Polyamine Technology –Reduced Iron Throw in the Steam Cycle

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Imagination at work

Air Cooled Condensers

Systems with ACC's face considerable challenges

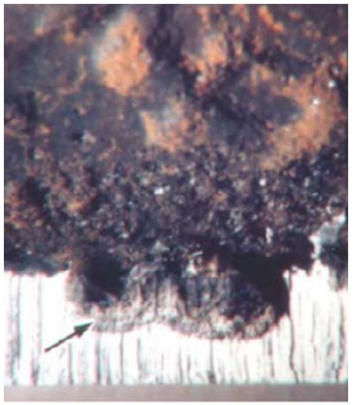
- A significant large increase in surface area compared to "wet condensers", where steel is in contact with steam/condensate
  - A very small corrosion rate amounts to significant amounts of iron
- Fluctuating velocities of steam entering into the streets
  - A "cold street" can cause a very high velocity due to the sudden vacuum created
- Fluctuating characteristics of the steam entering into the streets
  - Steam droplet size can vary depending on temperatures and operating conditions within the street. Droplets sizes of 0.1-50 microns have been reported in ACC's.[1]
  - As the droplets enter the ACC ducting they form ever larger droplets. These droplets have more mass and can impart higher energy when they hit the steel and tube entry surfaces
  - These droplets act in a similar manner as 2-Phase FAC corrosion.
  - Elevating the pH of the steam/condensate to 9.6-10.0 with a low volatility amine in conjunction with other ammonia and/or amines has shown significant reductions of corrosion and resultant iron throw in these areas

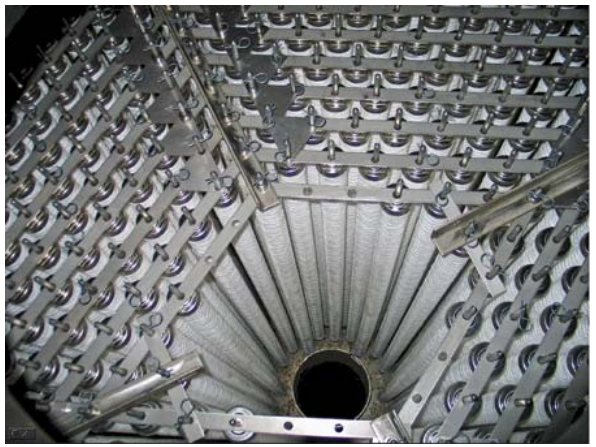
1 ACC Corrosion/FAC presentation, 5th Annual ACC Users Group, B. Dooley

