Waltron | EXPERTS IN WATER CHEMISTRY SINCE 1903

Instrumentation challenges in water steam cycles applying Film Forming Products

Flemington, NJ
July, 2026

The Unintended Corrosive Consequences of Film-Forming Products

- Why apply film forming products in water steam cycles
- What are the different FFA/FFP classes
- What are the effects of FFPs
- The unintended corrosive consequences
- The unintended effects on analytical equipment
- Mitigation strategies

Why apply film forming products in water steam cycles

- Asset protection and preservation (Layup)
- Safety and environment benefits
- Efficiency improvements
- Operational Flexibility

What are the different FFA/FFP Classes

- **Film Forming Amines (FFA)**
  -Octadecylamine (ODA)
  -Oleylamine (OLA)
  -Oleyl Propylenediamine (OLDA).

- **Film Forming Amine Products (FFAP)**
  These are commercially available blended products that contain an active Film Forming Amine

- **Film Forming Products (FFP)**
  These are commercially available products with film-forming properties that are *not* amine-based

What are the effects of FFPs

- Hydrophobic Barrier Formation
- Physical Shielding
- ➢ Corrosion Mitigation

The unintended corrosive consequences

- Thermal Degradation into Organic Acids
- Under-Deposit Corrosion (UDC)
- System Plugging and "Gunk Balls"
- Mixed Metallurgy Vulnerabilities

The unintended effects on analytical equipment

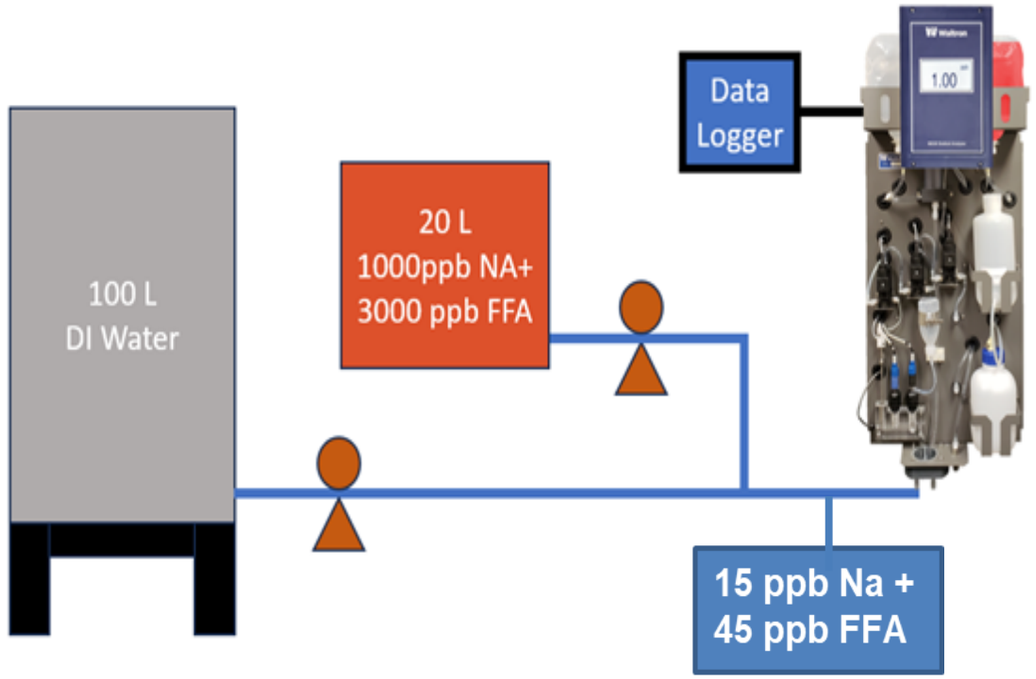
- **Sodium Analyzer "Blinding"**

Test Procedure

- The first test was to recreate the results at a lower spike level how FFAPs can affect the accuracy and response time of a Sodium analyzer
- A continuous flow of 15 ppb Sodium standard and 45 ppb FFA standard was fed into the analyzer, and the data were collected every 10 minutes
- Three times a day, a spike of 50 ppb Sodium was introduced to simulate an adverse event
- Three trials were run for each different FFAP, and the measuring and reference electrodes were thoroughly cleaned before each trial
- Results were combined by FFAP to track the analyzer's ability to detect a potential adverse event

