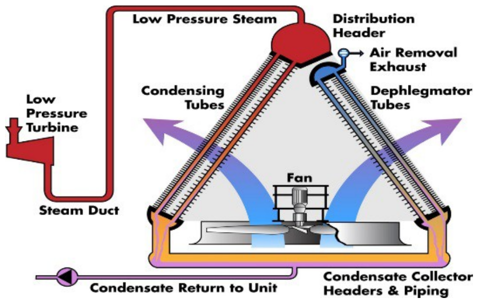
Air Cooled Condenser Users Group

Introduction for ACCUG Corrosion and Cycle Chemistry Section

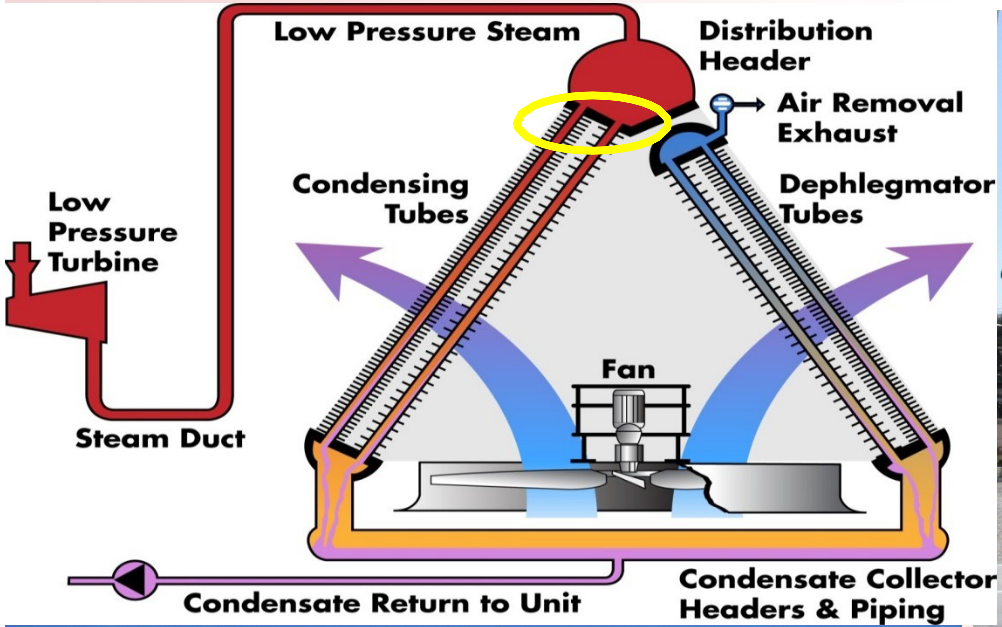


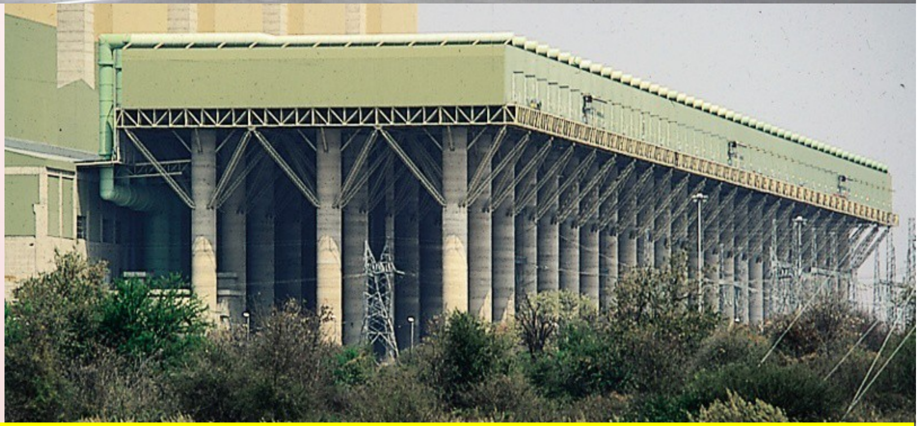
Fossil, Combined Cycle/HRSG and Industrial Plants
Review for new participants of key aspects from 2007
Updates on Film Forming Substances (FFS)

Barry Dooley

ACCUG 2021
Virtual Meeting
12th October 2021

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)**

Typical ACC Damage

Tube Entries, Support Structures and Transport Ducting

Corrosion/FAC in ACC and the Consequences

- High concentrations of iron around the cycle
  - Boiler/HRSG deposits (expensive chemical cleaning)
  - Boiler/HRSG Tube Failures (UDC, Overheating and TF)
  - 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)
- Overall, an ACC "controls" the unit cycle chemistry
  - International Guidelines are available for ACC and two-phase flow (ex. IAPWS Volatile Guidance)

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

DHACI

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

Dooley & Howell et al, PPChem 2009

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 later slides and in ACCUG Guideline on Internal Inspections

Dooley & Howell et al, PPChem 2009

DHACI for Lower / 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.