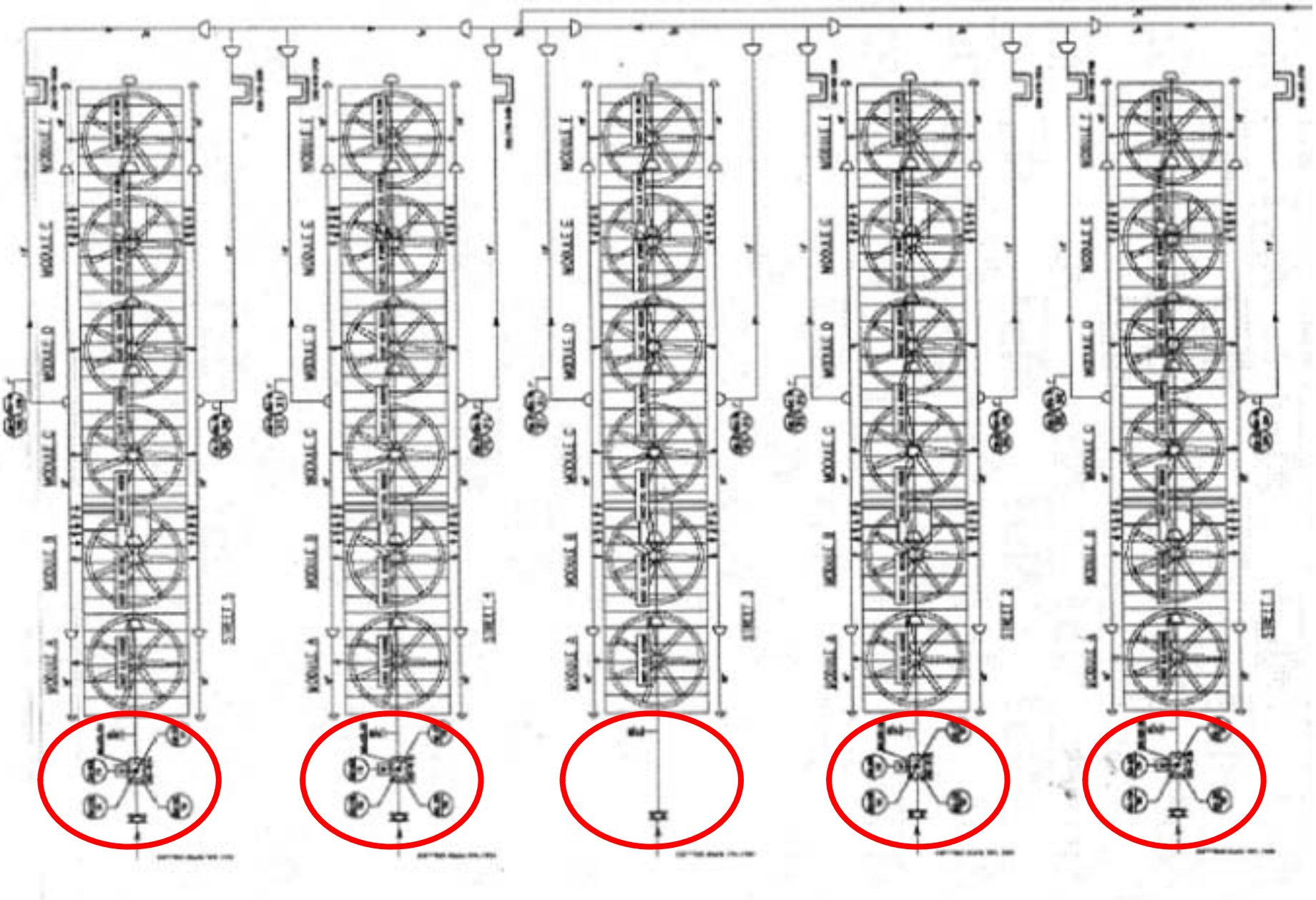
Air Cooled Condensers

The New Challenge!

- Cycling Operation
  - Frequent starts and stops.....
    - as many as two to three times a day
  - Breaking vacuum
  - No auxillary steam available
  - Limited nitrogen availability
  - Air leaks
  - Fluctuating chemistry from oxidizing to strongly oxidizing (or reducing to oxidizing)
  - All this leads to iron throw and loading on condensate polisher resins, filters, and ultimately iron deposition within the steam generators



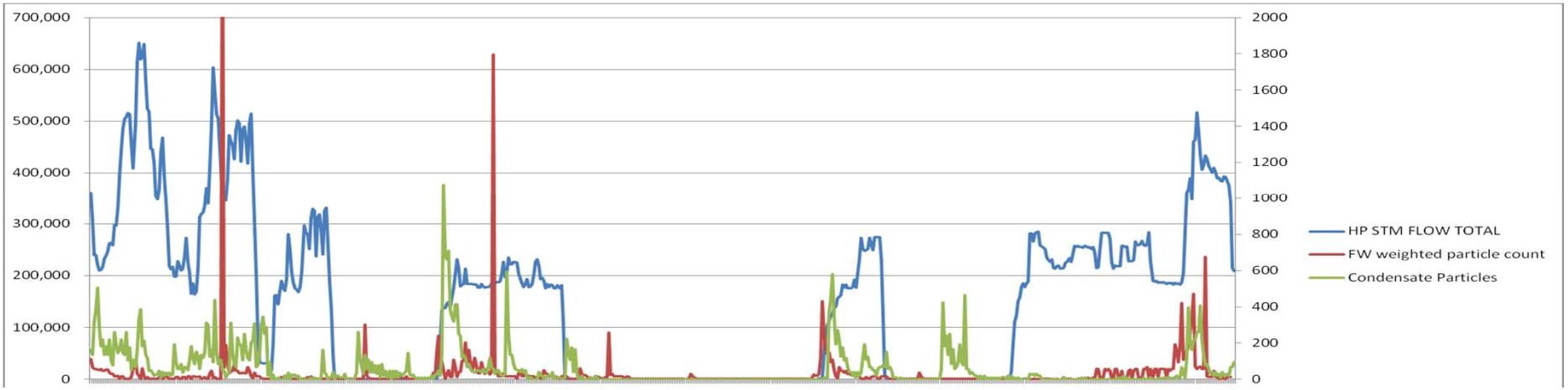




Street Valves[2]