Methodology for New Tests

- Two precise metering pumps supplying DI water and a concentrated solution of Sodium standard and FFA standard
- Two different solutions were prepared to deliver 15 ppb Na^+ and 45 ppb of FFA
- Waltron 9033X Sodium Analyzer
- Later tests used various Dissolved Oxygen, pH, and conductivity sensors
- Effects of filtration/mitigation devices were then tested before the analyzers



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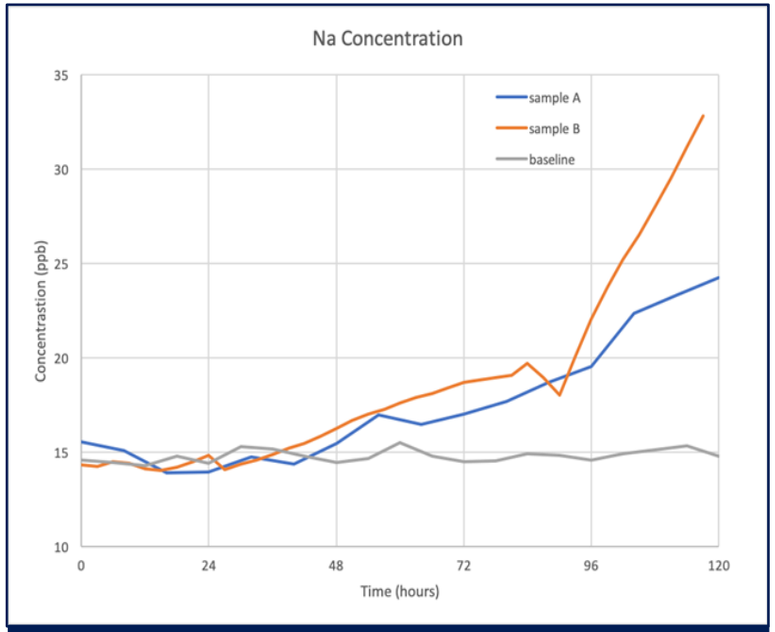
Initial Findings

- A **notable upward drift** in the reported Sodium concentration was observed
- Product A produced a significant accumulation of **microbubbles** on both electrodes, and the upward drift in measured concentration persisted even after manual removal of the bubbles
- The observed deviation was not solely due to the presence of bubbles, but also involved **electrochemical fouling** of the electrode surfaces, exacerbated by interferents adsorbed from the FFAPs



Likely Causes:

- *Progressive Electrode Fouling*
- *Direct Cationic Interference*
- *Electrochemical Degradation*

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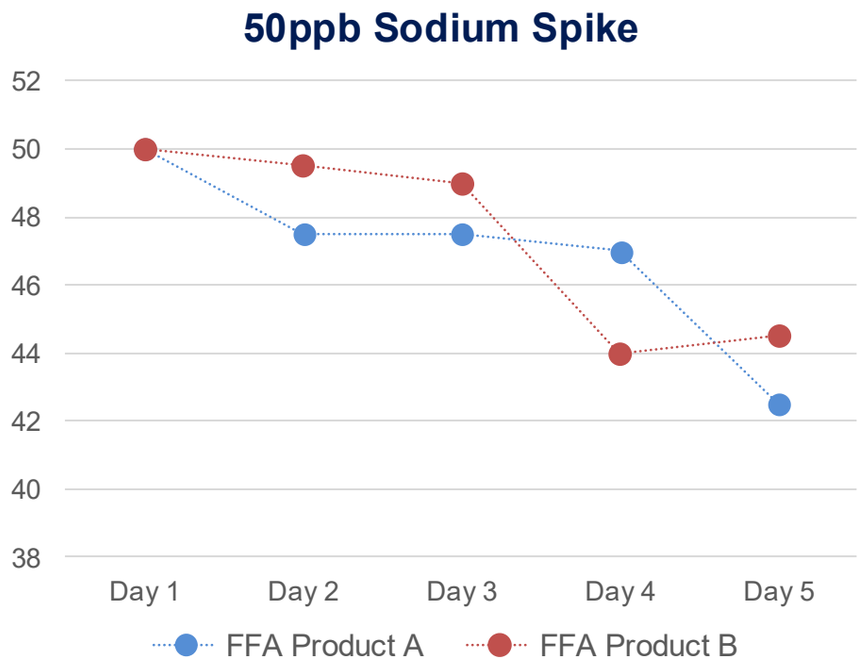
Adverse Event Test Results

