# Non-Toxic, OEM Compliant Metal Protection

## A Surface-Active Metal Passivation Technology For Low, Medium & High Pressure Boilers

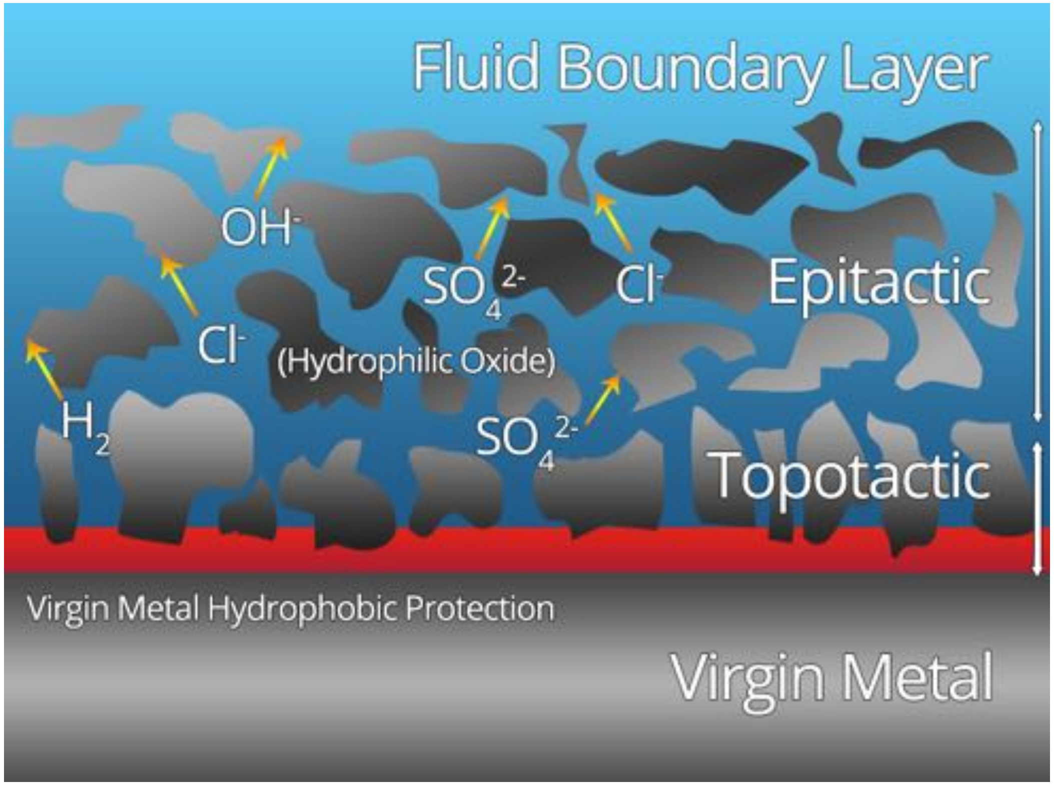
# **HOW** DOES IT WORK ?

Video Example of No Surface-Active Chemistry Protection

**Hydrophilic Oxide**

# Surface Active Chemistry SAC

**Stage 1** (real site images illustrating this stage next)

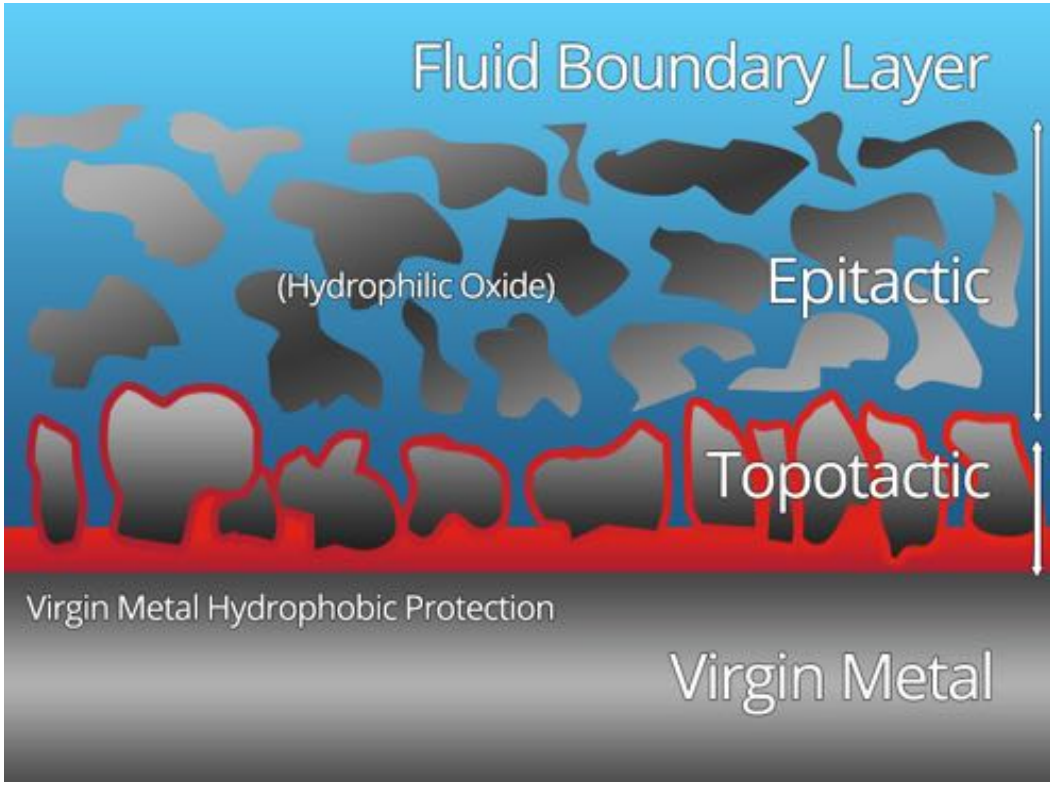



- Anodamine Permeation Through Oxide to Virgin Base Metal
- Cycle Clearance – Release of Trapped Inorganics, (Cation Conductivity Change).
- Limited Visual Topotactic Hydrophobicity
- Base Metal Protection & Hydrophobicity

# Surface Active Chemistry SAC

# Surface Active Chemistry SAC

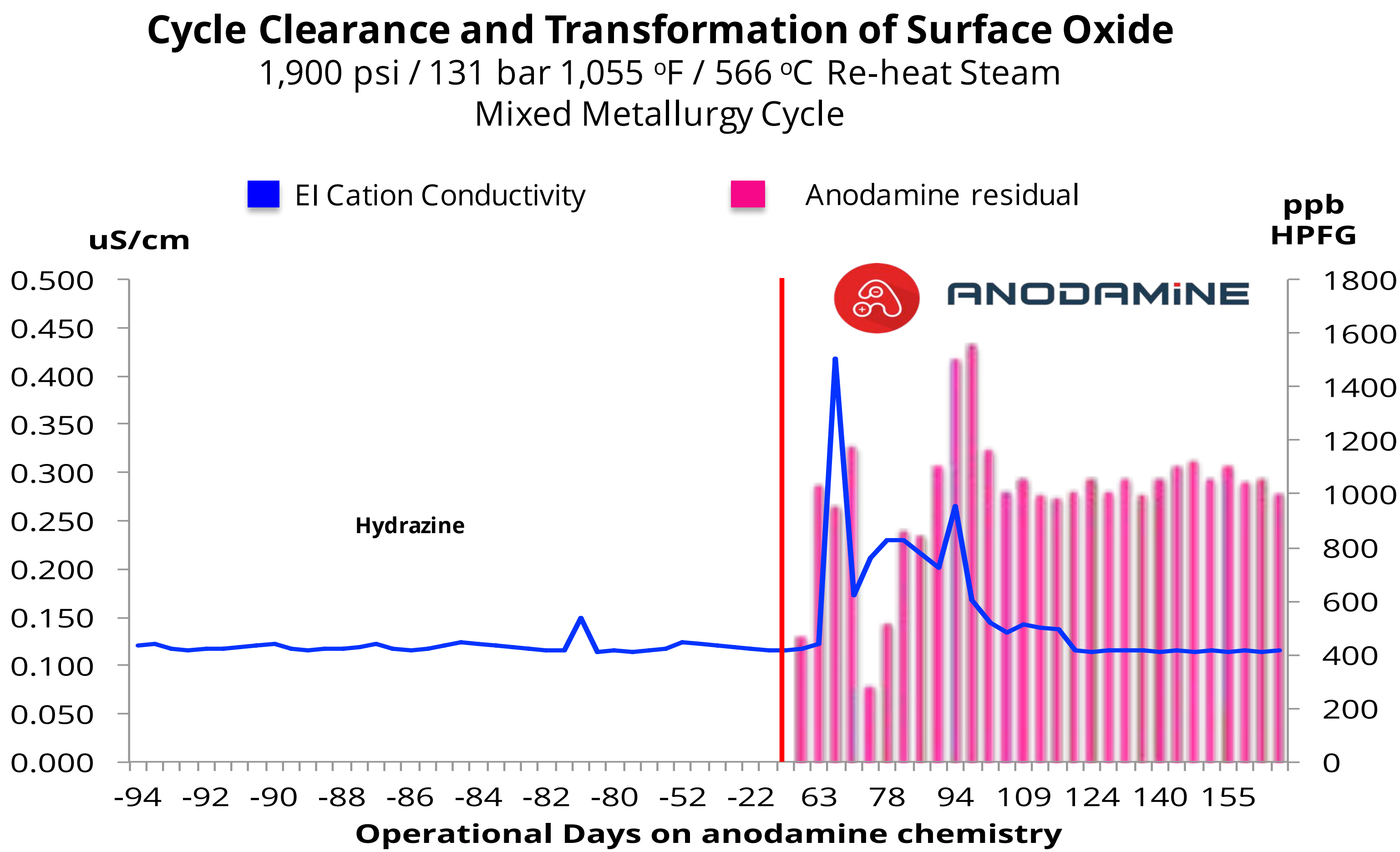
**Step 2** (real site images illustrating this stage next)




- Partial Epitactic Hydrophobicity
- Epitactic Oxide Free of Inorganic Contamination
- Base Metal Topotactic Hydrophobicity
- Base Metal Protection

# Surface Active Chemistry SAC

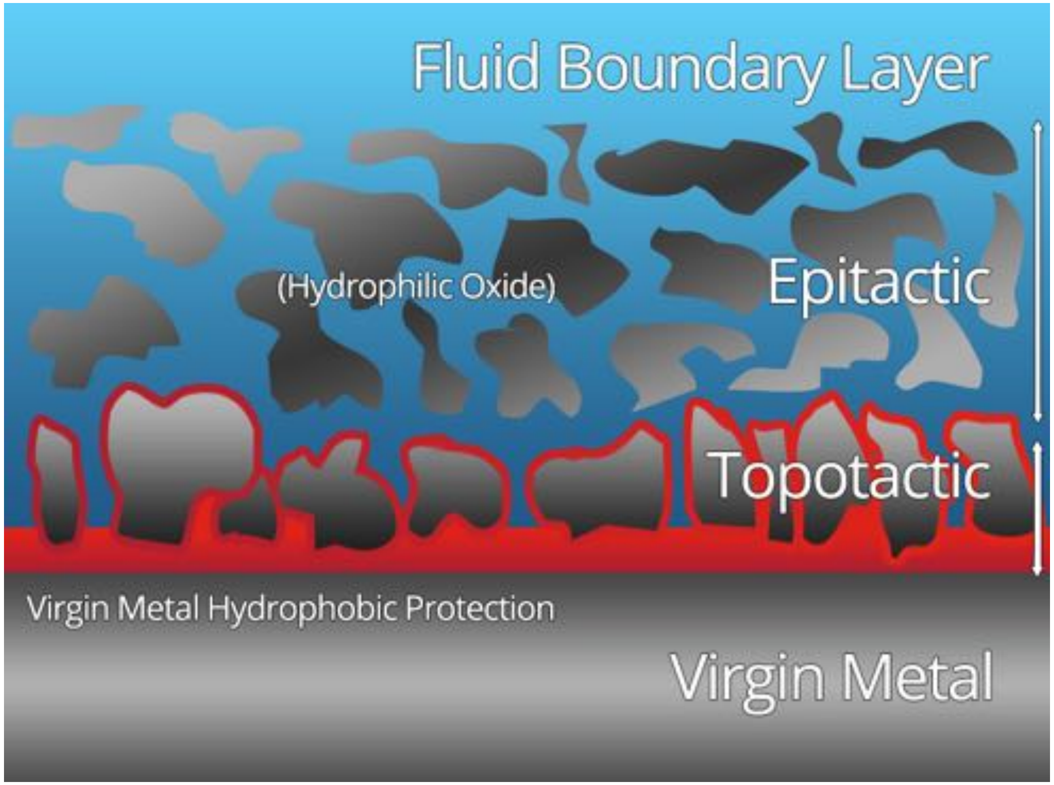
# Surface Active Chemistry SAC




*The Use of a Metal Passivation Additive to Eliminate Oxygen Scavenger in a Mixed-Alloy System* Bill Boyd, Arizona Public Service **IWT September October 2014**