Dooley & Howell et al, PPChem 2009

We know what the Corrosion Looks Like

DHACI 3

DHACI 4

DHACI 3

The FAC / Corrosion damage is the same worldwide with all cycle chemistries and plant types

and what Holes at Tube Entries Look Like

DHACI 5

Inspections Worldwide show the same Features

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

DHACI 4

Concentration of two-phase FAC at tube entries beneath supports

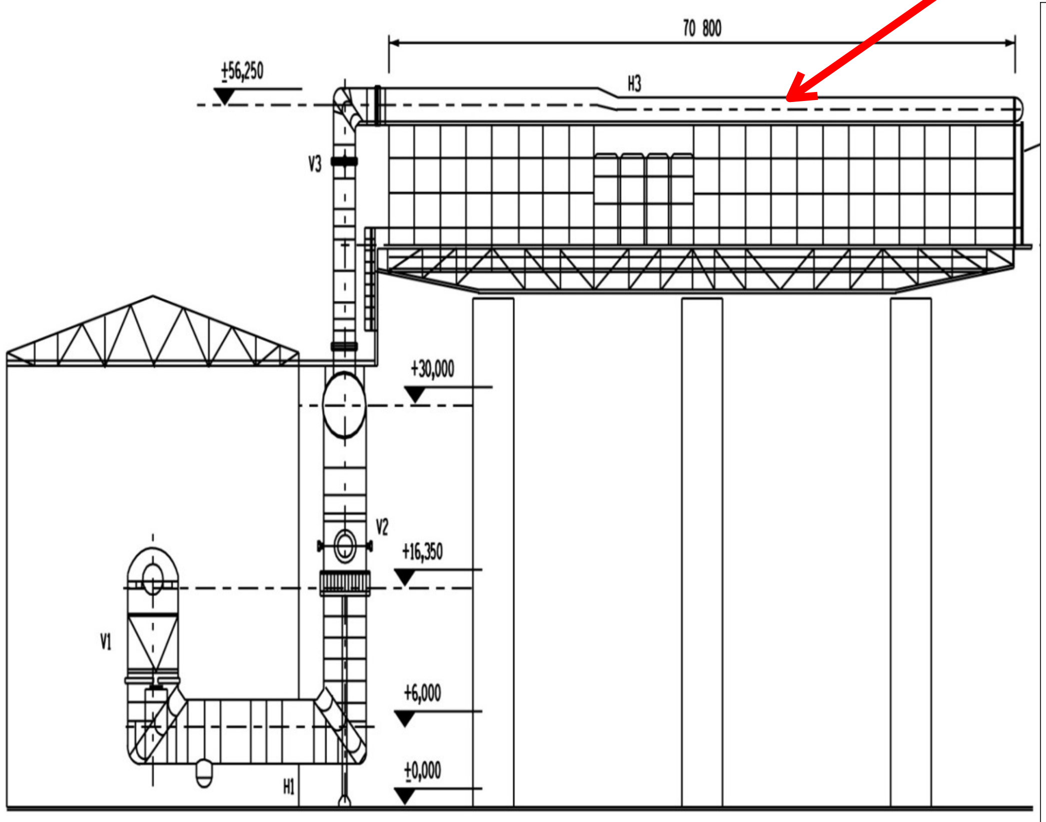
Inspections Worldwide show the same Features

