposit Map

34

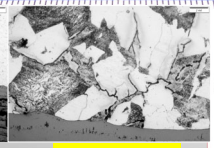
or you might end up with an HP Evaporator like this

(2x1 Triple Pressure HRSG, Operating on AVT(O) with FFA (polyamine) added)



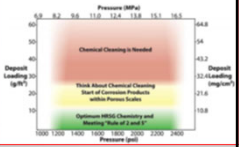


Multi-laminated scale – UDC* rapid process



Embrittled Material

(Please use the IAPWS Deposit Map to make assessment before application of FFS)



IAPWS Deposit Map

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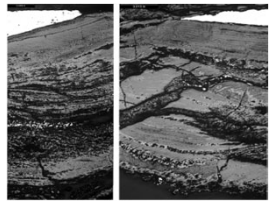
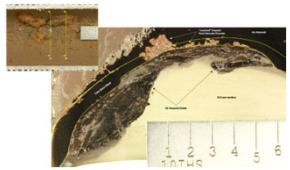
or like this: HP Evaporator Heavy Deposits and Failure

Double Pressure HRSG (9 and 0.5 MPa). HTF after FFAP Application without thorough upfront review (such as IAPWS Section 8)

Severe Under-deposit Corrosion (UDC)* in typical multi-laminated morphology. But no material degradation (voids)



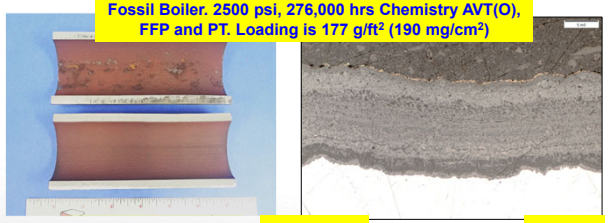


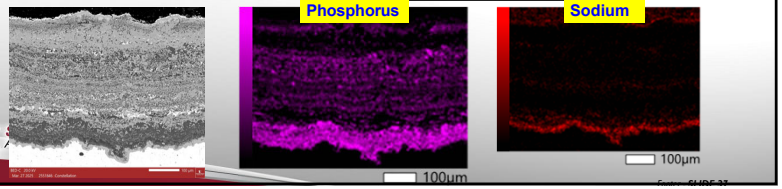
* Perhaps a new variant*

36

And beware of Increasing Fossil Waterwall Deposits after FFS Application (without detailed up-front Section 8 FFS TGD review)

Fossil Boiler. 2500 psi, 276,000 hrs Chemistry AVT(O), FFP and PT. Loading is 177 g/ft² (190 mg/cm²)

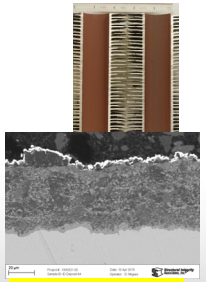




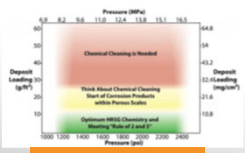
37

Beware of Increasing HP Evaporator Deposits after FFS Application

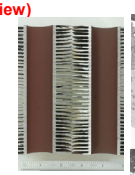
(without detailed up-front review)

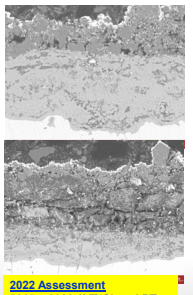


2018 Assessment
2003 - 2015 AVT(R) and PT
2015 - 2018 AVT(O) and PT
Total Loading 19 – 24 mg/cm²



IAPWS Deposit Map





2022 Assessment
2015 – 2020 AVT(O) and PT
2020 – 2022 AVT(O) + FFP
Total Loading 47 – 71 mg/cm²

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Biggest Question on FFS: Influences of FFS (FFA or FFP) on Oxide Growth Mechanisms around Generating Cycles?

Detailed Presentations by Dooley, Lister and Fandrich at 2019 and 2021 IAPWS FFS Conferences on oxides in condensate, feedwater, boiler/HRSG water and steam. This has not been addressed by any FFS supplier or any group working on FFS. So, it remains as the most important IAPWS Certified Research Need (ICRN).

First Example on Oxides in All-Ferrous Condensate and Feedwater

Here the interest in temperatures is up to 280 - 300°C. This is the main temperature range of interest for corrosion and FAC in fossil, combined cycle / HRSG and nuclear plants and for ACC

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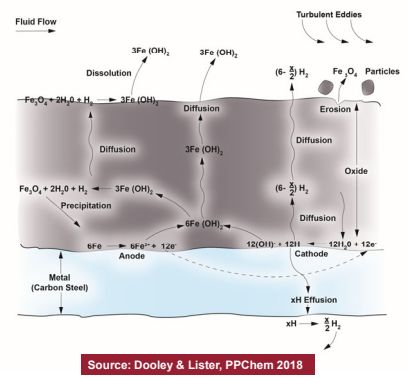
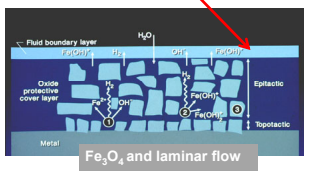
All-Ferrous Condensate, ACC and Feedwater & FAC on Carbon Steel

Normal Growth of Magnetite & FAC



Source: Dooley & Lister, PPChem 2018

Oxide growth ($Fe(OH)_2$) at M/O releases equal quantities of particulate and soluble Fe_3O_4 into fluid flow. Turbulence reduces boundary layer and accelerates the process. This is FAC. Mechanism and morphology well established.