2 How an ACC Unit Releases Iron presentation, 5th Annual ACC Users Group, P. Sehl, J Otis

Particle Burst Timing[2]

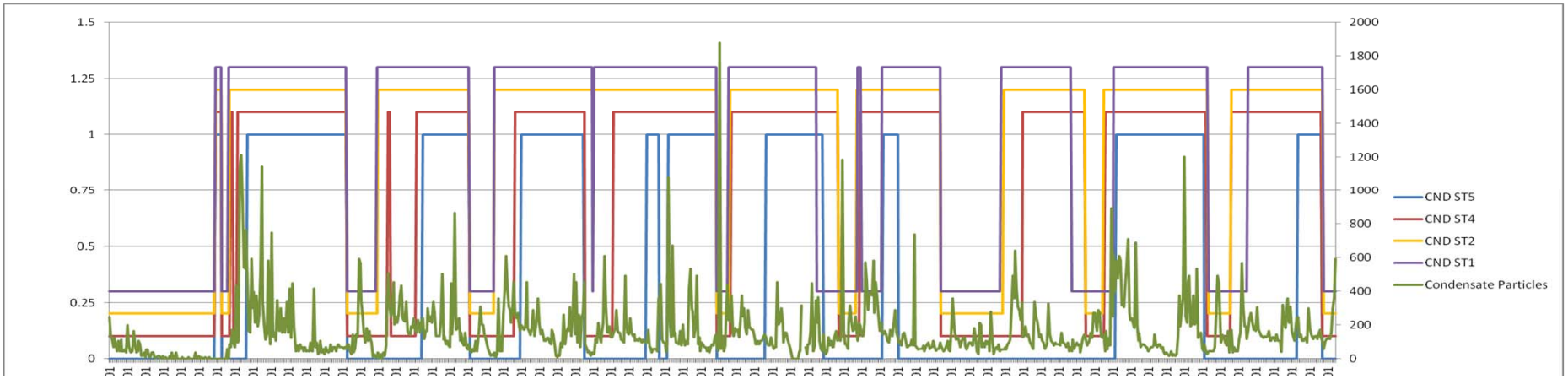


7-days

7-days

2 How an ACC Unit Releases Iron presentation, 5th Annual ACC Users Group, P. Sehl, J Otis

Particle Burst Intensity and Longevity[2]



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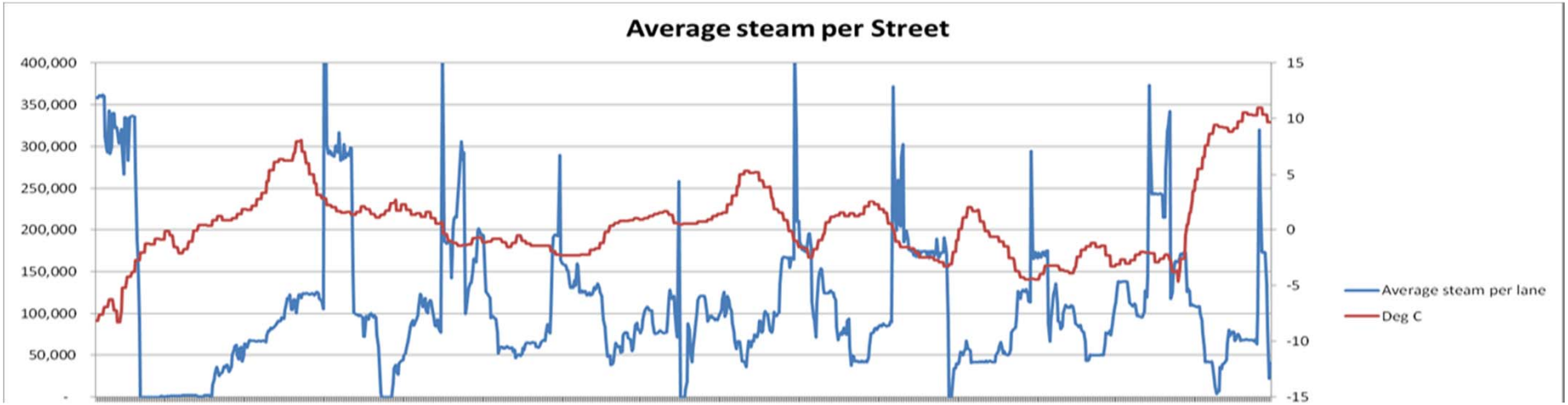


