The Latest International Activities on Film Forming Substances

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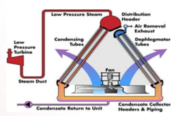
IAPWS Executive Secretary

ACCUG 2023
20th and 21st June 2023
Richmond, Virginia, USA



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This FFS Experience at ACCUG is a Compiled Version from Six IAPWS FFS International Conferences (6th in March 2023)
and has been presented at
Australasian Boiler & HRSG Users Group (ABHUG) (November 2022)
HRSG Forum (June 2023) and
European HRSG Forum (EHF) (May 2023)

ABHUG 2022 – IAPWS Australasian Boilers & HRSG Users Group Conference and Workshops, 15 - 17 November 2022, Brisbane Convention & Exhibition Centre, QLD

European Hrsg Forum – www.europeanHRSGforum.com

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HRSG FORUM

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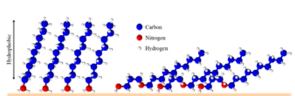

International Nomenclature

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 and this used internationally in most countries of the world.

Film Forming Substances (FFS)

- FFA/FFAP
- 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

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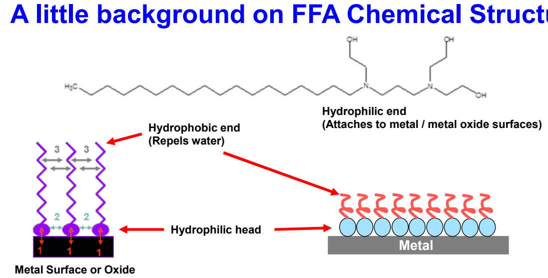
A little background on FFA Chemical Structure



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

Hydrophobic film has been thought to "protect" the steel by decreasing contact between water/metal

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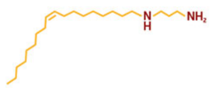
Film Forming Amines

Octadecylamine (ODA) - diamine
$CH_3(CH_2)_{16}CH_2NH_2$ or $C_{18}H_{37}NH_2$

Oleyamine (OLA) - diamine
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2NH_2$or $C_{18}H_{35}NH_2$

Oleyl Propylenediamine (OLDA) - polyamine
$CH_3(CH_2)_7CHCH(CH_2)_8NHCH_2CH_2CH_2NH_2$
$C_{21}H_{44}N_2$



NH_2 group is polar end for all molecules
End that bonds to the surface via N atom/Pi electrons

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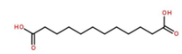
Film Forming Products

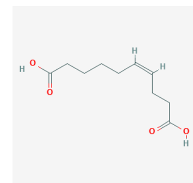
Could be things like di-carboxylic acids in various forms

Literature examples include

Dodecanedioic Acid (DDDA)



cis-4-decendionic acid



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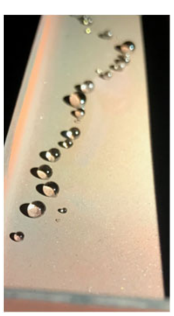
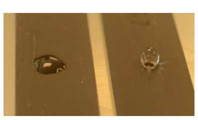
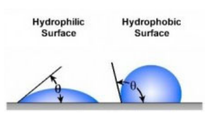
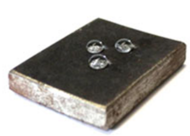
Film Forming Substances (FFS)
A little background – "hydrophobicity"







Source: www.sciencebrainwaves.com



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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 di-carboxylic acids/salts	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%	1-7.5%	<1-5%
Chemical & Thermophysical Properties Understood	Limited Understanding	Limited Understanding Except for ODA		

This Wide Range of FFS Makes Research into Common Solutions Difficult

Source: Dooley/Addison, IAPWS FFS Symposium, Sept 2022 & March 2023

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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, Veolia, Chemtreat, Helamin, Fineamin, Solenis
Film Forming Amines – Homogenization stabilized	Reicon, Kurita, Veolia
Film Forming Amines – pH stabilized and blended with dispersants	Helamin, Fineamin