# Surface Active Chemistry SAC

**Step 2** (real site images illustrating this stage next)

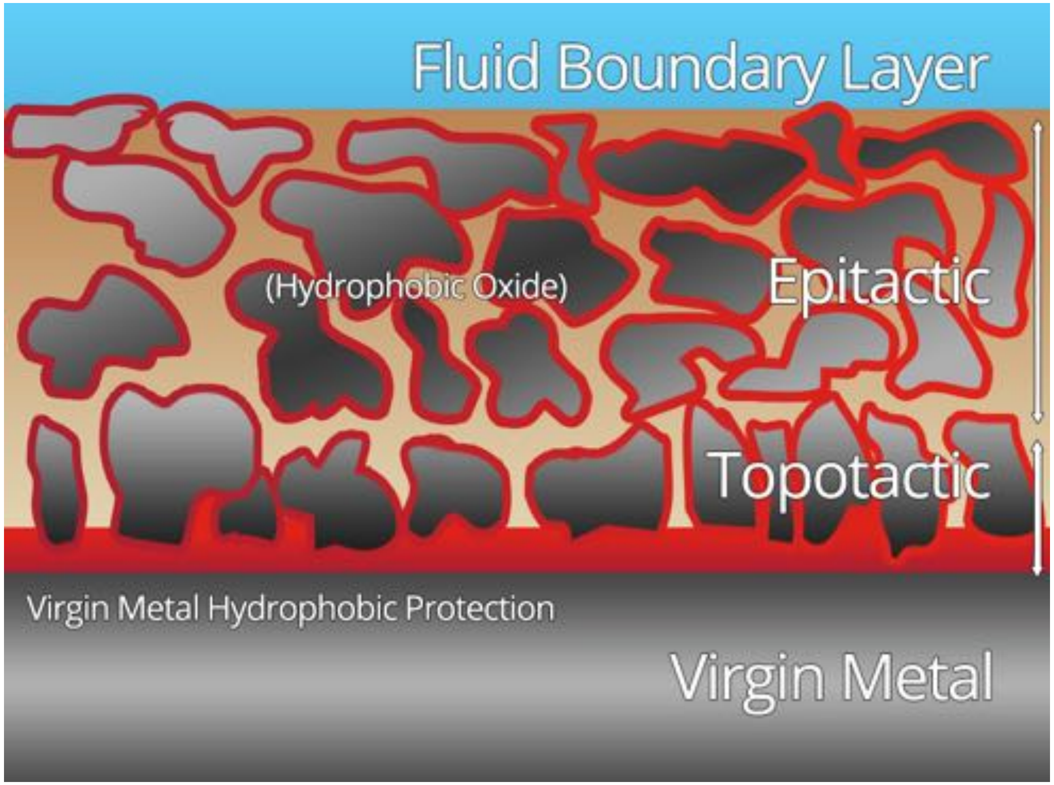



- Partial Epitactic Hydrophobicity
- Epitactic Oxide Free of Inorganic Contamination
- Base Metal Topotactic Hydrophobicity
- Base Metal Protection

# Surface Active Chemistry SAC

# Surface Active Chemistry SAC

**Stage 3**
(real site images illustrating this stage next)




- Achieved With Continuous 1000 – 1500 ppb Equilibrium Residual
- When Stage 3 is Achieved, (Time Dependent on Total Available Surface Area)
  - Dosage Can Be Reduced to Maintain 800 – 1000 ppb
- Complete Oxide Hydrophobicity
- Higher 3+ Oxide Content
- Base Metal Protection

# Surface-Active Chemistry (SAC)

## Video Example of Stage 3 Protection

Super-heater Tube Section from Super-critical 4500 psi Once Through

**Re-heat Tube (carbon steel) from a 3,600 psi / 870 MW Super-critical Once-through Unit with full-flow Powdex polishers.** The unit was commissioned in 1974 and was converted from Oxygenated chemistry to Anodamine AVT(O). The steam touched oxide was lightly sanded to expose the tube material.


Surface Active Chemistry SAC

# Conventional Film Forming Amines

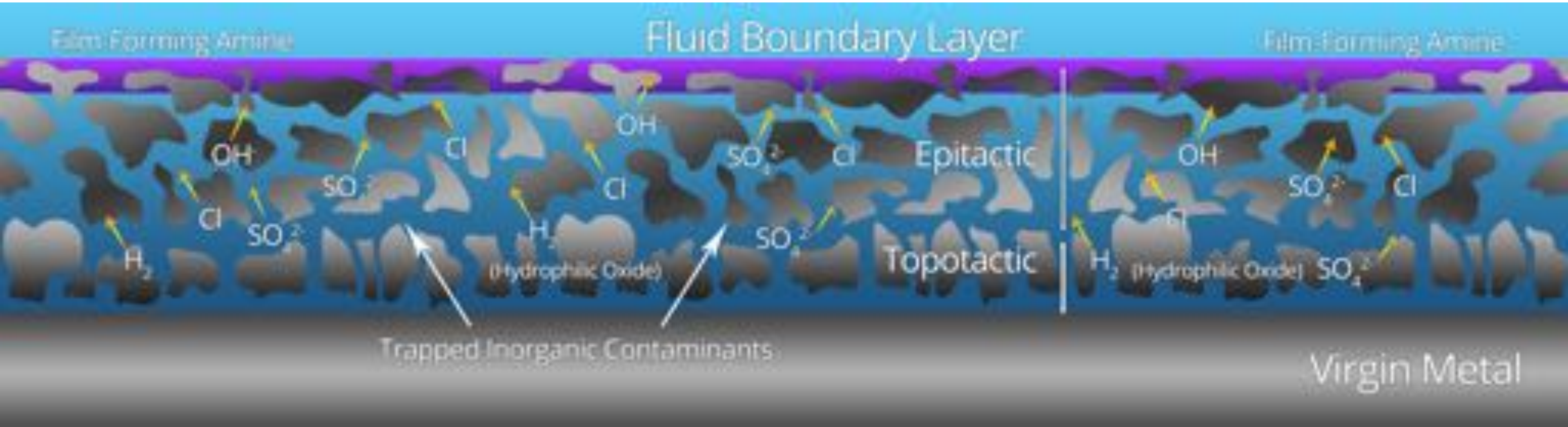
# Conventional Film Forming Amines

## FILM FORMING AMINES

- Mechanism of treatment is vastly different
- Do some treat the critical 2-phase locations.
- Are they OEM steam quality compliant?
- Selectivity of film formation?
- Compare MSDS.
- Check product toxicity LD50 aquatic organisms.
- Are they retained by soils, environmental concerns?
- Check product handling concerns.
- Check product flash point and flammability.
- Observe product solubility in water.
- Does the product contain neutralizing and/or alkalizing amines.........etc

# Limitations of Conventional FFAs

- **Non** OEM Compliant, **increased** CACE > 0.2uS/cm
- **Non-selective** film formation
- Dangerous **trapping** of inorganic contaminants
- **Under Deposit Corrosion** – base metal attack
- Degradation products (**waxy slime balls**)
- Film **degradation**



# Limitations of Conventional FFAs

# Limitations of Conventional FFAs

Due to differences in volatility and solubility between neutralizing amines and “all FFA chemistries” when neutralizing amines are lost, the FFA becomes in soluble in water and generates solids and/or a micro emulsion.

## Surface Active Chemistry SAC

# BENEFITS ?

# Surface Active Chemistry SAC

## BENEFITS OF USING **ANODAMINE**

1. Reduced/Elimination of both single and 2 phase FAC
2. Reduced/Eliminate Chemistry Holds.
3. No Chemistry Related Boiler Tube Failures.
4. No special layup precautions, Ability to layup wet or dry.
5. Potential to Eliminate Boiler Cleanings.
6. Improved Reliability & Availability, Irrespective of Mode of Operation.
7. No Negative Effect on CPP (Powdex or Whole Bead Polishers)

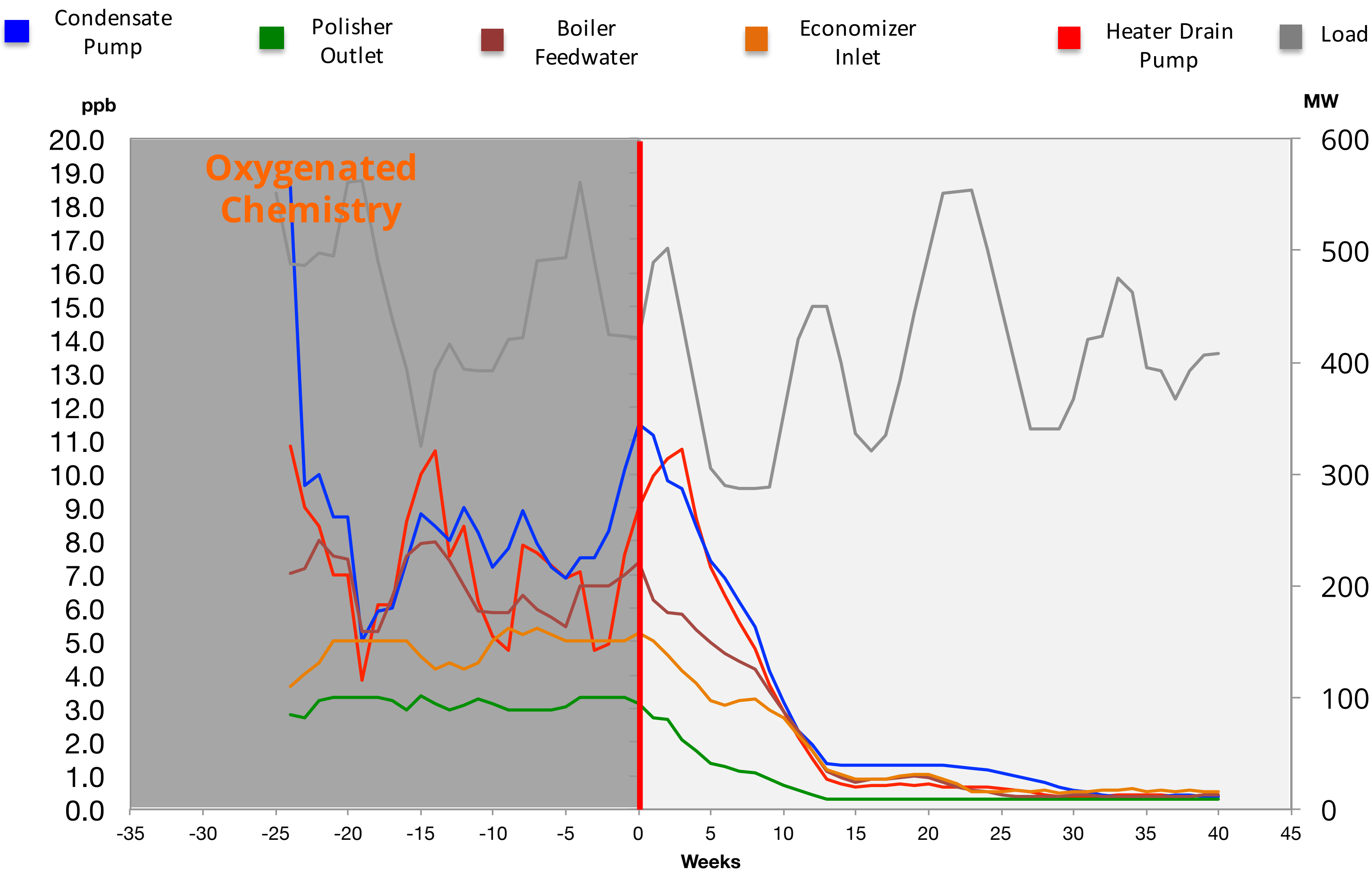
# REDUCED CHEMISTRY HOLDS

**Installation Data**

- 3 x 3,600 psi / 248 bar, CE super-critical once-through unit with a 870 WH Turbines. The unit was commissioned between 1978 and 1980. The condensate is passed through full-flow Powdex polishers. HP steam is reheated to 1,050 $^{o}$F / 566 $^{o}$C.
- Boiler feedwater is deaerated.
- The units were converted to Anodamine / OT and ammonia chemistry in 2013.

# Reduction in TOTAL Iron Transport

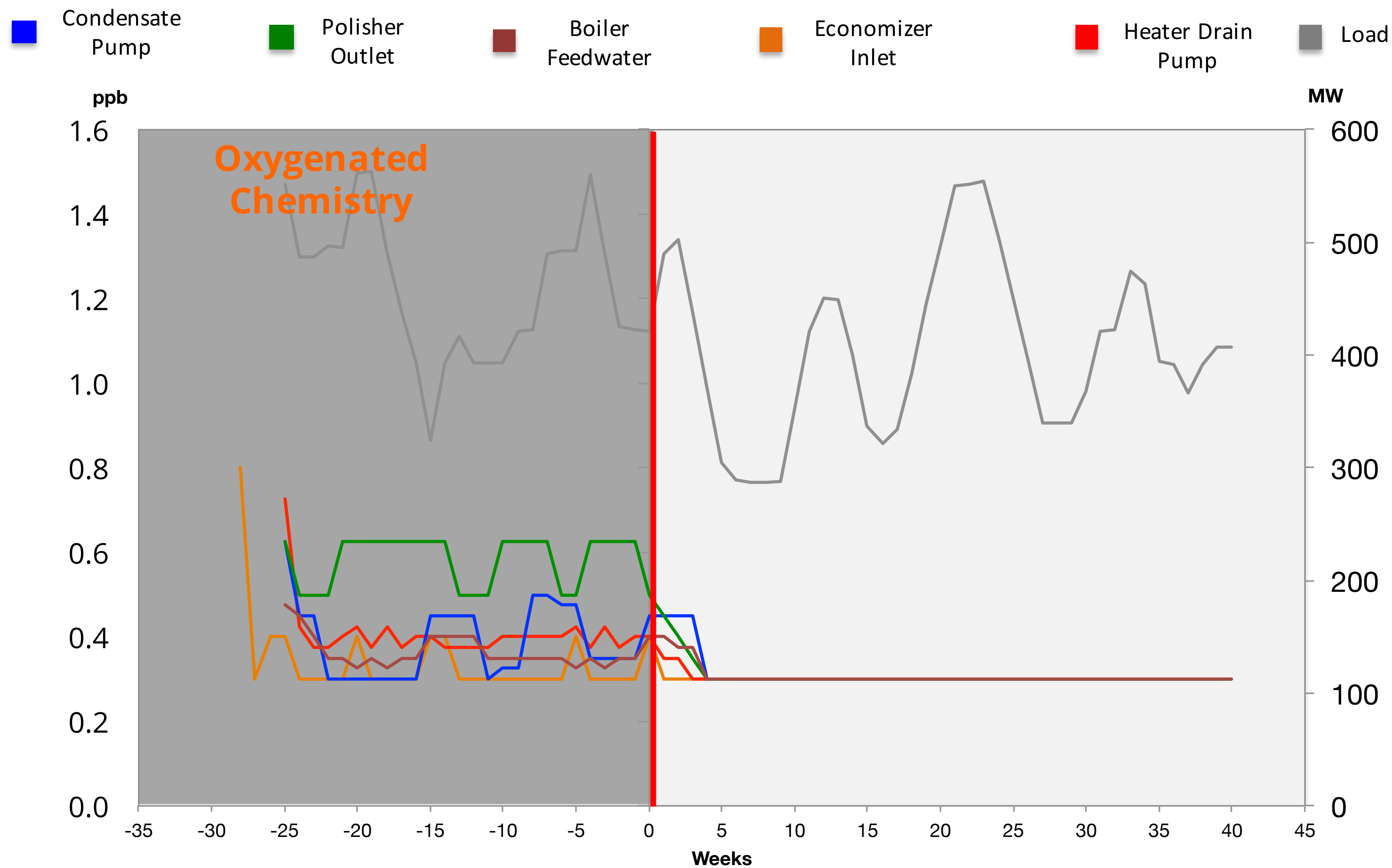
**Super-critical Once Through Boiler with Powdex**
**593 MW 3,600 psi / 248 bar (1,055°F / 568 °C)**