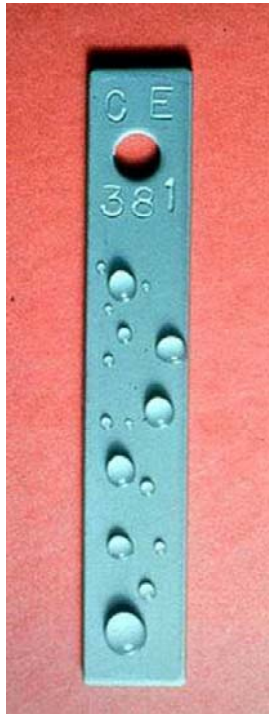
7-days

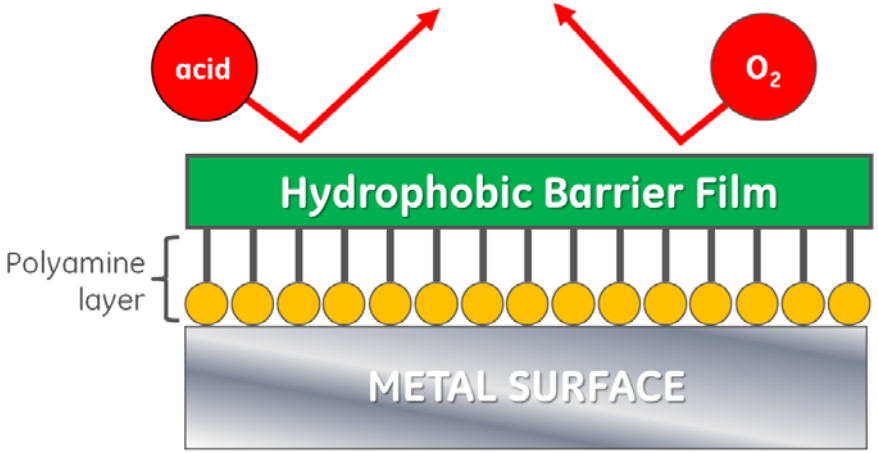
2 How an ACC Unit Releases Iron presentation, 5th Annual ACC Users Group, P. Sehl, J Otis

Evolving steam generator chemical treatment

Plant operations require cycle chemistry advancements

- Polyamine – latest evolution for asset protection
  - ✓ Volatile filmer: forms protective barrier throughout system
  - ✓ Evaluated thoroughly by in-house R&D
  - ✓ Continuous film adsorption and desorption
  - ✓ SG thermodynamic model for optimized application
    - Traditional fossil
    - HRSGs
  - ✓ Deployed in utility applications up to ~2600 psig