This Wide Range of FFS Vendors Makes Research and Common Solutions Difficult

Source: Dooley/Addison, IAPWS FFS Symposium, Sept 2022 & March 2023

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Film Forming Substances

2. History and Background

Extracted from

Six IAPWS International Conferences on Film Forming Substances (2017 - 2023)
and
Numerous Plant Assessments and Application Assistance Worldwide

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Film Forming Substances

From the literature, plant applications and previous IAPWS FFS Conferences the following have been claimed and/or documented:

- Suitable for all-ferrous and mixed-metallurgy (copper alloys) feedwater systems
- Lower corrosion product (Fe & Cu) generation and transport
- Shutdown protection under wet and dry conditions
- Cleaner steam turbines
- Benefits for oxidizing and reducing chemistries
- Avoids BTF / HTF due to Under-deposit Corrosion & Corrosion Fatigue
- Arrests FAC (single- and two-phase)

Most obvious and visible example in ACC →

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

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

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)

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Film Forming Substances

IAPWS has organized six FFS Conferences (2017, 2018, 2019, 2021, 2022 & 2023)
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 always results from a thorough up-front review (such as Section 8 in IAPWS TGDs)**
- **Thermal decomposition / thermolysis, stability – effect of residence time, temperature, for ODA and OLDA (but what about FFP?)**
- **Film formation - detection visually (multiple plants), Laboratory –** Xray Photoelectron Spectroscopy (XPS), Electrochemical Impedance Spectroscopy (EIS)
- **Adsorption on surfaces. Laboratory work on metal surfaces for mainly ODA (but what about on oxides, other FFA and FFP?)**
- **In-situ film formation, thickness and porosity – effectiveness of nm films with ODA is good at 80°C and 120°C (but other FFA and FFP?)**
- **Flow-accelerated Corrosion (FAC) and FFS in the laboratory– good representation for single-phase but still some disconnects with some two-phase results from plants**

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Sources at IAPWS FFS Confs: Xue, De Mayer & Vidojkovic (Ghent), Roy (CEA), Hater (Kurita), Pébère (U of Toulouse), Lister (UNB), Fandrich & Ramminger (Framatome)

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Key Highlights from Fossil and Combined Cycle/HRSG FFS Applications

- **Universal reductions in feedwater Fe and Cu transport but no equivalent understanding of the mechanism of oxide growth reductions**
- **General observations of hydrophobic films on water-touched surfaces, but it is underlined that hydrophobicity (contact angle) does not prove presence of a film or any protection** (see examples)
- **Generally good shutdown protection of water-touched surfaces**
- **Film formation remains very questionable on steam-touched surfaces**
- **Adsorption of film onto metal (oxide ?) surfaces as a function of FFS will provide (?) information for changing the FFS applied ****
- **Arresting FAC is difficult to "see" other than by reduction of Fe. ACC corrosion / FAC is the exception** (see example)
- **Problems occurring in plants worldwide** (but not openly published)(see examples)**: 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**

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Highlights compiled from 6 IAPWS International FFS Conferences and many assessments

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Hydrophobicity

Poorly understood and often incorrectly applied "metric" for assessment of FFS dosing effectiveness

Most common – visual method via different "techniques"
Demin water or FFS dosed feedwater?
Sprayed or carefully dropped on the surface?
Direct onto surface in as found stage vs special surface preparation?
Result required immediately or after a time period?
Assessment "by eye" or actual contact angle measured?

Unclear if this is a key aspect of corrosion control
(in solution some FFAs are actually hydrophilic and **INCREASE** surface wetting)

Source: Addison & Dooley, FFS2023, Prato, Italy. March 2023

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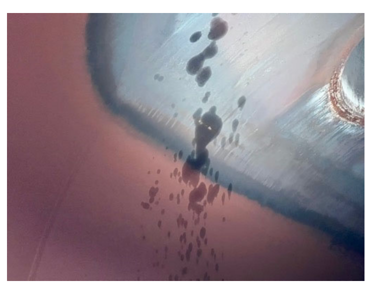
FFS Dosed or Not? 20 bar saturated steam industrial geothermal reboiler internals