**Ferrozine® ULR Method** – TOTAL Iron LDL 0.3ppb; *Adapted from Stookey, L.L., Anal. Chem., 42(7), 779 (1970)*

# Reduction in DISSOLVED Iron Transport

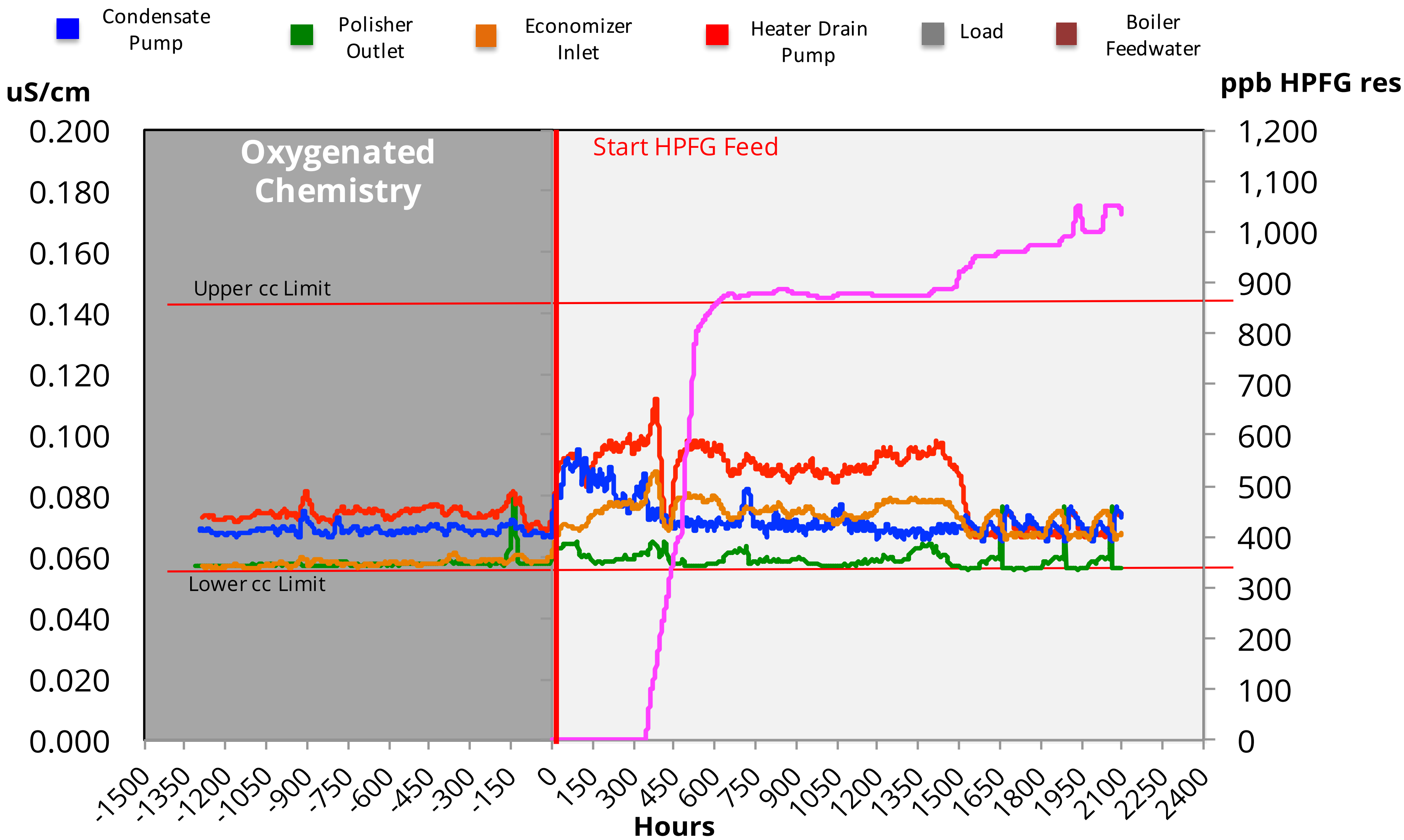
**Super-critical Once Through Boiler with Powdex**
**593 MW 3,600 psi / 248 bar (1,055ºF / 568 ºC)**




**Ferrozine® ULR Method** – TOTAL Iron LDL 0.3ppb; *Adapted from Stookey, L.L., Anal. Chem., 42(7), 779 (1970)*

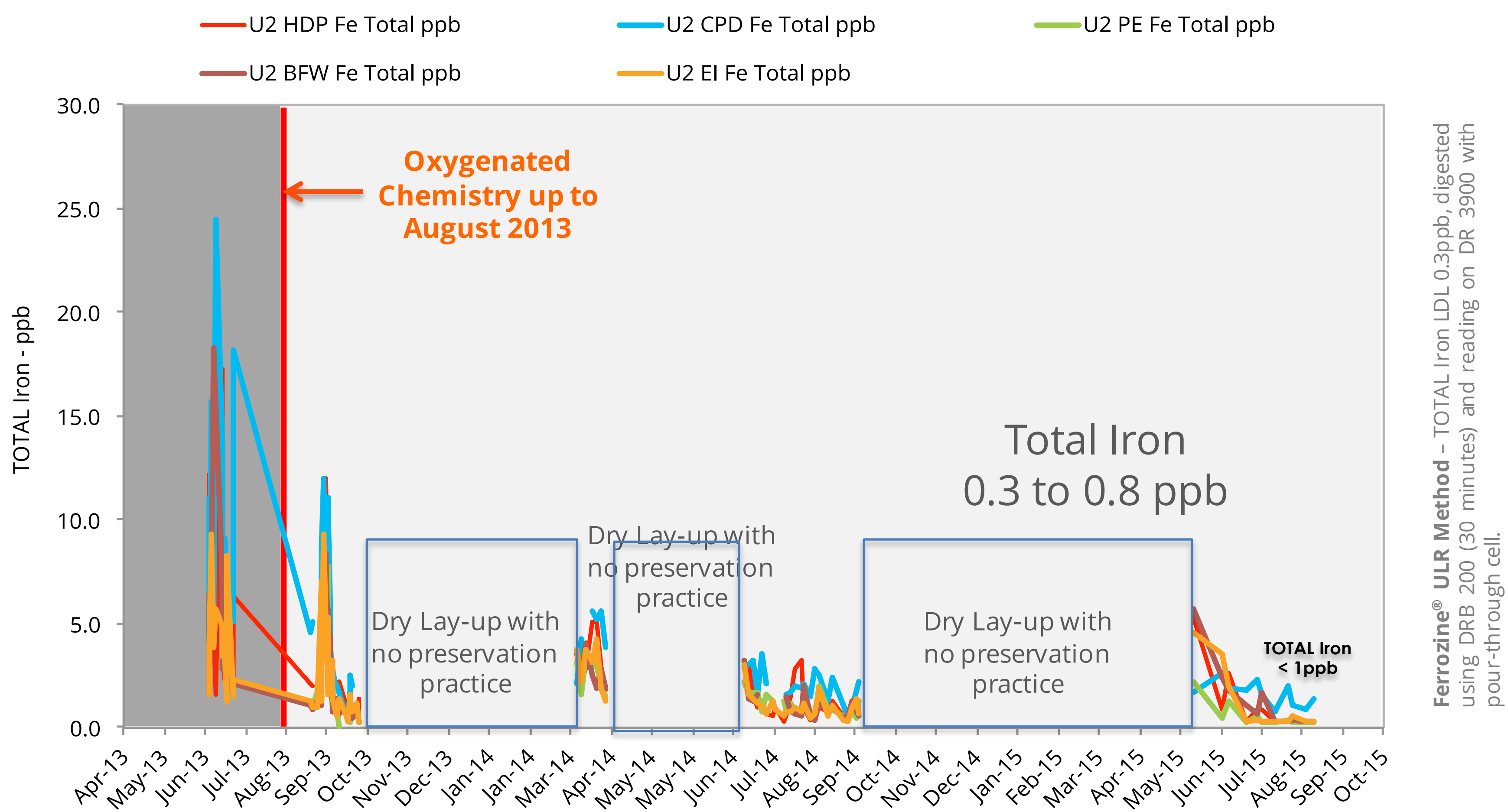
# Cation Conductivity / Cycle Clearance

**Super-critical Once Through Boiler with Powdex**
**593 MW 3,600 psi / 248 bar (1,055°F / 568 °C)**



# Corrosion Product Transport during Cyclic Load Operation

593 MW 3,500psi / 241 bar,
1,055 $^oF$ / 566 $^oC$ Re-heat steam



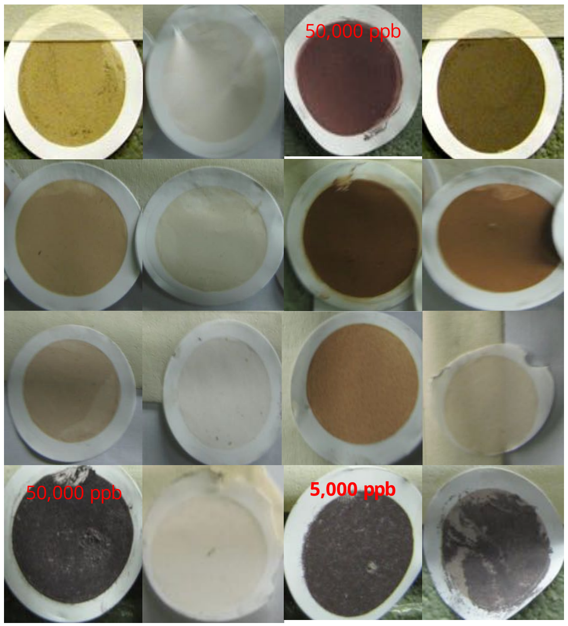

Typical corrosion product transport with OT / Ammonia chemistry was between 1 and 25 ppb. Under the same operating conditions with Anodamine chemistry, the total iron in the feedwater, superheat and reheat steam is < 0.5 ppb.

# Reduction in Corrosion Product Transport during Unit return-to-service

593 MW 3,500psi / 241 bar,
1,055 ºF / 566 ºC Re-heat steam

**Unit return to service with Conventional Chemistry, typical 4 days**

CPD | Polisher Outlet | Boiler feedwater | Economizer Inlet



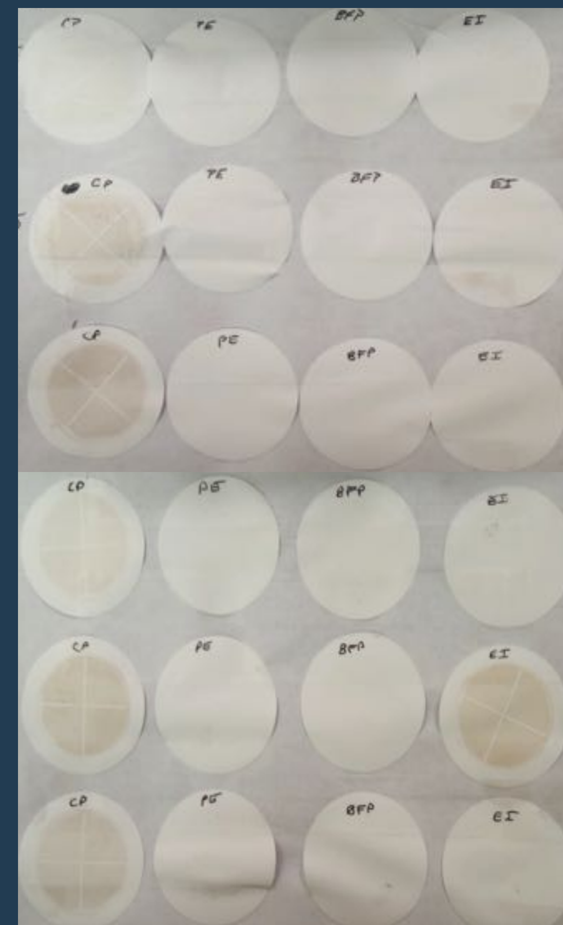

**The unit typically remained in chemistry hold for days before the cycle chemistry complied for Turbine**
**(estimated operation cost in excess of U$ 100,000 per hour)**

Please note. Due to extremely high corrosion product transport, some Millipore pads only represent 200 ml samples instead of 1 liter.