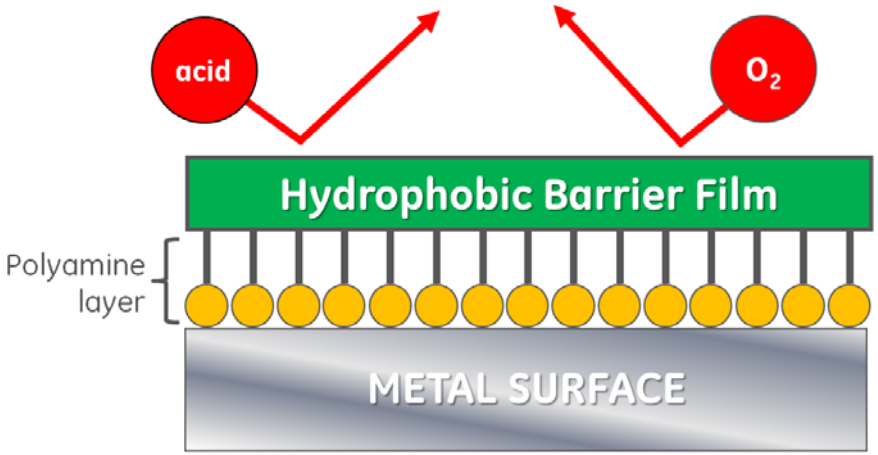
Evolving steam generator chemical treatment

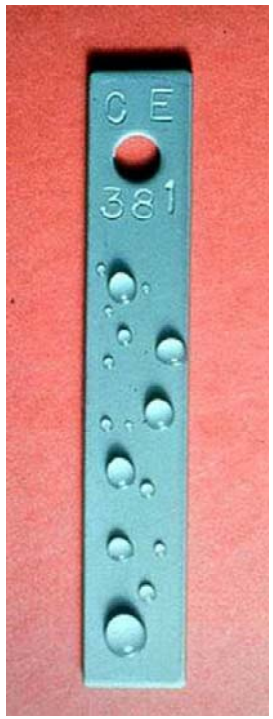
What is a polyamine?