- A spiked solution was introduced via grab sample for *only 15 minutes*
- A downward value was observed for each subsequent day's result
- The Sodium measurements had still not stabilized by the end of each 15-minute spike, showing a significant **degradation in response time**
- This confirms the ever-worsening ability to detect adverse events due to severe physical and chemical fouling, where the analyzer has become **less and less responsive**



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Dangers of Progressive Fouling

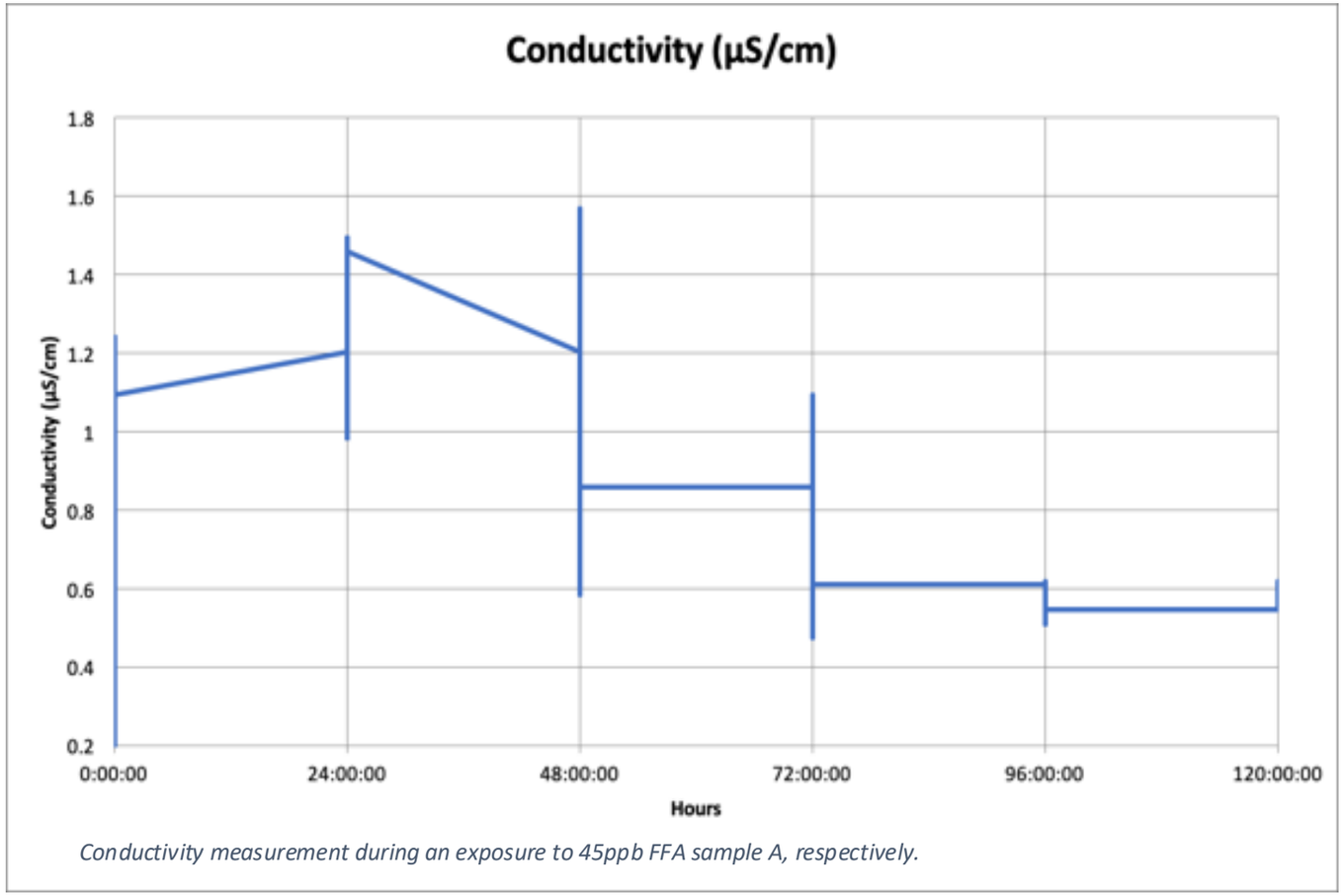
- Critical Loss of Sensitivity: Severe loss of sensitivity caused by growing film of FFA on the electrode, which acts as a barrier and prevents the sensor from accurately reading the calibration standards
- Reference Electrode Drift: This test showed a classic sign of reference electrode fouling, where the FFA film alters the stable reference potential, introducing a progressive error into every measurement
- False Sense of Security: An operator performing infrequent calibrations would be completely unaware of this rapid, daily degradation in analyzer performance
- Masking Adverse Events: The primary risk is that the fouled, "blinded" analyzer will fail to detect a genuine Sodium contamination event, such as a serious condenser leak