Elimination of chemical hold periods

**Unit return to service with Surface Active Chemistry, typical 4 hours**

CPD | Polisher Outlet | Boiler feedwater | Economizer Inlet



# Surface Active Chemistry SAC

Using Anodamine treatment improvements in unit start-ups accompany:

1. reduced oxide transport
2. full steam water cycle protection
3. improved performance of full flow Powdex Polishers

many super critical units are noticing an appreciable reduction in chemistry holds, often **reduced from approx. 2 days down to 4 - 5 hours.**
The financial benefit derived by this performance characteristic can be summarized as follows:

# Surface Active Chemistry SAC

- Typical chemistry holds pre-Anodamine range from **2 days** depending on length of outage and success of the layup procedure. Chemistry holds have been reduced to < 5 hours
- Est. 27,000 MW gained due to entire cycle protection, & rapid start using Anodamine.
- Average of x lbs coal per MW produced, coal price $ x per ton

- = **$540,000** **(Saving in MW produced due to rapid start – excluding contractual dispatch, loss production penalties.)**

= **$ 130,0000** **(Reduction in fired fuel saved due to rapid start) - $10,000 of fuel oil burnt per hour whilst on chemistry hold.**

*Calculation based on supercritical once through cyclic operation, 840 MW day operation, 450 MW night operation, 3600 psig full flow Powdex polishers. ($20 per MW)

# Surface Active Chemistry SAC

**DURING CONTINUED CYCLIC OPERATION**
**(TREATMENT WITH ANODAMINE)**

1. Extended Powdex runs between pre-coats (pressure drop)
   - Before: 3 weeks between pre-coats
   - After: 12 weeks between pre-coats
2. Visual change in resin when replacing/pre-coating.
3. Full cycle chemistry compliance.
4. Resultant Savings In Extended Powdex Runs = **$39,000**
   **(projected annual savings @ $3,000 each)**

*Calculation based on supercritical once through cyclic operation, 840 MW day operation, 450 MW night operation, 3600 psig full flow Powdex polishers.

# Surface Active Chemistry SAC

**RETURN TO SERVICE FROM 7 - 8 MONTH EXTENDED OUTAGE**
(ROUTINE TREATMENT AND OFFLINE PROTECTION WITH ANODAMINE).

| | |
|---|---|
| Powdex polisher pre-coats required on startup (before Anodamine) | **35 – 40 pre-coats** @ $3,000 each<br>$105,000 |
| Powdex polisher pre-coats required on startup (treated with Anodamine) | **4 – 5 pre-coats** @ $3,000 each<br>$13,500 |

## SAVINGS IN POWDEX REPLACEMENT:

## $91,500

*Calculation based on supercritical once through cyclic operation, 840 MW day operation, 450 MW night operation, 3600 psig full flow Powdex polishers.

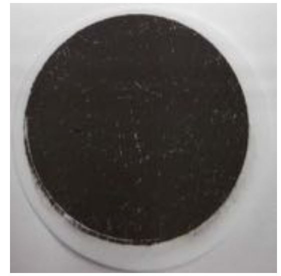
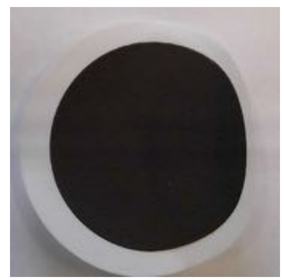
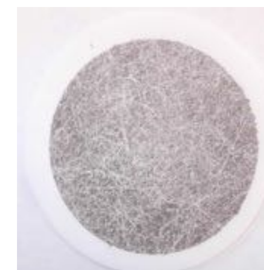
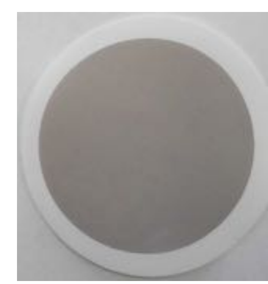
# REDUCED CHEMISTRY HOLDS

# 870MW CCGT, The Netherlands

After only 2.5 months after starting Anodamine dosing, chemical holds have been eliminated and total iron concentrations are all well within OEM compliance.

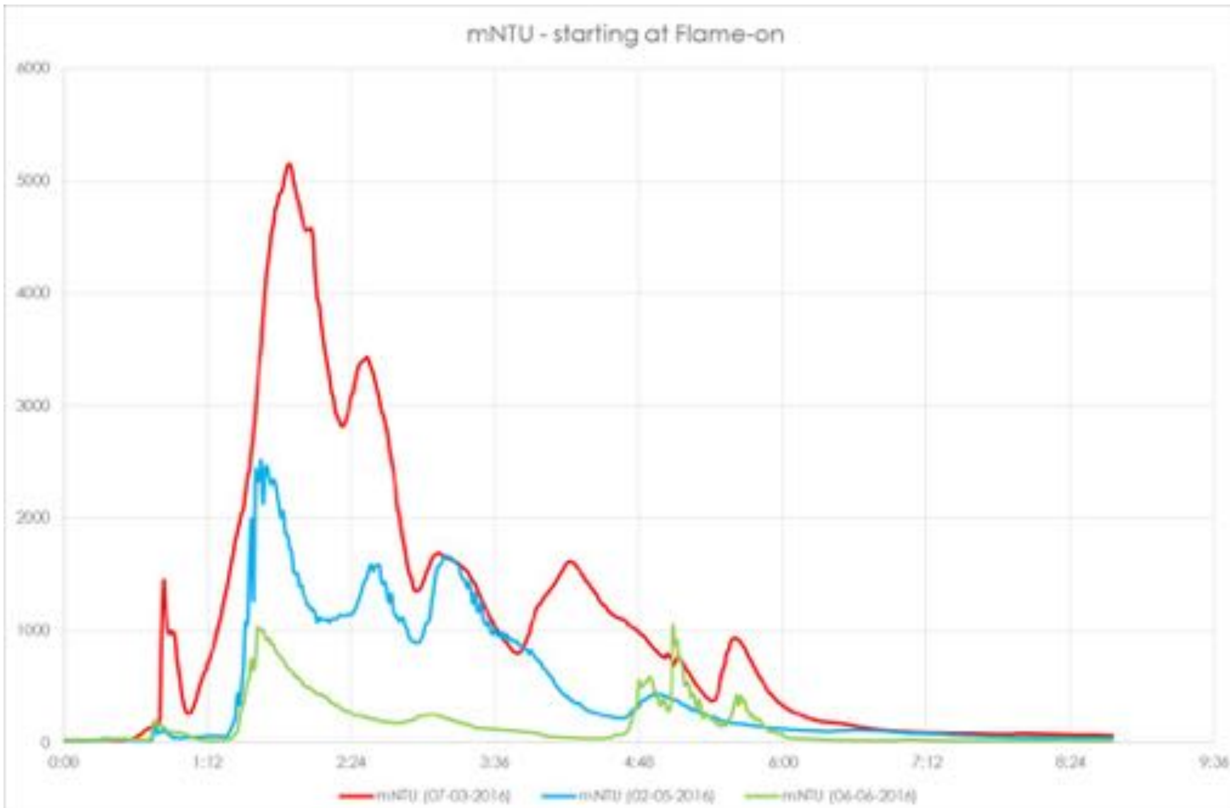
(LP 2.0 µg/l; IP 23 µg/l; HP Once Through 5.9 µg/l total Iron).

# CCGT START UP COMPARISON WITH SWITCH TO ANODAMINE

| | LP Feed Water | IP Feed Water | LP Drum | LP Superheater Steam | Condensate |
|---|---|---|---|---|---|
| **Before** Anodamine |  |  |  |  |  |
| | 129 µg/L total iron | 14,3 µg/L total iron | 25800 µg/L total iron | 130 µg/L total iron | 829 µg/L total iron |
| **39 days** on Anodamine |  |  |  |  |  |
| | 21 µg/L total iron | 3,5 µg/L total iron | 87100 µg/L total iron | 22 µg/L total iron | 285 µg/L total iron |
| **74 days** on Anodamine |  |  |  |  |  |
| | 3,7 µg/L total iron | 2,1 µg/L total iron | 16 µg/L total iron | 2,0 µg/L total iron | 94 µg/L total iron |

# 870MW CCGT

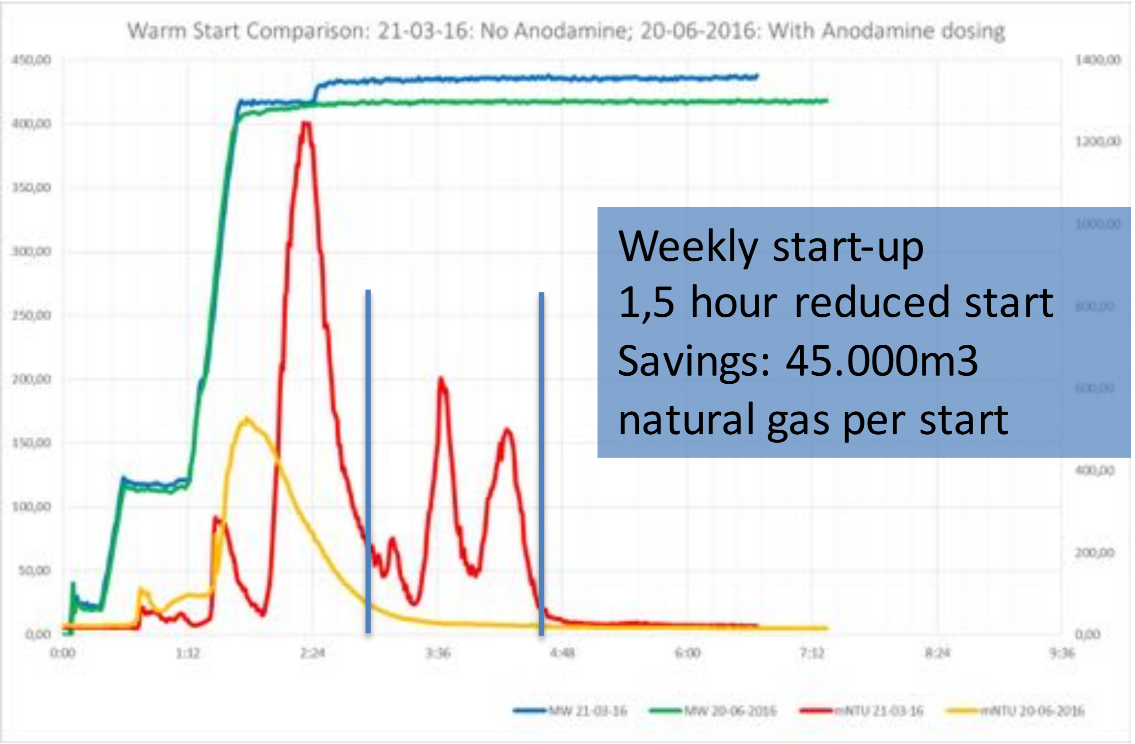
## COLD START COMPARISON WITH SWITCH TO ANODAMINE




**BEFORE** ANODAMINE **39 DAYS** ANODAMINE **74 DAYS** ANODAMINE

# 870MW CCGT

## WARM START COMPARISON WITH SWITCH TO ANODAMINE




**BEFORE** ANODAMINE **88 DAYS** ANODAMINE

*The outage for both starts was 53 hours. The start-curve used is the same which can be seen in the MW curve for both starts.