Dosed with a FFA – OLA/OLDA

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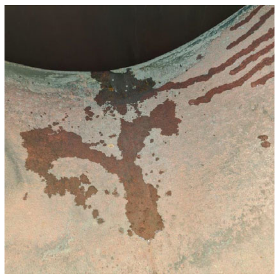
FFS Dosed or Not? Deaerator of Fossil Boiler



Dosed with one FFP for 8 months followed by 5 months with alternate FFP

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FFS Dosed or Not? – CCGT Plant Condenser, LP and HP Drums

Dosed with a FFA –
OLA/OLDA + NA
But only for 3 weeks before outage

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FFS Dosed or Not? – 180 Bar Subcritical Conventional Boiler, Waterwall Boiler Tube

Never dosed with a FFS

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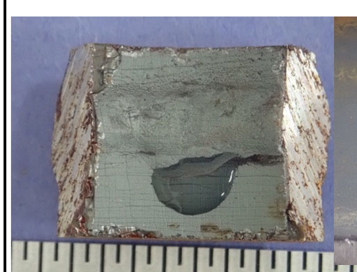
FFS Dosed or Not? – Conventional Subcritical Plant Reheater Tubes



Dosed with a FFP (non amine)

Never dosed with a FFS

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Problem Areas Observed

Source: Dooley, FFS2023, Prato, Italy. March 2023

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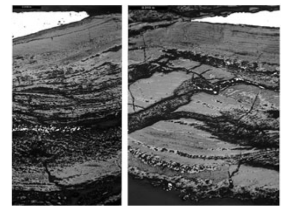
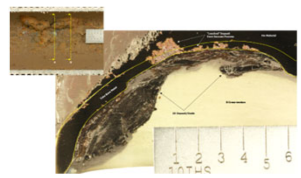
HP Evaporator Heavy Deposits and Failure

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 in typical multi-laminated morphology





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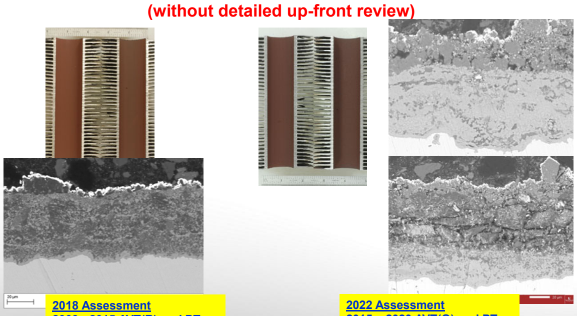
Beware of Increasing HP Evaporator Deposits after FFS Application

(without detailed up-front review)



2018 Assessment
2003 - 2015 AVT(R) and PT
2015 - 2018 AVT(O) and PT
Total Loading 19 – 24 mg/cm^2

2022 Assessment
2015 – 2020 AVT(O) and PT
2020 – 2022 AVT(O) + FFP
Total Loading 47 – 71 mg/cm^2

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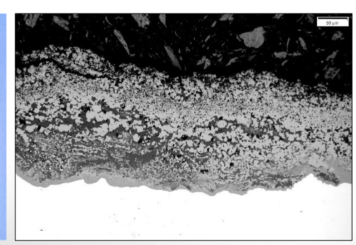
Please do not add FFS if your HP Evaporator looks like this

(use the IAPWS TDG to make an assessment)



2023 Assessment
Total Loading ~65 mg/cm^2

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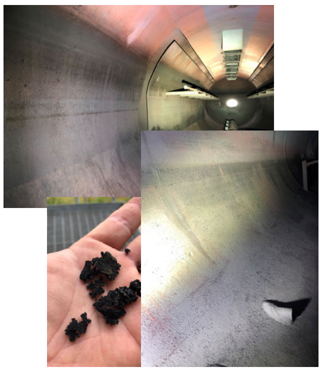
LP Drum Deposits

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.