The unintended effects on analytical equipment

- **Sodium Analyzer "Blinding"**
- **Probe Coating on pH/ORP and Conductivity Sensors**

Effects on pH / ORP probes

- **Conductivity**: A noticeable decline in conductivity values was observed after prolonged exposure to the same FFA concentration
- **pH**: Did not observe any adverse effects on our Refex pH combination sensor; other pH glass electrode sensors showed similar fouling effects as Sodium



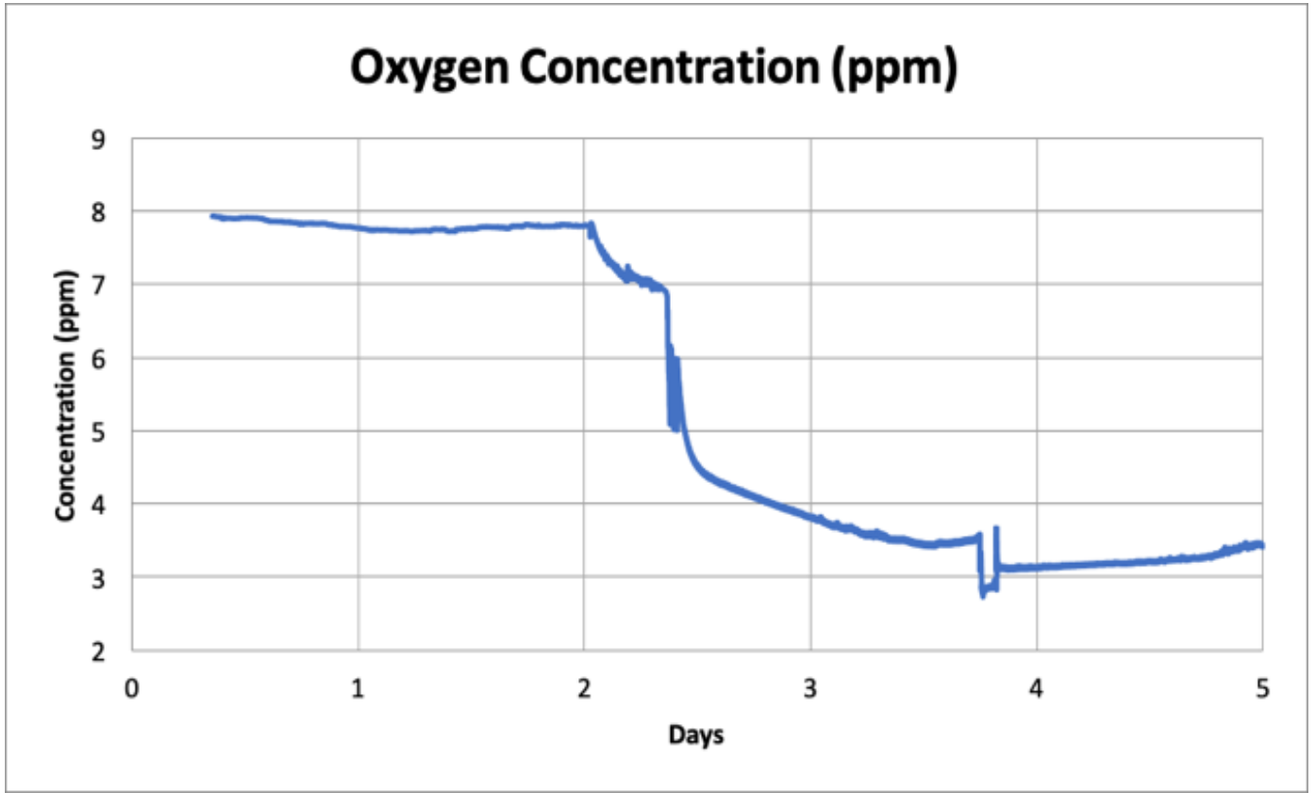
Conductivity measurement during an exposure to 45ppb FFA sample A, respectively.