# Surface Active Chemistry SAC

Calculated annual savings in natural gas = 45,000 Nm3 (per start)

Estimated US natural gas cost $ 0.2225 Nm3 = **$10,012 per start.**

(calculated on US industrial pricing) – Netherlands pricing est. $0.75/Nm3

Reference pricing estimate Public Policy Institute - Source: Energy Information Administration
http://www.ppinys.org/reports/jtf2004/naturalgas.htm

# IMPROVED RELIABILITY

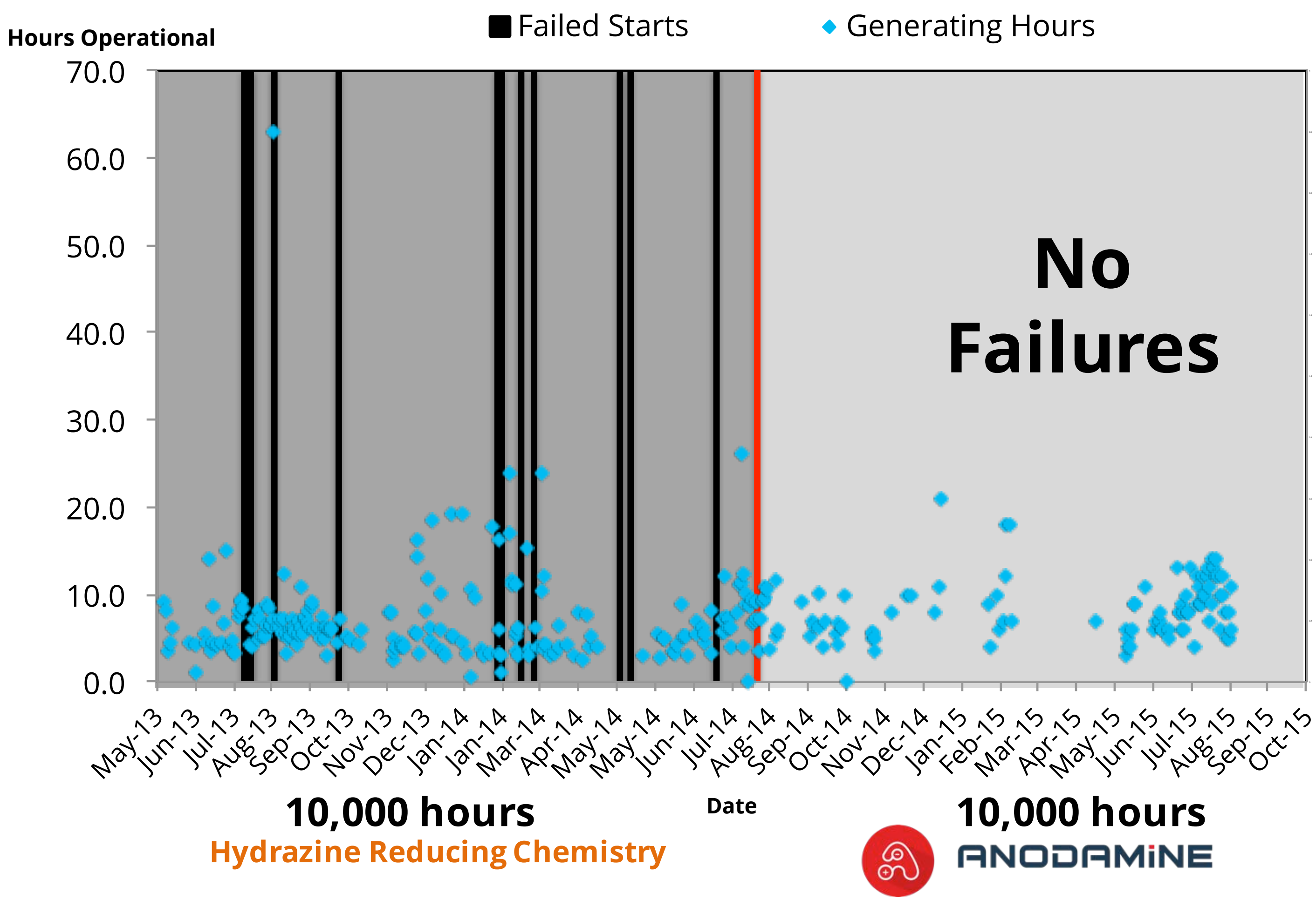
# Preventing Corrosion Fatigue CF

- 1 x 2,600 psi / 179 bar, CE Natural circulation, mixed metallurgy drum units with 475 MW WH Turbines, commissioned in 1964. HP steam is reheated to 1,050 ºF / 566 ºC.
- 1 x 1,935 psi / 133 bar, B&W Natural circulation, mixed metallurgy drum units with 125 MW GE Turbines, commissioned in 1958. HP steam is reheated to 1,050 ºF / 566 ºC. (retired)
- Unit 1 is retired, Unit 2 was converted from AVT(R) – Hydrazine / CT to Anodamine / AVT(O) / CT in 2013.
- Unit 2 is a peaking unit operating anywhere from 2 to 20 hours per start-up.
- The unit operates at 10 to 15% of available time.

# Unit Failure Frequency

## (Hydrazine chemistry = failure every 143 hours)

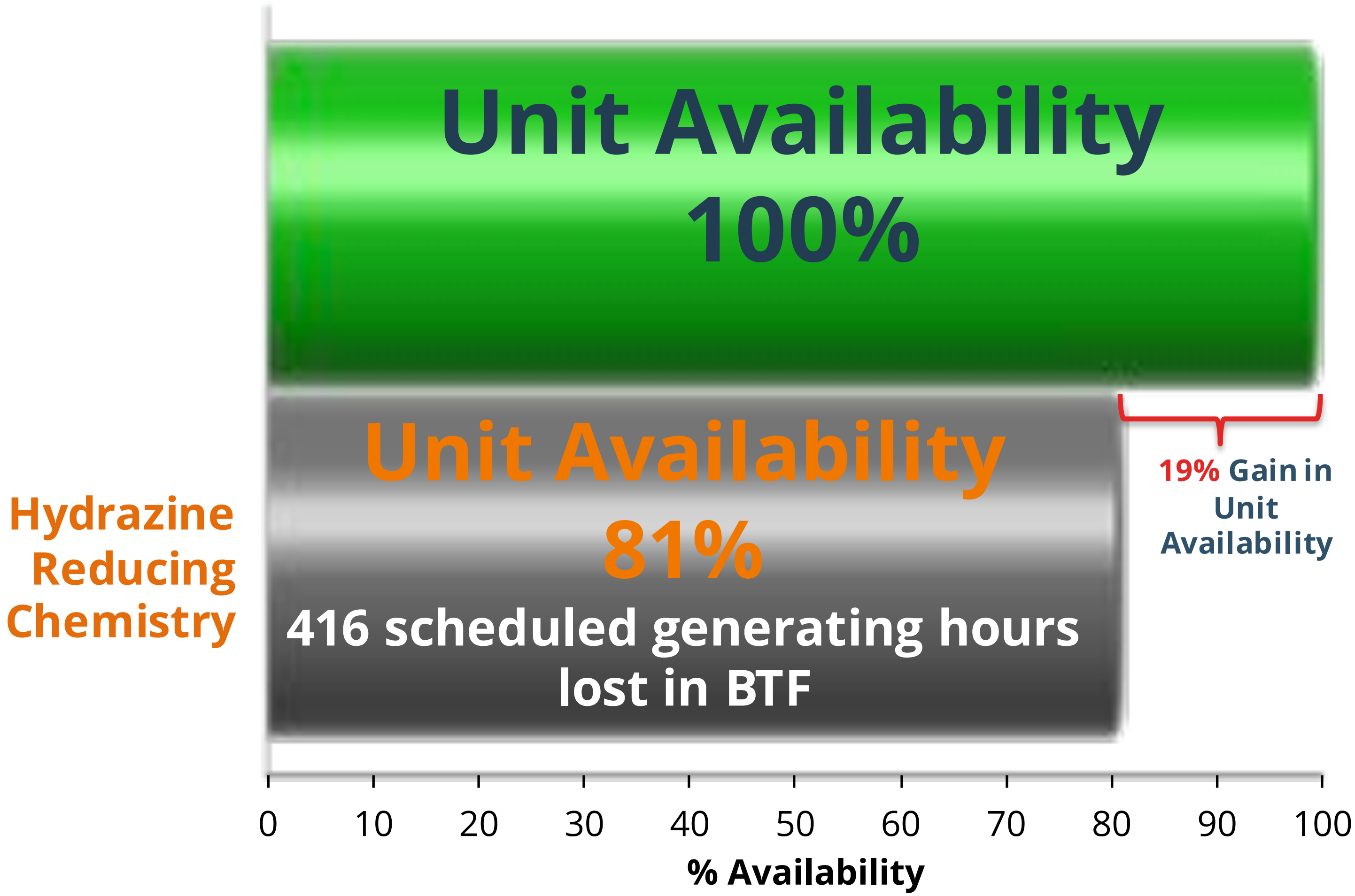
475 MW 2,600 psi / 179 bar, 1,005°F re-heat
Mixed Metallurgy Drum Unit




| The number of times the unit failed to return-to-service | Hydrazine Reducing Chemistry | Anodamine |
|---|---|---|
| | **12 failures** (failure every 143 hours) | **ZERO failures** |

# Unit Availability on Start-up

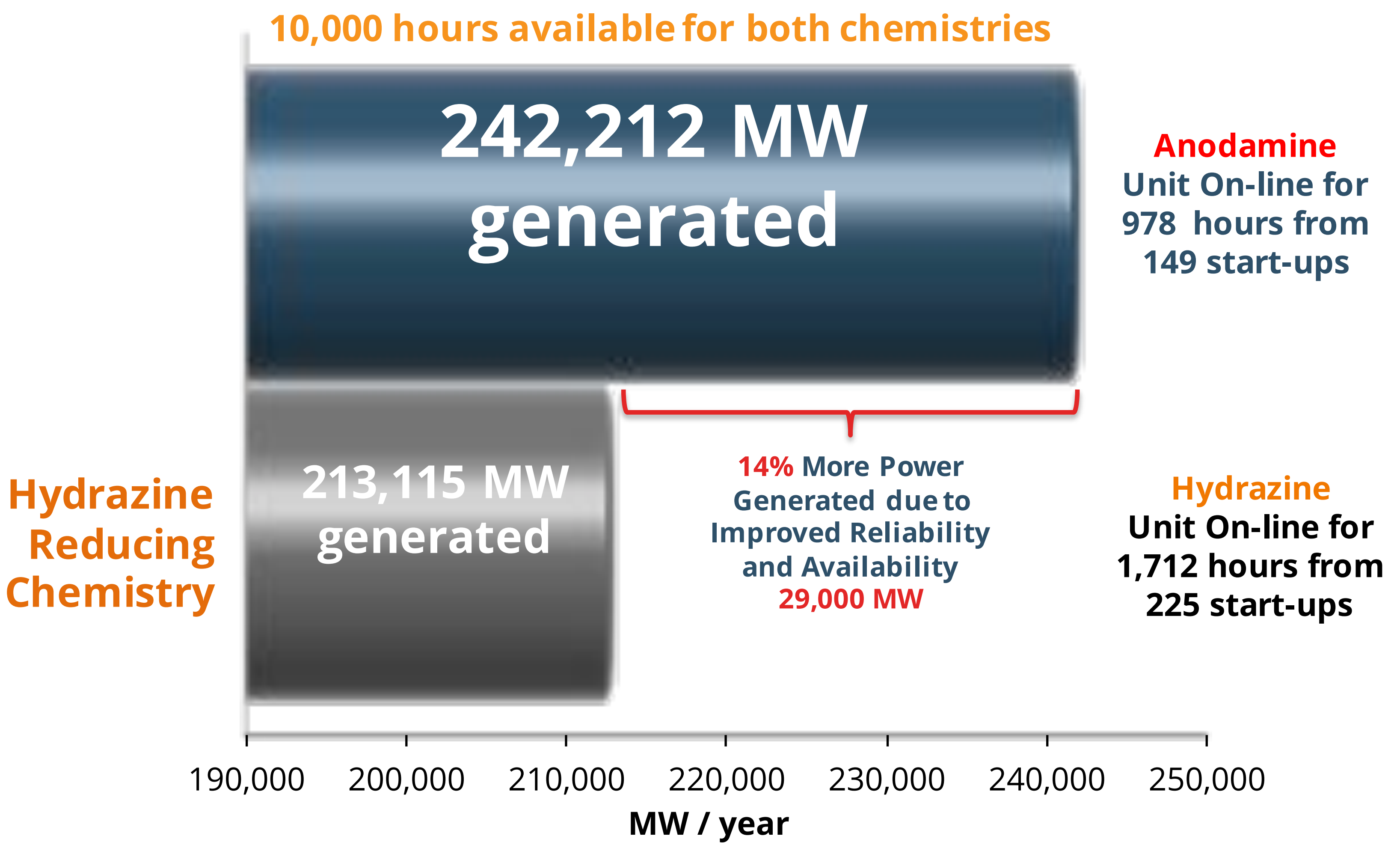
475 MW 2,600 psi / 179 bar, 1,005°F re-heat
Mixed Metallurgy Drum Unit




| Unit Availability | Hydrazine Reducing Chemistry | Anodamine | 19% gain in unit availability |
|---|---|---|---|
| | 81% available on start-up | 100% available on start-up | |