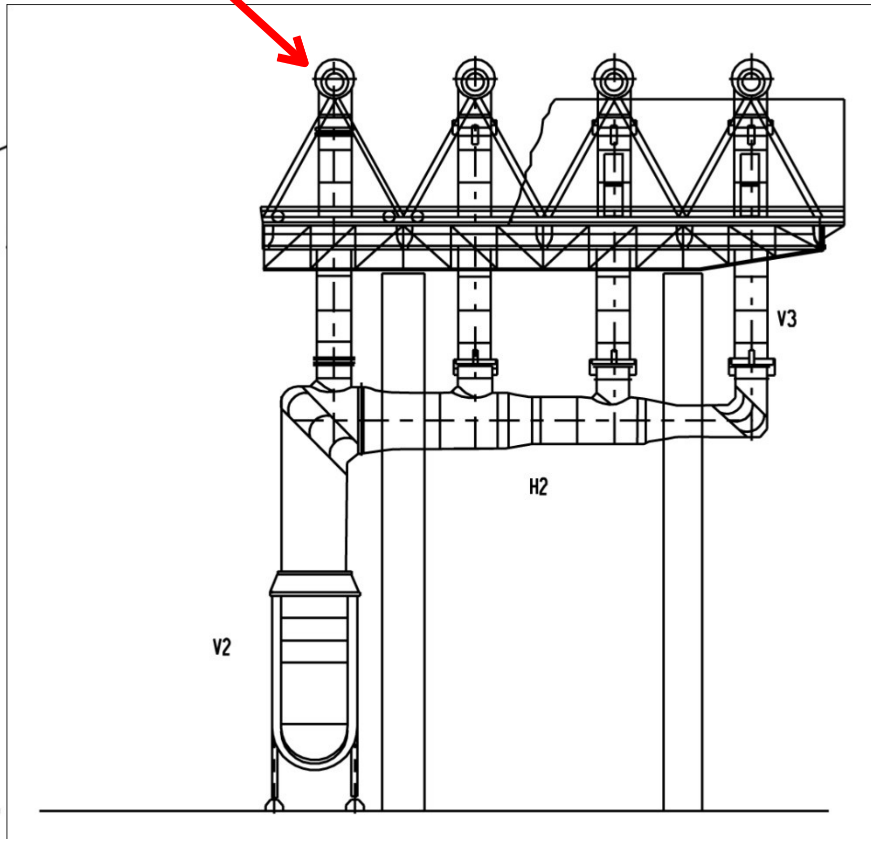
750 MW Supercritical on OT at pH 9, ~4,000 hrs.

DHACI 4

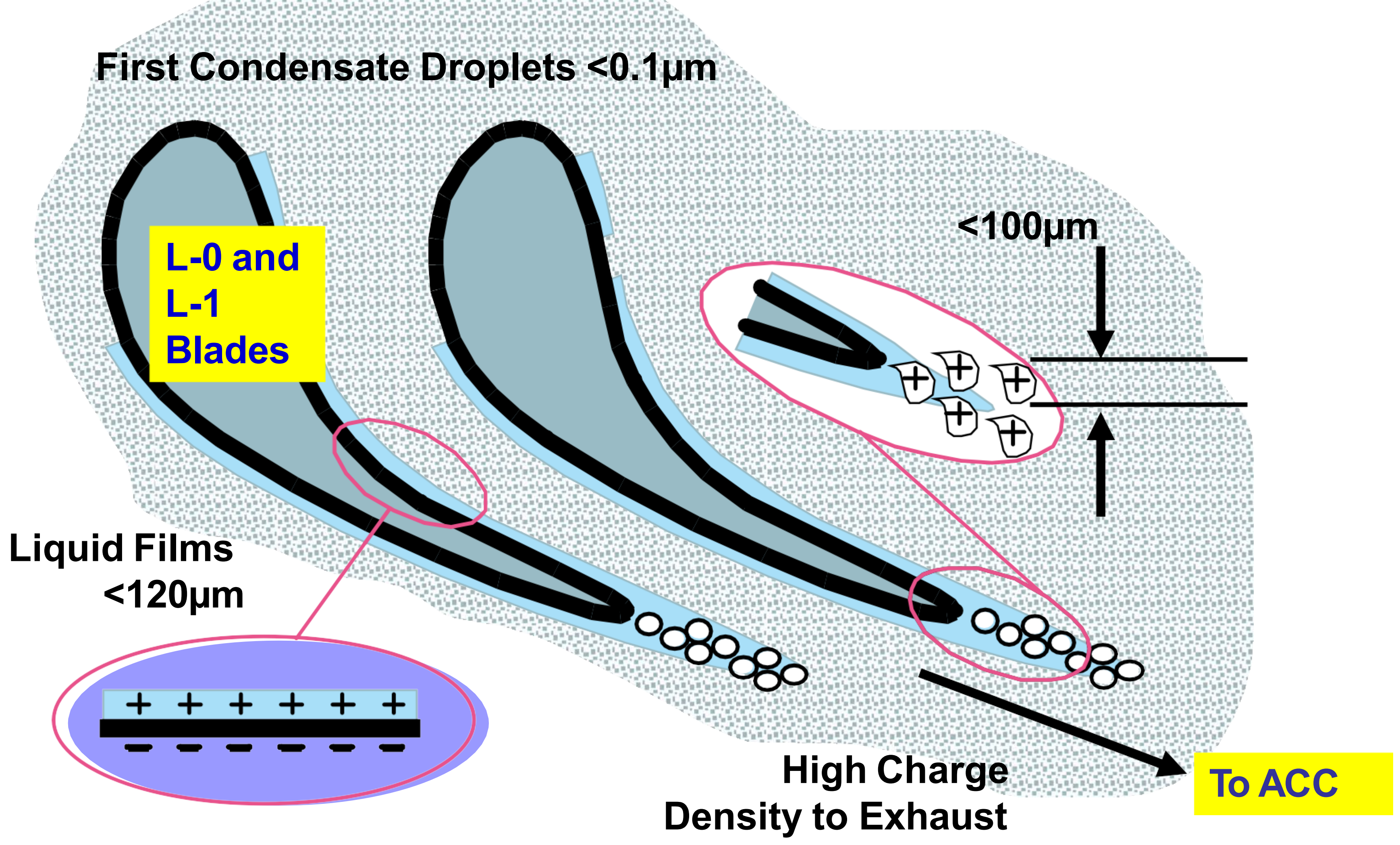
Concentration of two-phase FAC at tube entries beneath supports