The unintended effects on analytical equipment

- **Sodium Analyzer "Blinding"**
- **Probe Coating on pH/ORP and Conductivity Sensors**
- **Probe Coating on dissolved Oxygen Sensors**

Effects on Other Parameters

Dissolved Oxygen: No effect was seen on the Waltron 9165S Luminescent DO Sensor, but a significant decrease in sensitivity of older galvanic DO was consistent with electrochemical fouling from the Sodium experiments



Oxygen measurement during an exposure to 45ppb FFA sample A, respectively.

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The unintended effects on analytical equipment

- Sodium Analyzer "Blinding"
- Probe Coating on pH/ORP and Conductivity Sensors
- Probe Coating on dissolved Oxygen Sensors
- Elevated Cation Conductivity (CACE)
- Grab Sampling Adsorption

Mitigation Strategies, Measures to guarantee good cycle chemistry monitoring

- Continuous FFA Monitoring
- DCACE Monitoring
- LDO Dissolved Oxygen (DO) Sensors
- Sodium Analyzer Maintenance and Filtration
- Corrosion product monitoring
- Robust grab sampling protocols for FFA analysis

References and useful guidance documents

- **Corrosion Product Sampling, Monitoring and Analysis for Flexible and Fast Starting Plants**. Power Cycle Chemistry (PCC) Working Group of the IAPWS, published via PPCHEM AG (2025).
- **Document download: Application of Film Forming Substances in Fossil, Combined Cycle, and Biomass Power Plants (TGD8-16)**. International Association for the Properties of Water and Steam (IAPWS) (2019).
- **EPRI Layup Guidance for Fossil Power Plants (Ready for Service)**. Warren, C., EPRI Journal (2016).
- **Film Forming Amines Process Study: Fouling Effect of Film Forming Amine on a Sodium Analyzer**. Dong, H., Waltron.
- **Film Forming Products: Application, Corrosion Reduction, Layup Benefits, and Heat Transfer Improvement (IWC 23-35)**. Patrick, G. (Veolia Water Technology & Solutions), Engineers' Society of Western Pennsylvania.
- **Film-Forming Amines: Harmonizing Industrial Water Treatment**. Kurita America, featured in Process Heating (2022).
- **IAPWS TGD11-19 The International Association for the Properties of Water and Steam Technical Guidance Document: Application of Film Forming Substances in Industrial Steam Generators**. IAPWS (2019).

References and useful guidance documents

- **IAPWS TGD7-16 - Technical Guidance Document: HRSG High Pressure Evaporator Sampling for Internal Deposit Identification and Determining the Need to Chemical Clean**. IAPWS (2016).
- **Mastering Film-Forming Amines: Preservation Procedures**. Wagner, R., REICON Wärmetechnik und Wasserchemie Leipzig GmbH (2025).
- **Technical Guidance Document: Air In-leakage in Steam–Water Cycles (IAPWS TGD9-18)**. IAPWS (2018).
- **Technical Guidance Documents for Cycle Chemistry**. IAPWS.
- **The International Association for the Properties of Water and Steam - Technical Guidance Document: Application of Film Forming Amines in Fossil, Combined Cycle, and Biomass Power Plants (TGD8-16)**. IAPWS / Competitive Power Resources (2016).
- **VGBE-010-00-2023-08-EN: Feed Water, Boiler Water and Steam Quality for Power Plants/Industrial Plants**. vgbe energy e.V. (VGB PowerTech) (2023).

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