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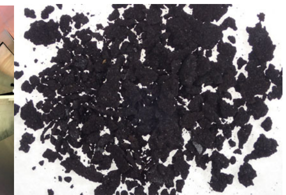
LP Drum Deposits

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



Analysis of "gunk" deposits indicated 80 - 85% Carbon. FTIR indicated the presence of hydrocarbon and functional groups of *carbonyl or carboxylic* acid.

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Film Forming Substances

3. On the Path to Needed Research

Originally Presented

IAPWS 5th and 6th International Conferences on Film Forming Substances (FFS2022 & FFS2023)
and
IAPWS Symposium, November 2022
for the development of an ICRN
(IAPWS Certified Research Need)

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Film Forming Substances Research Needs

The following require more definitive results and/or research and will be focused in an IAPWS Certified Research Need (ICRN)

- Much work is on metal surfaces rather than oxide surfaces as present in plants
- Needed fundamental work:
  - effect of FFS on growth mechanisms of Fe, Cu and Cr oxides in water and steam (three examples originally provided)
  - effect of FFS on BTF/HTF (UDC and CF) and SCC
  - film formation, kinetics, structure and porosity on water- and steam-touched oxide surfaces
  - uncertainty of stability limit and decomposition products for all FFA and especially FFP
  - uncertainty of adsorption onto oxide surfaces as a function of FFS
  - and protection of superheated steam surfaces as a function of FFS
  - increased steam turbine performance for amine-based FFS (ODA) but what about other FFA and FFP. Surface tension data needed
  - information to change from one FFS to another.

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Influences of FFS on Oxide Growth Mechanisms around Generating Cycles

Detailed Presentations by Dooley, Lister and Fandrich at 2019 and 2021 FFS Conferences on oxides in condensate, feedwater, boiler/HRSG water and steam.

First Example on Oxides in <u>All-Ferrous</u> 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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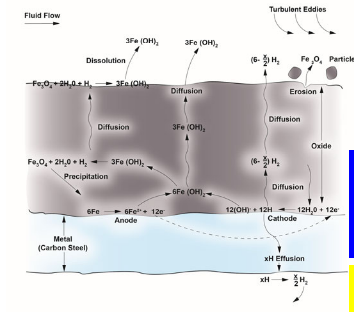
All-Ferrous Condensate, ACC and Feedwater

Normal Growth of Magnetite & FAC



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

2 Formation of an FFS Film on/in oxide is expected to: a) change mechanism, b) reduce dissolution? 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) ??

Source: Dooley & Lister, PPChem 2018

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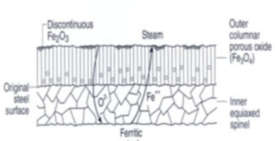
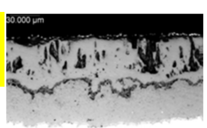
Oxide Growth and Exfoliation (OGE) in Steam

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 <u>ferritic</u> and <u>austenitic</u> 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

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The Importance of Understanding Oxides in Relation to FFS

- Oxide growth mechanisms are completely understood around generating cycles.
- Oxides provide protection and can release corrosion products which lead to deposits.
- Literature and FFS Conference presentations suggest water-touched oxide growth rates change and corrosion product transport is lower with FFS addition. But how does this take place?
- In some cases FFS applications lead to problems (deposits).
- We are somewhat removed from a detailed understanding of how FFS films change these processes in water, and much removed from understanding the adsorption process and any influence in steam.
- Overall suggests that much more work is needed in the future on the effect of a wide range of FFS additions to allow more rugged and permanent advantages such as the ability to change FFS.

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A few concluding remarks:

- **Well established and understood chemistries for > 30 yrs**
  - **AVT(O), AVT(R), OT, PT and CT + PTZ Failure/Damage in ST**
- **FFS for last 8 - 10 years have been applied without the same level of detailed basic understanding, and now**
- **The most common question is: "how do we change from one FFS to another?" (particularly FFP to FFA)**
- **In the interim before this understanding is more complete: Rule 1: make sure plant chemistry is optimized before application of an FFS, and**
- **Rule 2: conduct a comprehensive review before an FFS application (example: IAPWS TGD Section 8)**

Discussed and developed during FFS2023 Panels

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