To Understand the Corrosion Here we need to Apply the Understanding of the Environment in the PTZ





Generation of the ACC Environment is in the PTZ



Adapted from Dooley and Dooley and Rieger, 2001

We now Fully Understand the Environment but Can we Prevent the Corrosion Mechanism?

“Solutions” are being applied

Increase bulk condensate pH up to 9.8 – Works and is Validated

Apply an amine (including FFS) – Appears to work but science not fully understood / explained

Filters (average and absolute) and condensate polishers – Can lower total iron but doesn’t stop FAC/Damage at tube entries

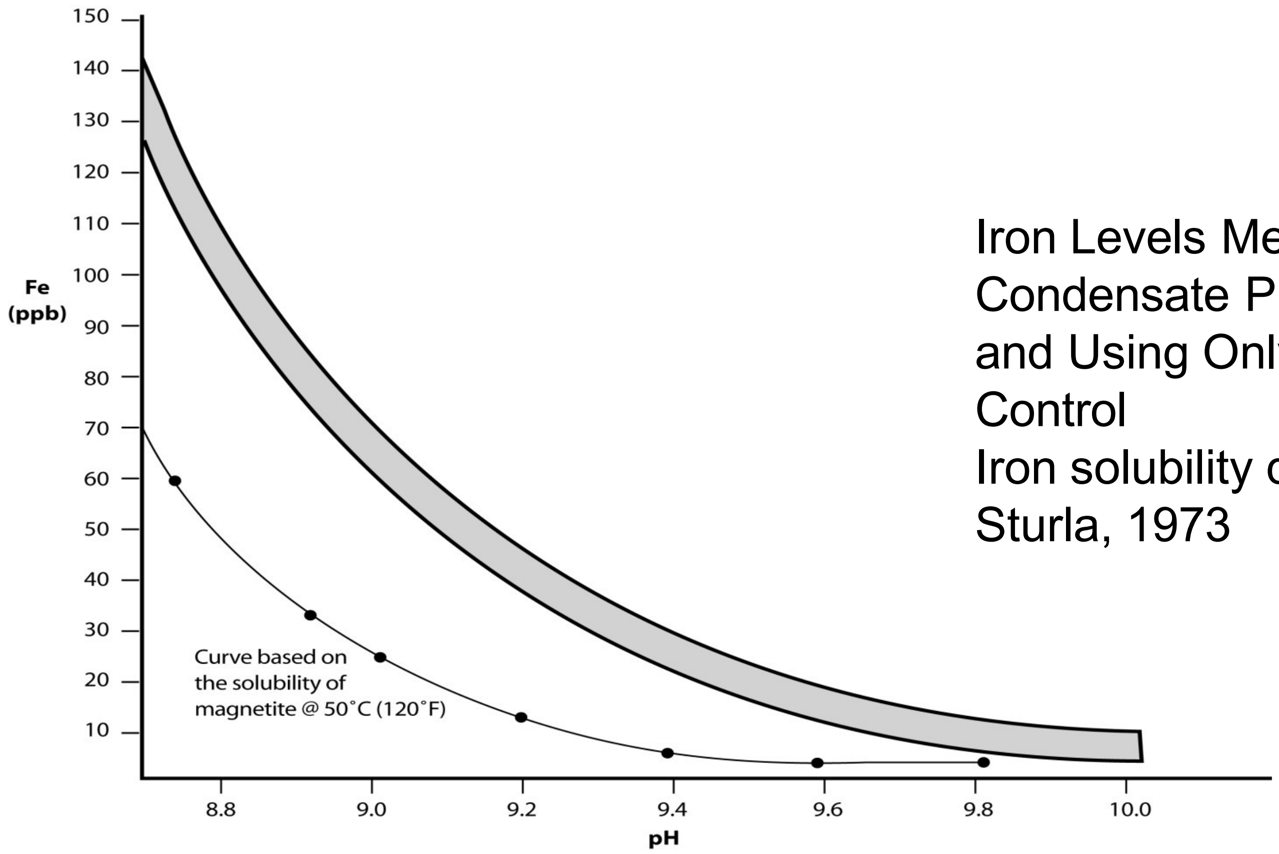
Coatings (epoxy), Sleeves, Inserts – Not sufficient information