# Reliability and Availability vs. Power Generated

475 MW 2,600 psi / 179 bar, 1,005°F re-heat
Mixed Metallurgy Drum Unit

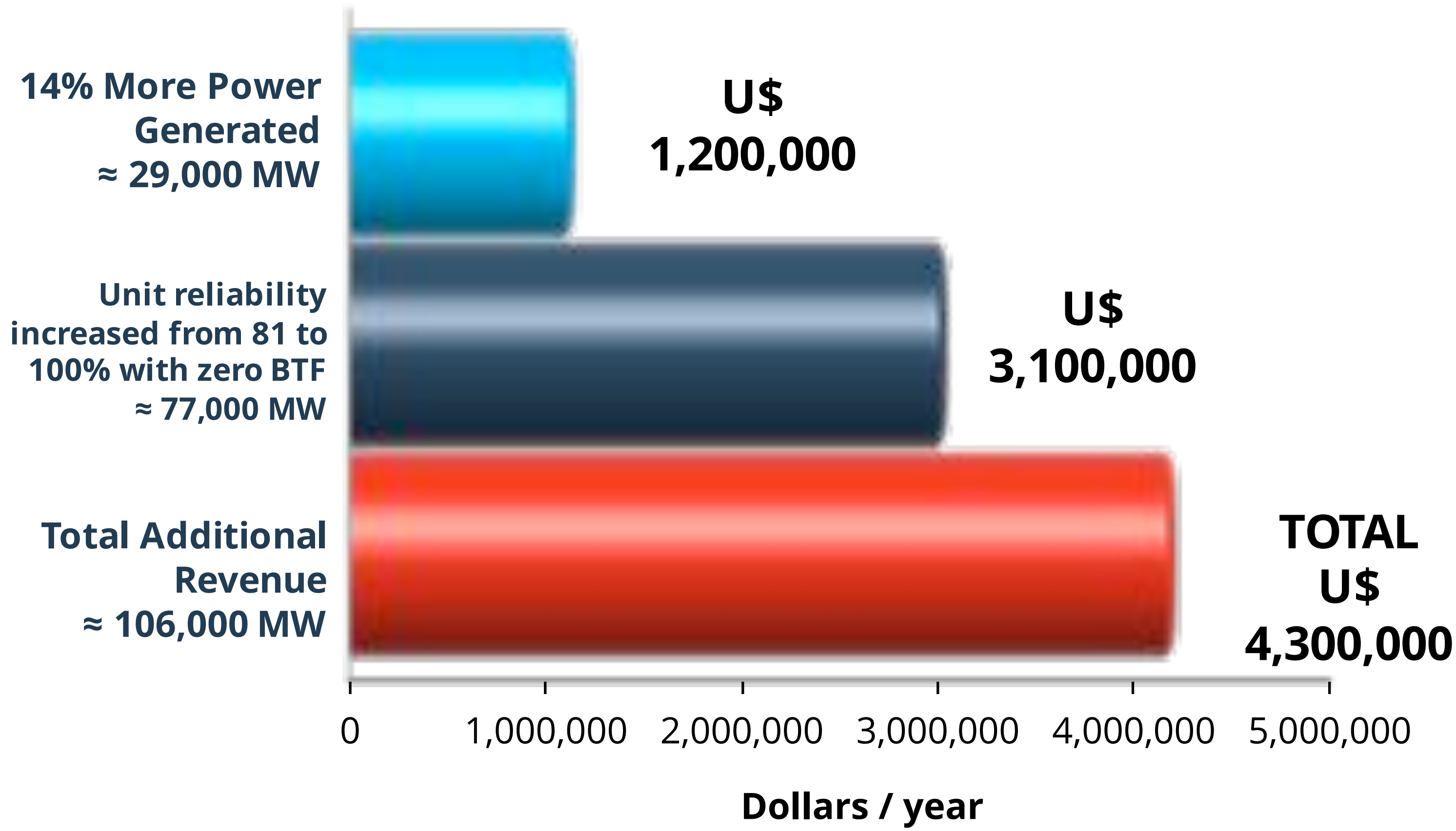



| | | | |
|---|---|---|---|
| **Power Generated** | **Hydrazine Reducing Chemistry**<br>**213,115 MW generated** | **Anodamine**<br>**242,212 MW generated** | **29,000 MW additional Power Generated** |

# The Cost Of Poor Reliability and Availability

475 MW 2,600 psi / 179 bar, 1,005ºF re-heat
Mixed Metallurgy Drum Unit

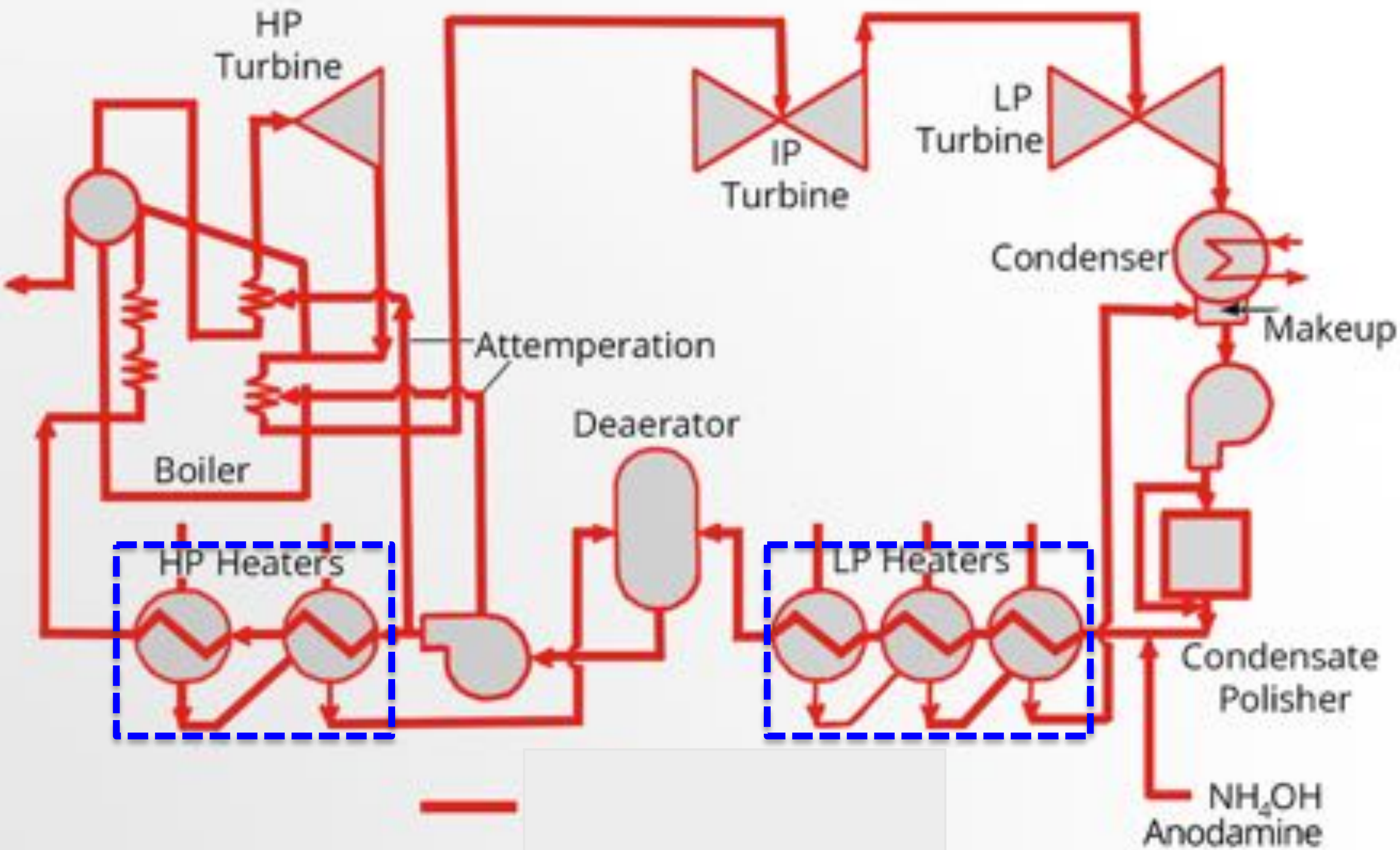
**Data represents approximately 10,000 hrs. on Hydrazine chemistry vs. 10,000 hrs. on Anodamine chemistry**




| Cost savings with improved availability and reliability | Improved Reliability (No lost time)<br>**U$ 1,200,000** | Additional MW generated with 100% unit availability<br>**U$ 3,100,000** | **U$ 4,300,000** |
|---|---|---|---|

# 2 PHASE PROTECTION

# Anodamine distribution throughout the water steam cycle




HPFG target concentration 800 – 1,000 ppb

The Anodamine chemistry is normally introduced into the condensate pump discharge. With a 50/50 volatile-to-liquid ratio at boiler temperatures, 50% of the product is transferred to the saturated steam. The chemistry is stable to superheat temperatures and will therefore provide surface-active protection of all water and steam touched surfaces throughout the turbine stages, reheat steam and extraction steam to the feedwater heaters. During steam condensation, 50% of the chemistry is transferred to the liquid fluid, providing the necessary surface-active chemistry protection in the two-phase flow locations

# High Intermediate Pressure (HIP) 3rd (Bottom Tubes)

| | |
|---|---|
| Manufacturer | Foster Wheeler |
| Date Stamped | 1996 |
| Number of Tubes | 391 |
| Tube OD (inches) | 3/4 |
| Tube Gauge | 18 B.W.G. |
| Tube X-Sec. Area (sq. ft.) | 0.002319 |
| Tube Material | Admiralty |
| Design Feedwater Flow (lb./hr.) | 1349655 |
| Design Flow Velocity (ft./sec.) | 6.63 @ 60 F |


**High Intermediate Pressure (HIP) 3rd (Bottom tubes) from a 2,200 psi / 253 MW, 1,000ºF / 538ºC re-heat steam, natural-circulating, mixed metallurgy drum unit** The unit was commissioned in 1963 and was converted from all-volatile-reducing hydrazine chemistry to Anodamine AVT(O). The unit retired for decommission in December 2013. The feedwater heater tubes were removed one year later and sent to our laboratory for inspection. The condition of the tubes as received by the client without preservation or protection.

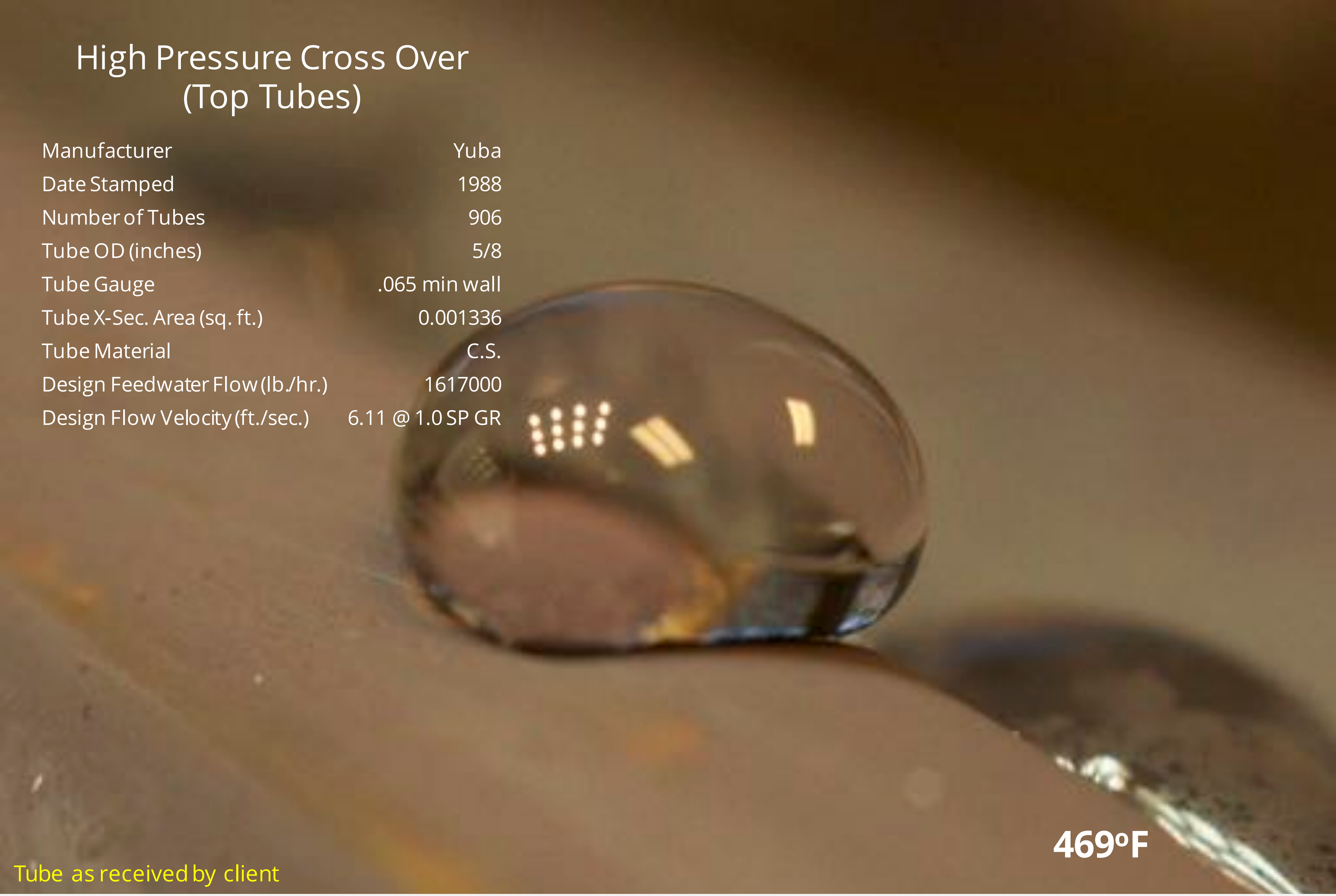
## High Intermediate Pressure (HIP) 3rd (Top Tubes)

| | |
|---|---|
| Manufacturer | Foster Wheeler |
| Date Stamped | 1996 |
| Number of Tubes | 391 |
| Tube OD (inches) | 3/4 |
| Tube Gauge | 18 B.W.G. |
| Tube X-Sec. Area (sq. ft.) | 0.002319 |
| Tube Material | Admiralty |
| Design Feedwater Flow (lb./hr.) | 1349655 |
| Design Flow Velocity (ft./sec.) | 6.63 @ 60 F |


**High Intermediate Pressure (HIP) 3rd (TOP tubes) from a 2,200 psi / 253 MW, 1,000ºF / 538ºC re-heat steam, natural-circulating, mixed metallurgy drum unit** The unit was commissioned in 1963 and was converted from all-volatile-reducing hydrazine chemistry to Anodamine AVT(O). The unit retired for decommission in December 2013. The feedwater heater tubes were removed one year later and sent to our laboratory for inspection. The condition of the tubes as received by the client without preservation or protection.