Fe_3O_4 and laminar flow

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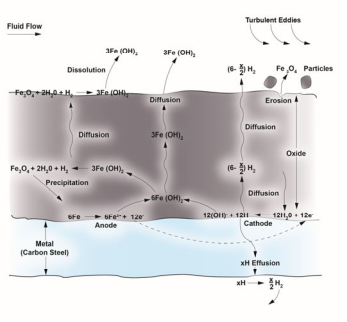
All-Ferrous Condensate, ACC and Feedwater

Normal Growth of Magnetite & FAC



Source: Dooley & Lister, PPChem 2018

1. Oxide growth ($Fe(OH)_2$) at M/O releases equal quantities of particulate and soluble Fe_3O_4 into fluid flow. Turbulence reduces boundary layer and accelerates the process. This is FAC. Mechanism and morphology well established

2 Formation of an FFS Film on/in oxide is expected to: a) change mechanism? b) reduce dissolution? or c) ?? Ultimately reducing total iron levels. How?

3. But does a 10 nm FFS film on/in the oxide:
a) reduce liquid on surface and restrict access of H_2O to M/O, b) restrict $Fe(OH)_2$ growth and flow into fluid flow, or c) ??

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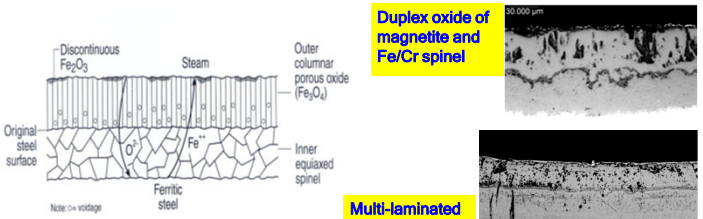
Oxide Growth and Exfoliation (OGE) in Steam

Here the oxides are semiconductors and grow by ionic diffusion processes. Not dependent on chemistry (oxygen). Considering superheated steam with temperatures up to 600C +

Morphologies of OGE are well understood for ferritic and austenitic alloys*



Duplex oxide of magnetite and Fe/Cr spinel

Multi-laminated oxides prior to exfoliation

*Wright & Dooley, Materials at High Temperatures, 2011
*Dooley & Wright, Oxide Growth and Exfoliation. PPChem, 2019

Very Improbable that an FFS (FFA or FFP) can affect growth of steam grown oxides.

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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 (IAPWS) suggested levels (5 - 10 ppb) at CPD. Documented by a decreasing DHACI. FFS sometimes will work but not sufficient detailed documentation of ACC 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? Depth of damage down into ACC tube needs investigation?

FFS appears in some cases 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 (FFA and FFP).

Use of the IAPWS Decay Map can show definite improvement or not.

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Air Cooled Condenser Users Group

Summary

- **Some aspects relate to (LT Two-phase) FAC**
  - Adjacent black and white areas in severe turbulent areas
  - Increasing local pH reduces damage
- **But some aspects don't** (normal FAC scalloped appearance and white areas on cross members is probably LDI)
- **Environment is known and has been measured**
  - Two-phase mixture formed in PTZ of the steam turbine well understood
  - Concentrating liquids on PTZ surfaces (**Higher in chloride/sulphate, organics**)
  - Lower in pH (0.5) and very low in dissolved oxygen (close to zero) on ACC surfaces
- **"Arrested" two-phase FAC areas turn red slowly**
  - ACC Mechanism is thus not totally understood & what are amines/FFS doing?
  - Red coloration is known to form during shutdown (not during operation)
- **Results from a number of plants indicate increased Al levels in turbine and drum deposits**
  - This may result from initial operation

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IAPWS Technical Guidance Documents for Fossil and 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 — **Carryover**
- **Instrumentation for monitoring and control of cycle chemistry for the steam-water circuits of fossil-fired and combined-cycle power plants (June 2024)**. 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(2024) — **Instrumentation**
- **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. Added guidance for fast and/or frequently started units. TGD3-10(2015) — **Volatile Treatments. AVT and OT**

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

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IAPWS Technical Guidance Documents Fossil and 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 drum units. TGD4-11(2015) — **Phosphate & NaOH. PT & CT**
- **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 — **Steam Purity**
- **Corrosion Product Sampling and Analysis (May 2014).** This document covers the optimum procedures and techniques for sampling and monitoring total iron and copper. Includes a table of achievable Fe/Cu levels for plants including those with ACC. TGD6-13(2014) — **Corrosion Products**

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IAPWS Technical Guidance Documents Fossil and 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 — **HRSG HP Evap Deposits**
- **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) — **Film Forming Substances**
- **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 — **Air In-Leakage**

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

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IAPWS Technical Guidance Documents Fossil and 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 poor makeup. TGD11-19 — **FFS Industrial Plants**
- **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 — **Generators**

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Resources for all areas of water and steam

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