Alternate Materials to CS – Very few cases and no validation

Designs – Various have been applied but FAC/Damage still occurs

The Total Iron vs pH is Consistent Worldwide

(Dooley/Aspden pH Versus Iron Relationship)

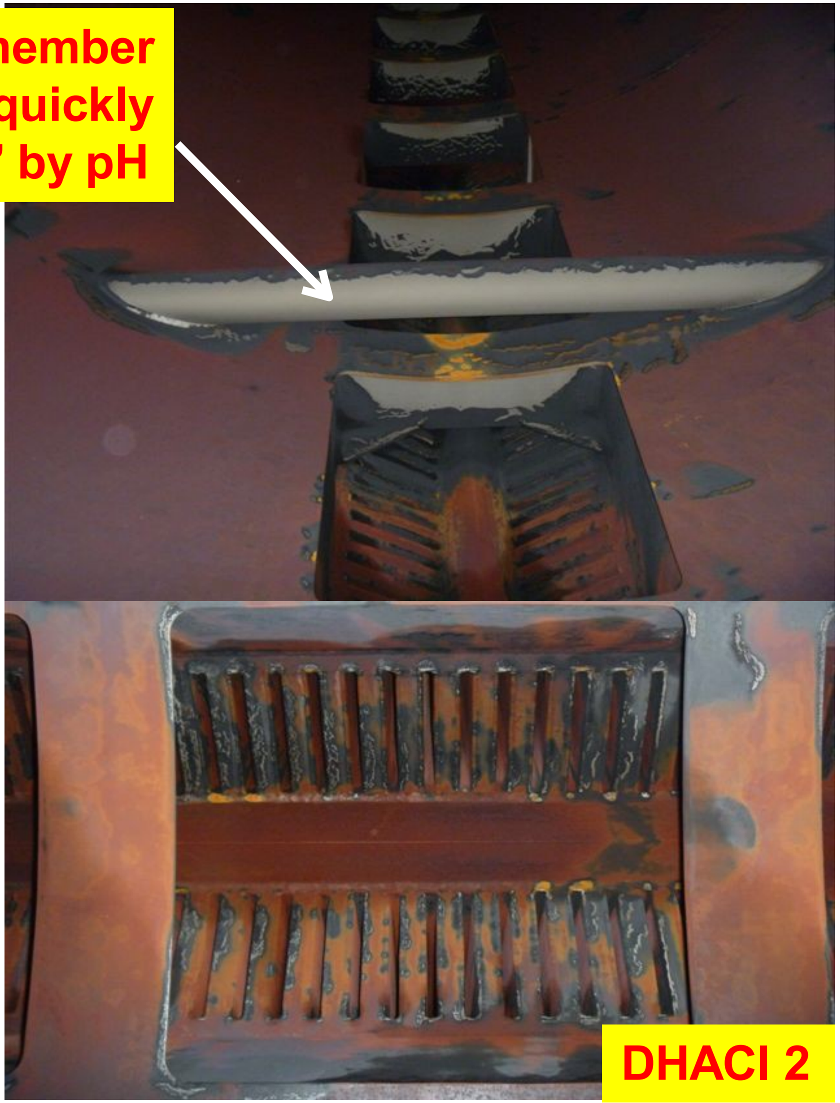


Iron Levels Measured at Condensate Pump Discharge and Using Only Ammonia for pH Control

Iron solubility data extracted from Sturla, 1973

Dooley, Aspden, Howell & DuPreez, PPChem 2009

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



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

DHACI 4

DHACI 2

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

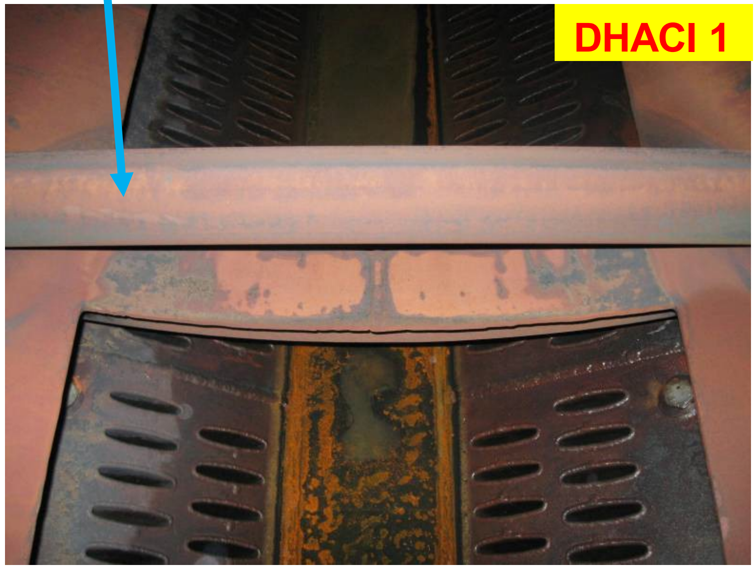
(Indicative that FAC/Corrosion is "under control")