# High Pressure Cross Over (Top Tubes)

| | |
|---|---|
| Manufacturer | Yuba |
| Date Stamped | 1988 |
| Number of Tubes | 906 |
| Tube OD (inches) | 5/8 |
| Tube Gauge | .065 min wall |
| Tube X-Sec. Area (sq. ft.) | 0.001336 |
| Tube Material | C.S. |
| Design Feedwater Flow (lb./hr.) | 1617000 |
| Design Flow Velocity (ft./sec.) | 6.11 @ 1.0 SP GR |



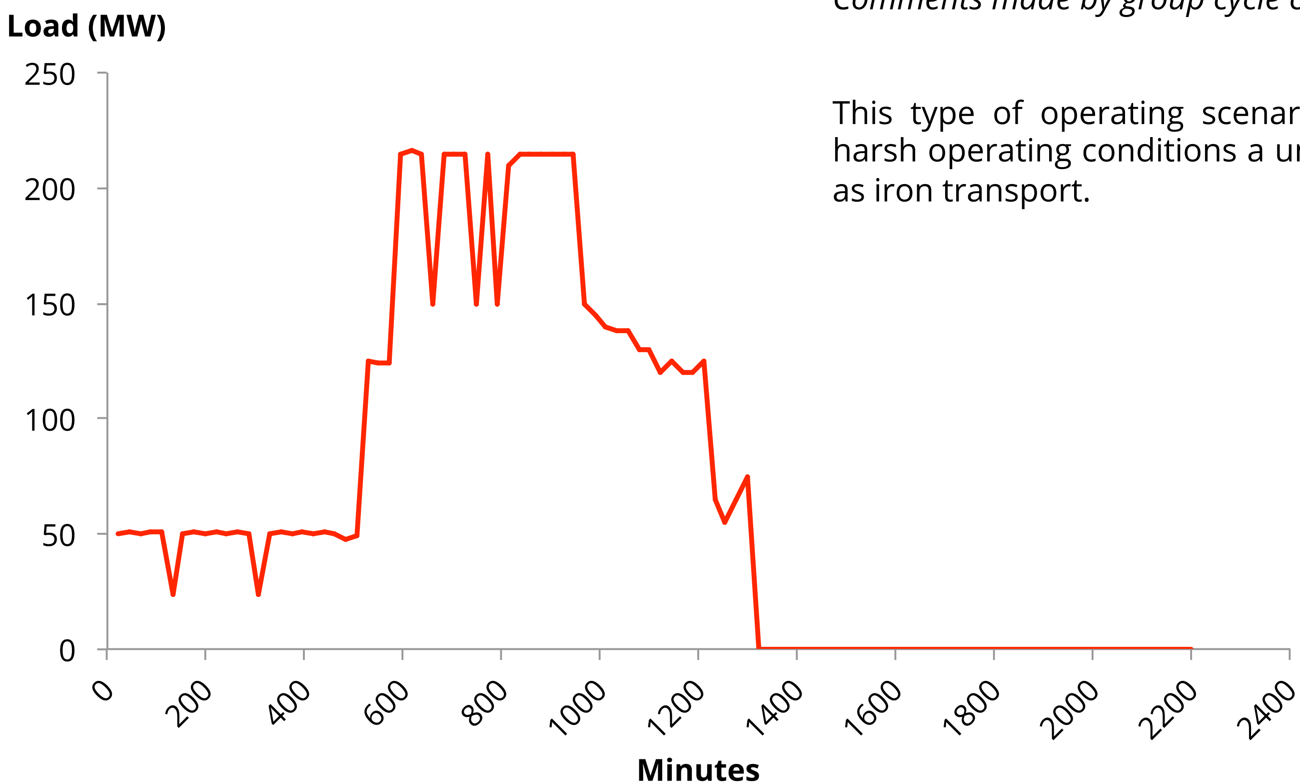

**High Pressure Cross over (TOP tubes) from a 2,200 psi / 253 MW, 1,000°F / 538°C re-heat steam, natural-circulating, mixed metallurgy drum unit** The unit was commissioned in 1963 and was converted from all-volatile-reducing hydrazine chemistry to Anodamine AVT(O). The unit retired for decommission in December 2013. The feedwater heater tubes were removed one year later and sent to our laboratory for inspection. The condition of the tubes as received by the client without preservation or protection.

# HRSG’s & ACC’s Protection Single & 2 Phase FAC Using Anodamine

The plant utilizes two highly efficient Siemens-Westinghouse 501FD2 combustion turbines to produce electricity. Additionally, the exhaust from the two turbines is recycled to produce steam for an Alstom STF30C steam turbine to make additional electricity.

- 2 x Alstom Triple pressure HRSG, Steam pressure for LP / IP / HP units is 129 / 721 / 2,781 psi & 9 / 50 / 192 bar. HP steam is reheated to 1,055 ºF / 568 ºC. Total generation capacity is 530 MW with two 134 MW Alstom Turbines.

# Triple Pressure HRSG with ACC's Total Iron Corrosion Product Transport during Two-shifting



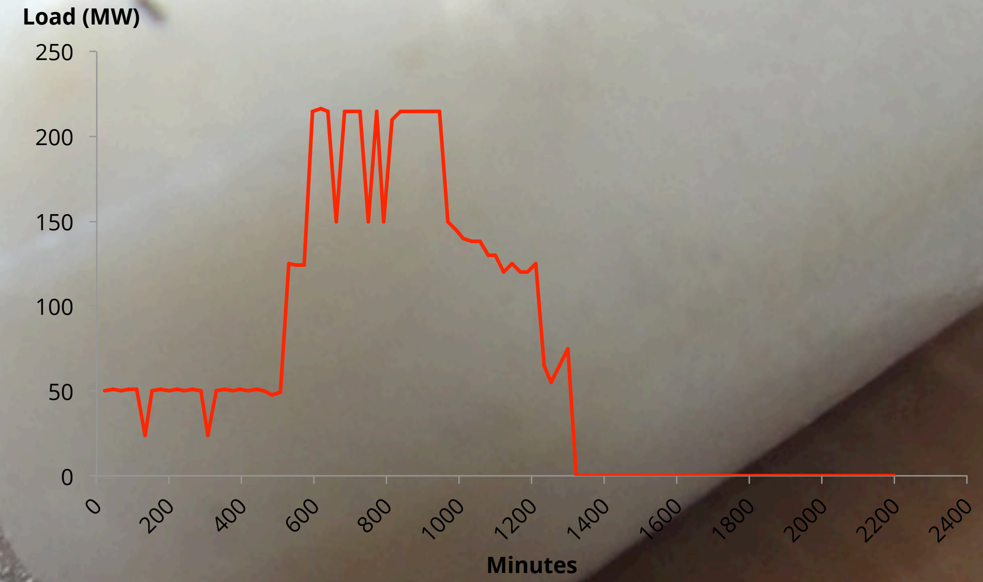

*Comments made by group cycle chemist:*

This type of operating scenarios is one of the most harsh operating conditions a unit can experience as far as iron transport.

This Triple pressure combined cycle with massive ACC's operates at cyclic load, shutting down during low power demands at night and returning to service during peak demands in the morning.  A 0.45 um Millipore sample was collected over a period 24 hours, with unit operation at low load during the day, peaking during high demand and reserve lay-up during the night. Total particulate iron collected was only 2.9 ppb.

# Triple Pressure HRSG with ACC's Total Iron Corrosion Product Transport during Two-shifting

0.45 um Millipore pad



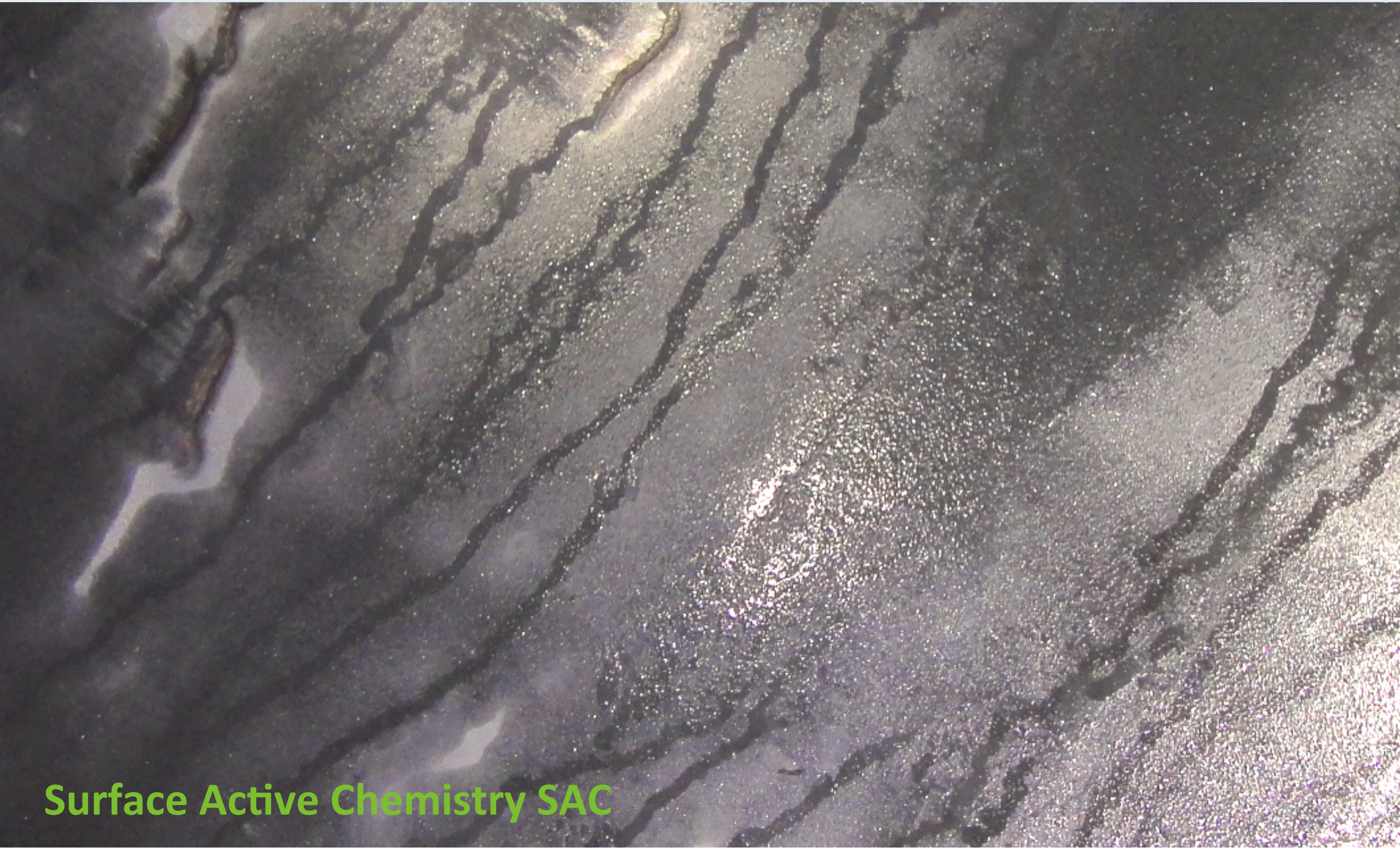

**2.9 ppb Total Iron**

During reserve lay-up the auxiliary boiler provides steam to operate the steam air injector which maintain the vacuum on the boilers. The condensate system provides feed water to the auxiliary boiler and any looses are compensated with make up water. Comments made by group chemist: Comments made by group cycle chemist: “This type of operating scenarios is one of the most harsh operating conditions a unit can experience as far as iron transport”.

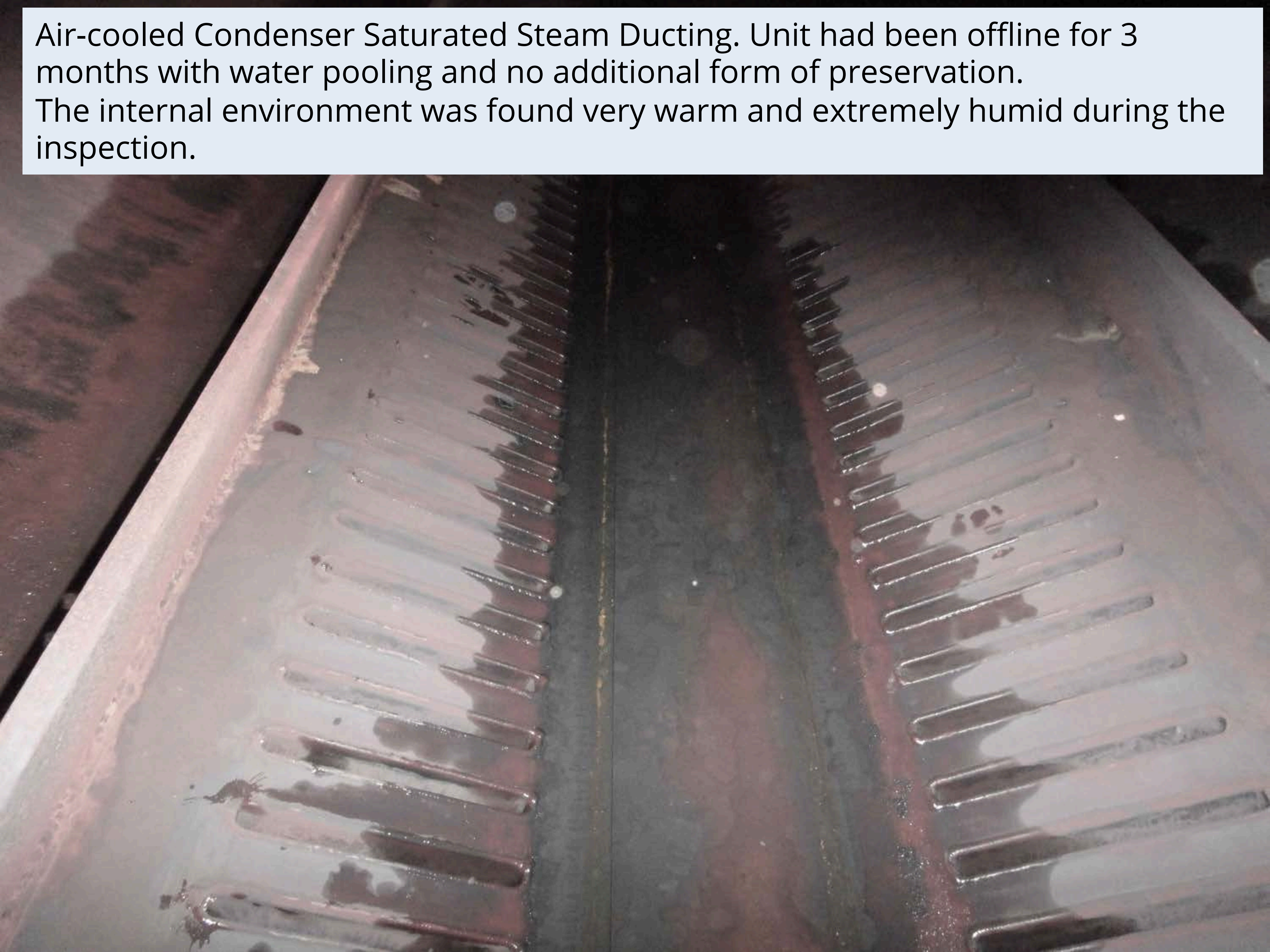
LP turbine exhaust lower distribution duct. The operational environment is supplied with steam having approx. 5 – 6 % moisture, image taken after the LP section of the turbine just prior to steam distribution vanes.