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 (ppb)
Post Condensate Filter:	Total Fe =	< 5 µg/kg (ppb)

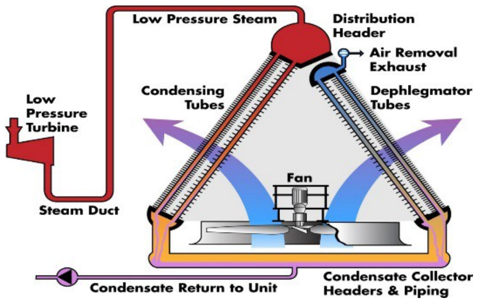
ACC Two-phase FAC can also be "Arrested" with FFS

(Significant Reduction in DHACI for FAC at Tube Entries in ACC Accompanied by Significant Reduction in Total Iron in Condensate)

Cross member appear to arrest using FFS



Discussion Item for ACCUG 2021



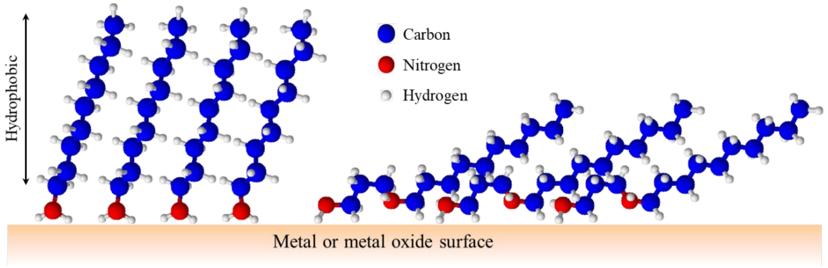
Film Forming Substances (FFS)
Three ACCUG presentations on FFS application
Summary of International Experience & Missing Information

Extracted from IAPWS Symposium

15th September 2021

B. Dooley, UK

D. Addison, New Zealand



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 TGD

Film Forming Substances (FFS)

- FFA/FFAP
- FFP

Film Forming Amines (FFA)

Octadecylamine – ODA
Oleyamine – OLA
Oleyl Propylenediamine – OLDA

Film Forming Products (FFP)

Proprietary

Film Forming Substances – Wide Range of Products and Mixtures

Product Type	Film Forming Products (None Amine)	Film Forming Amines – pH stabilized	Film Forming Amines – Homogenization stabilized	Film Forming Amines – pH stabilized and blended with dispersants etc
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		

Film Forming Substances – Wide Range of Vendors Globally

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

Film Forming Products (None Amine)	Nalco, Anodamine, Cortec etc.
Film Forming Amines – pH stabilized	Nalco, Suez, Chemtreat, Helamin, Finamin, Solenis etc.
Film Forming Amines – Homogenization stabilized	Reicon, Kurita, Suez etc.
Film Forming Amines – pH stabilized and blended with dispersants etc	Helamin, Finamin, etc.

Film Forming Substances

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

- Plant applications: fossil, combined cycle/HRSG and industrial plants w and w/o ACC, and nuclear, ammonia, fertilizer, 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
- Film formation - detection visually (multiple plants), Laboratory – Xray Photoelectron Spectroscopy (XPS), Electrochemical Impedance Spectroscopy (EIS)
- Adsorption on surfaces. Laboratory work on metal surfaces.
- In-situ film formation, thickness and porosity – effectiveness of nm film with ODA is good at 80°C and 120°C
- 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 & Vidojkovic (Ghent), Roy (CEA), Hater (Kurita), Pébère (U of Toulouse), Lister (UNB)

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

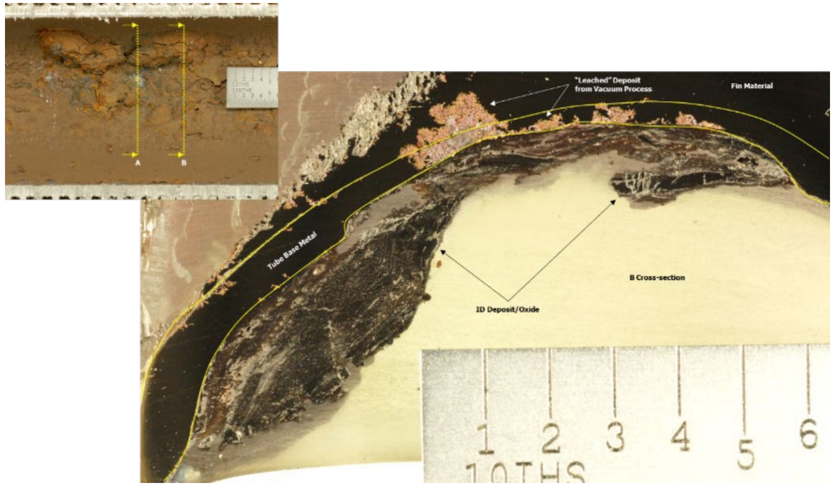
- Universal reductions in feedwater Fe and Cu Transport but no equivalent understanding of the mechanisms of oxide growth "formation/reductions" in condensate (ACC), feedwater, boiler water and steam
- General observations of hydrophobic films on water-touched surfaces, but it is underlined that hydrophobicity (contact angle) does not prove presence of film or protection
- Film formation remains very questionable on steam-touched surfaces
- Basic understanding has improved worldwide since 2014
- 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

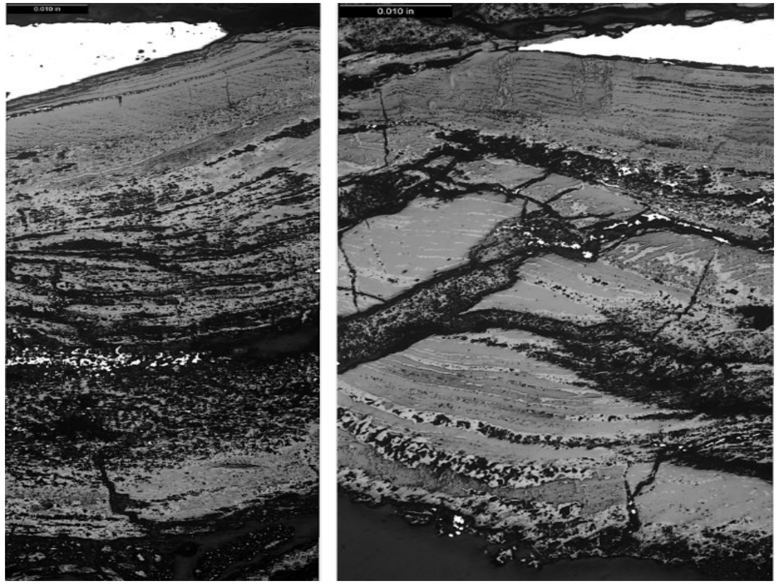
A couple of examples →

HP Evaporator Heavy Deposits and Failure

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

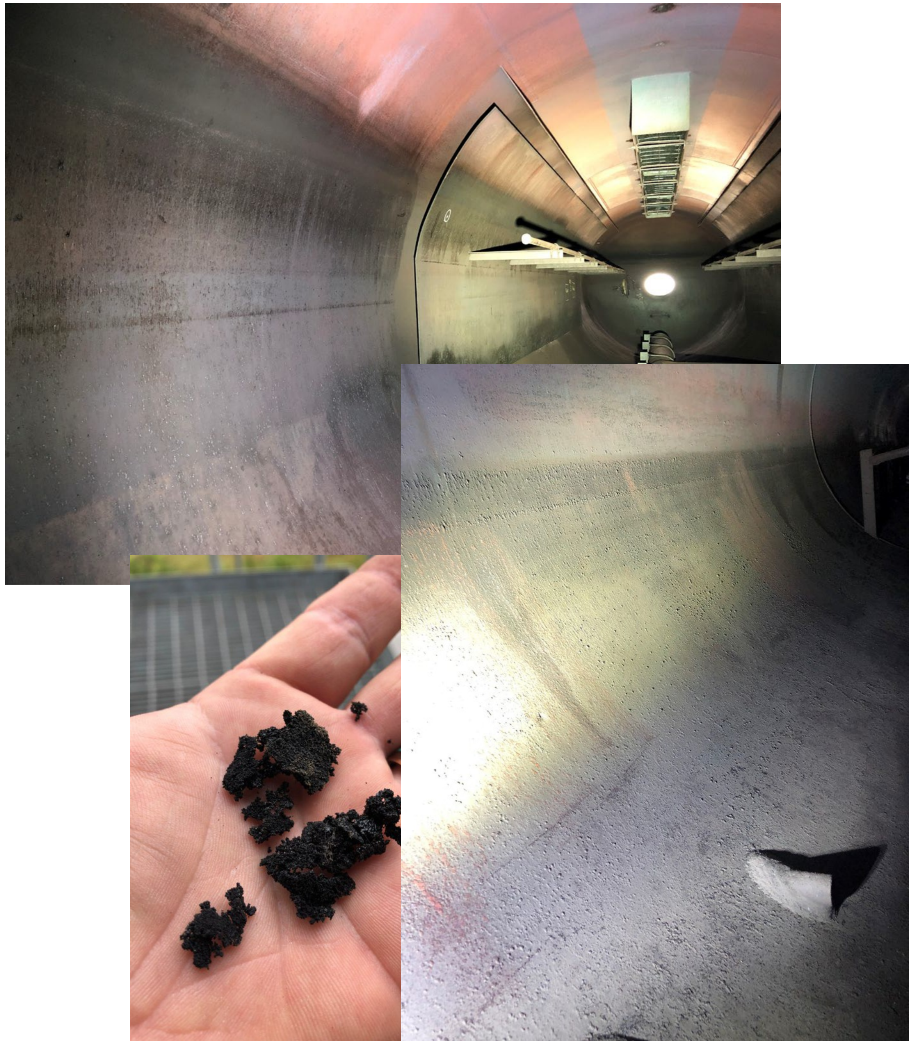
Severe Under-deposit Corrosion in typical multi-laminated morphology