The entire lower pipe sections were found wet with lots of water pooling.

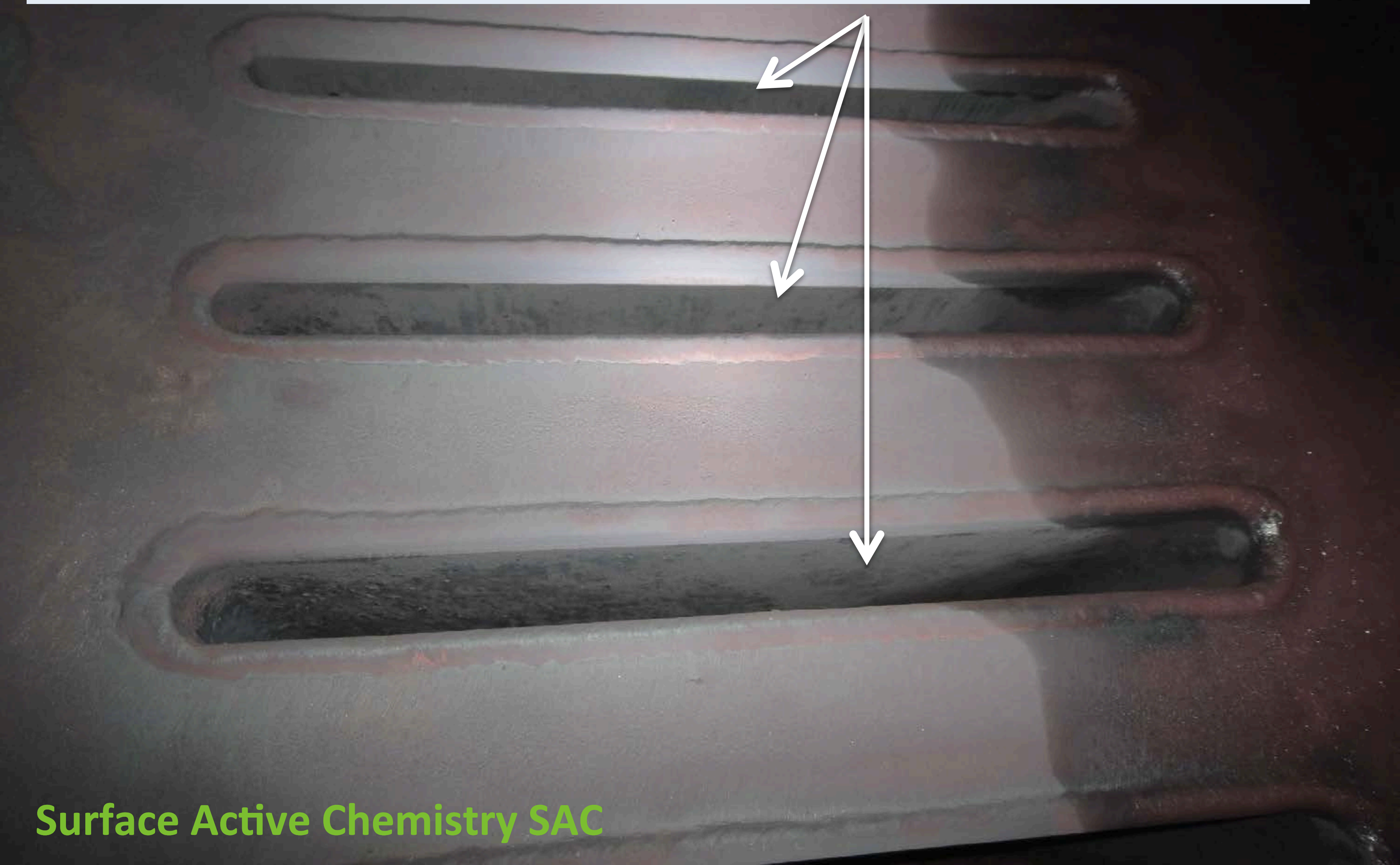
The unit had been offline for 3 months with no external form of preservation.



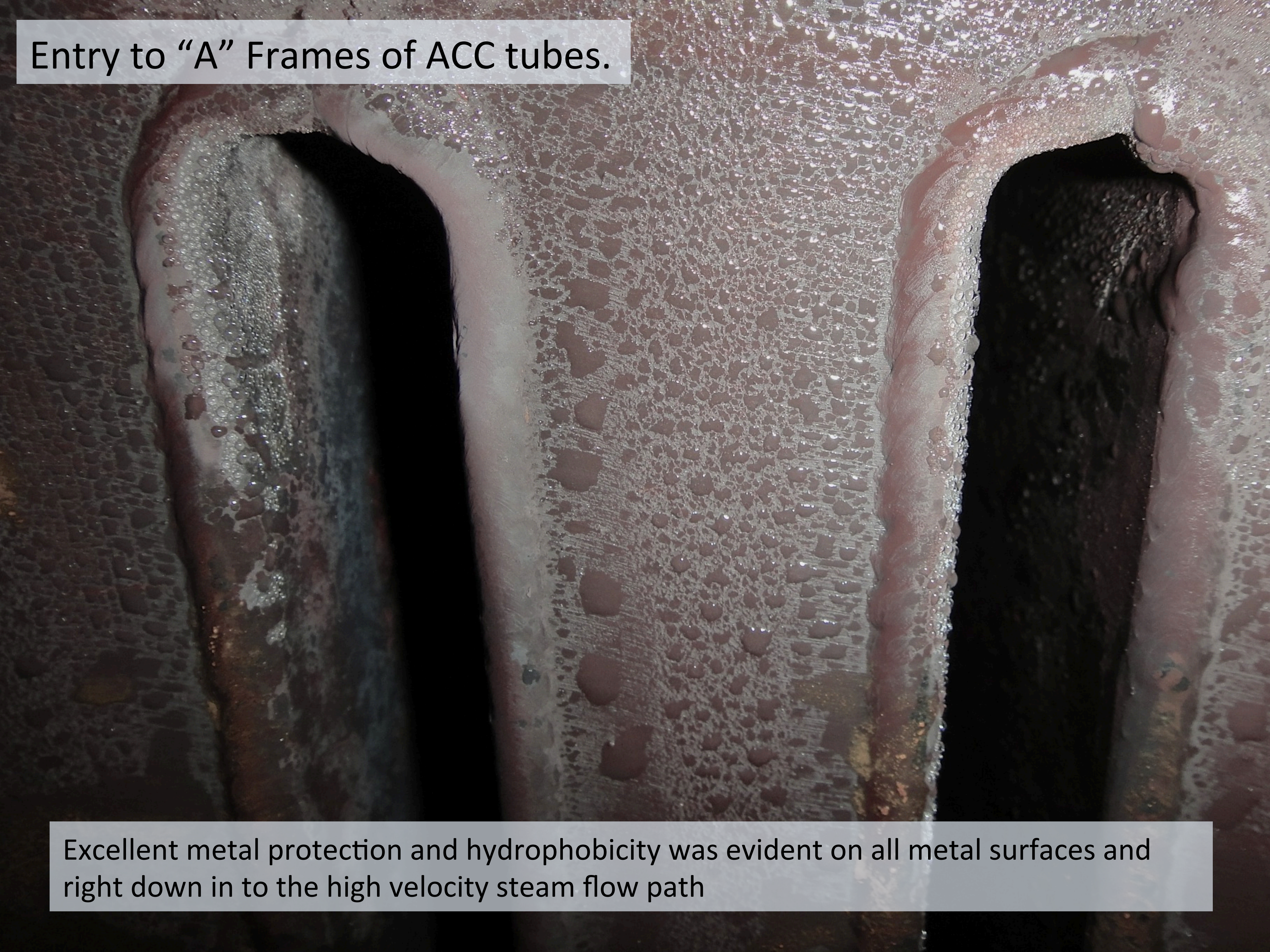
Air-cooled Condenser Saturated Steam Ducting. Unit had been offline for 3 months with water pooling and no additional form of preservation.
The internal environment was found very warm and extremely humid during the inspection.



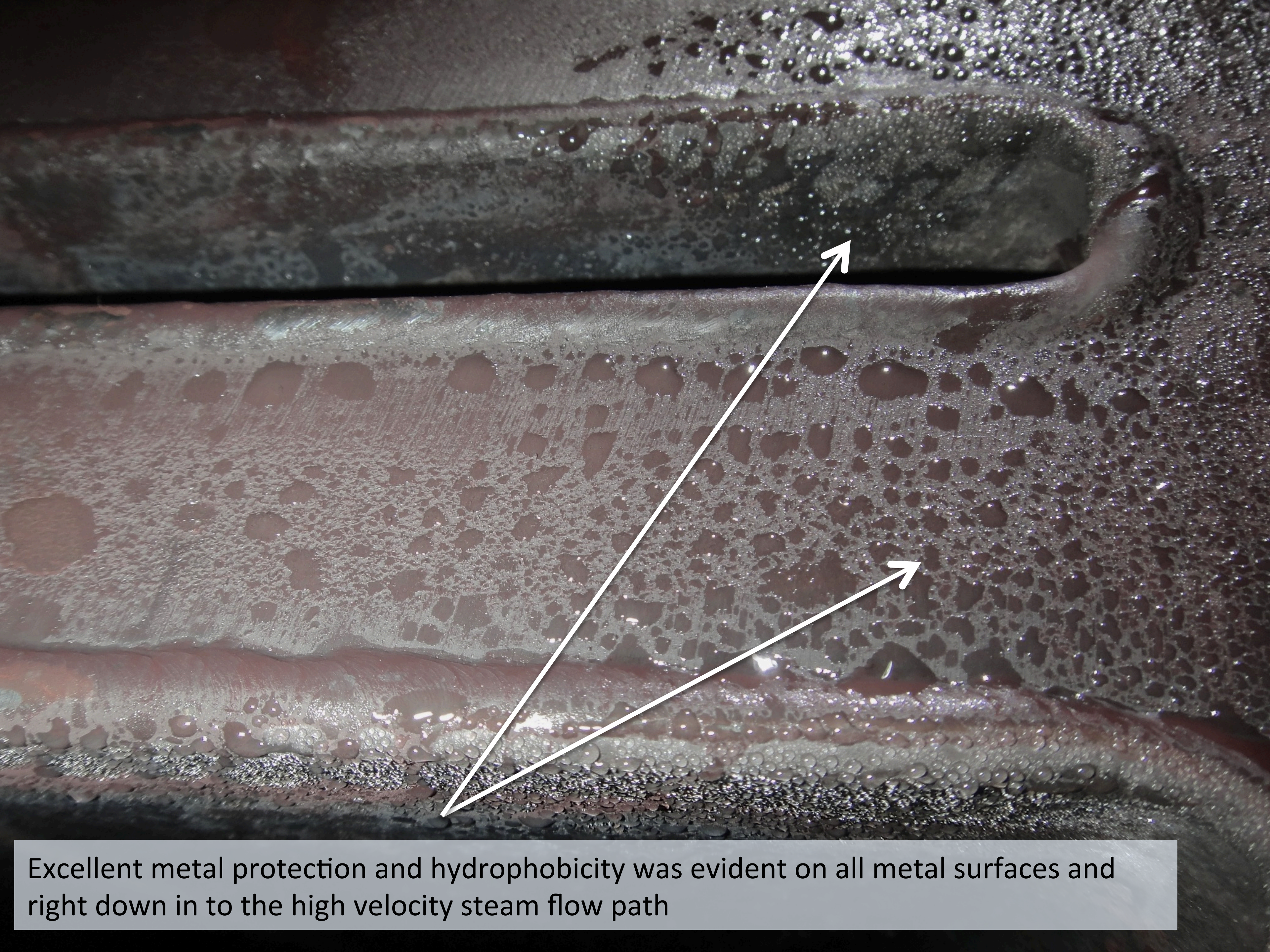
Entry to "A" Frames of ACC tubes.
No visible signs of FAC in any of the steam flow path areas.
It was reported by site inspections that old areas noted as being previously affected by FAC damage had now been terminated.



# Entry to “A” Frames of ACC tubes.



Excellent metal protection and hydrophobicity was evident on all metal surfaces and right down in to the high velocity steam flow path



Excellent metal protection and hydrophobicity was evident on all metal surfaces and right down in to the high velocity steam flow path

# THANK YOU

Questions?