LP Drum Deposits

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



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

Influences of FFS on Oxide Growth Mechanisms around Generating Cycles

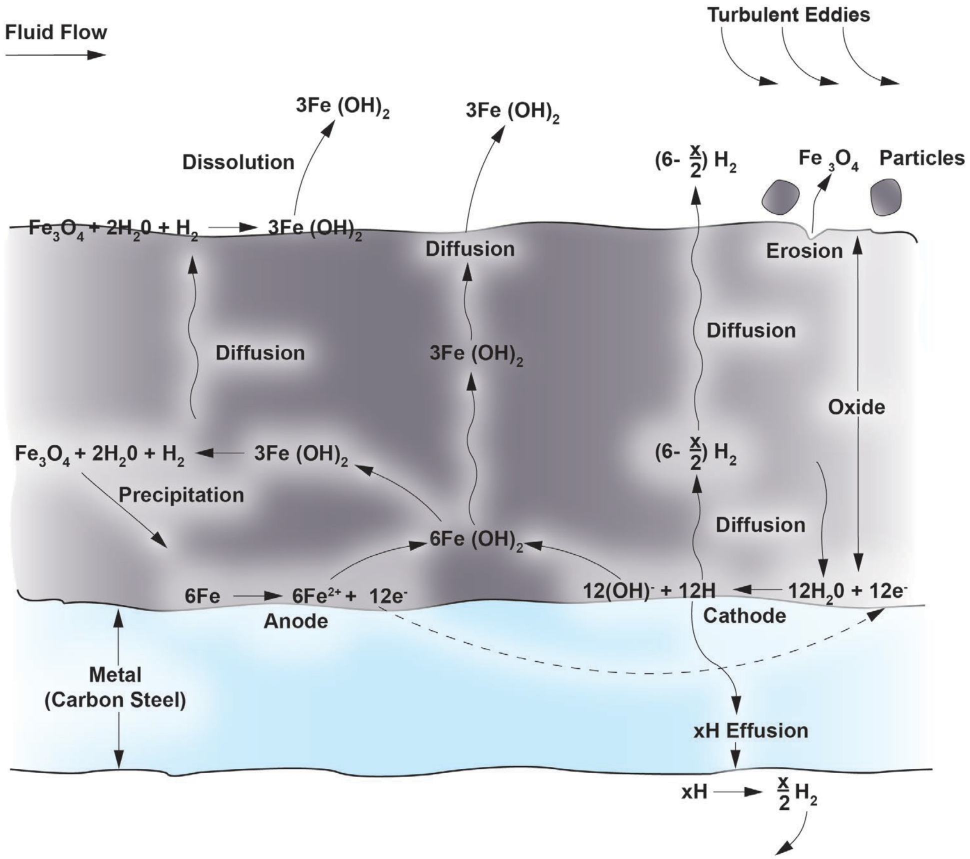
Extracted from: Dooley, Lister and Fandrich,
IAPWS FFS2019, Heidelberg, Germany

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 FAC in fossil, combined cycle and nuclear plants and ACC

All-Ferrous Condensate, ACC and Feedwater

Normal Growth of Magnetite & FAC



Source: Dooley & Lister, PPChem 2018

1. Growth (at M/O) releases particulate and soluble iron into fluid flow. Turbulence reduces boundary layer and accelerates the process. Mechanism and morphology well established.

2 Formation of FFS Film on/in oxide is expected to: reduce dissolution? Ultimately reducing total iron levels

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) ??

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?

Much care is required when using FFS for possible problems in remainder of plant (boiler/HRSG tube failures, drums, valves, etc).