In MSDS terms (CAS 7173-62-8) it is called Alkyl diaminopropane,

It has the following chemical description R_1-NH-R_2-NH_2

Breakdown products would be ammonia and other smaller chains

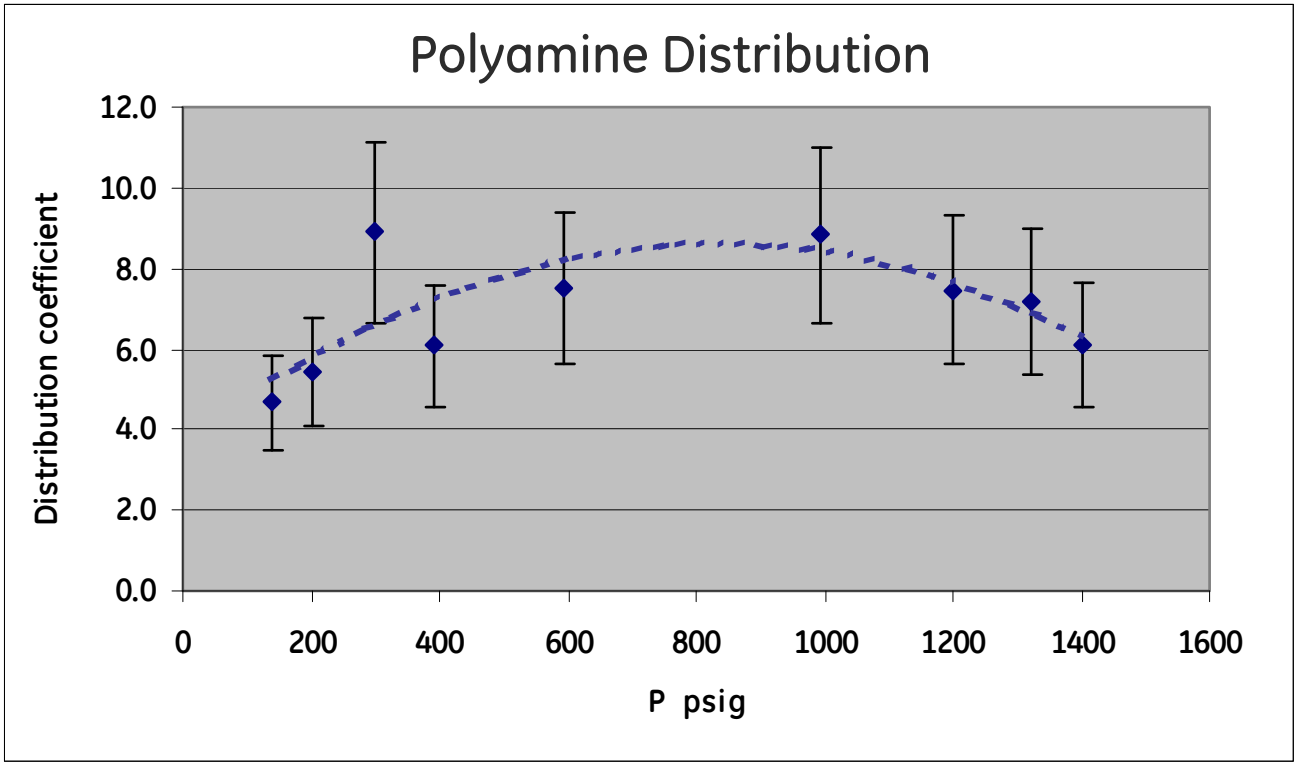




R&D: volatility versus pressure

Laboratory study: steam-liquid distribution ratio

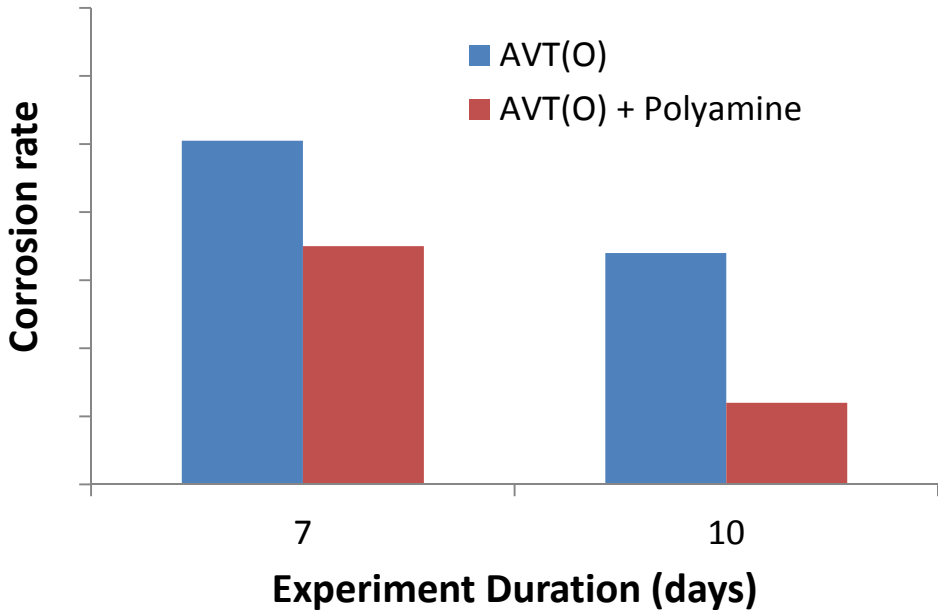
- significant volatility observed
- DR: Polyamine > MOPA (MPA) > MEA (ETA) > ODA

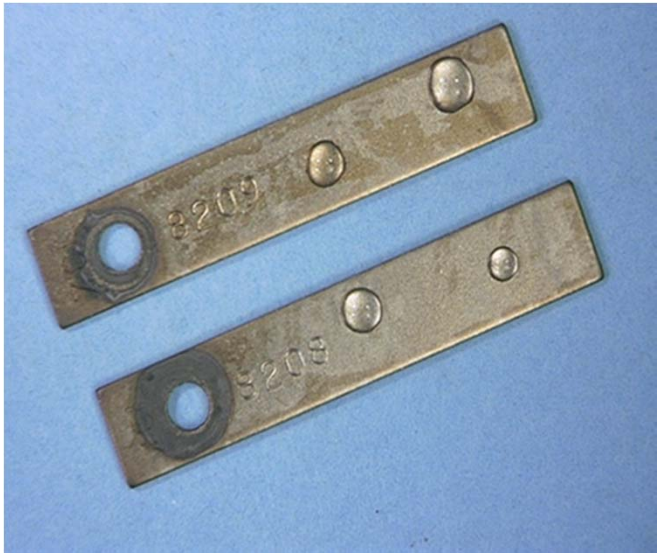


R&D: corrosion experiments

Laboratory product development: corrosion tests

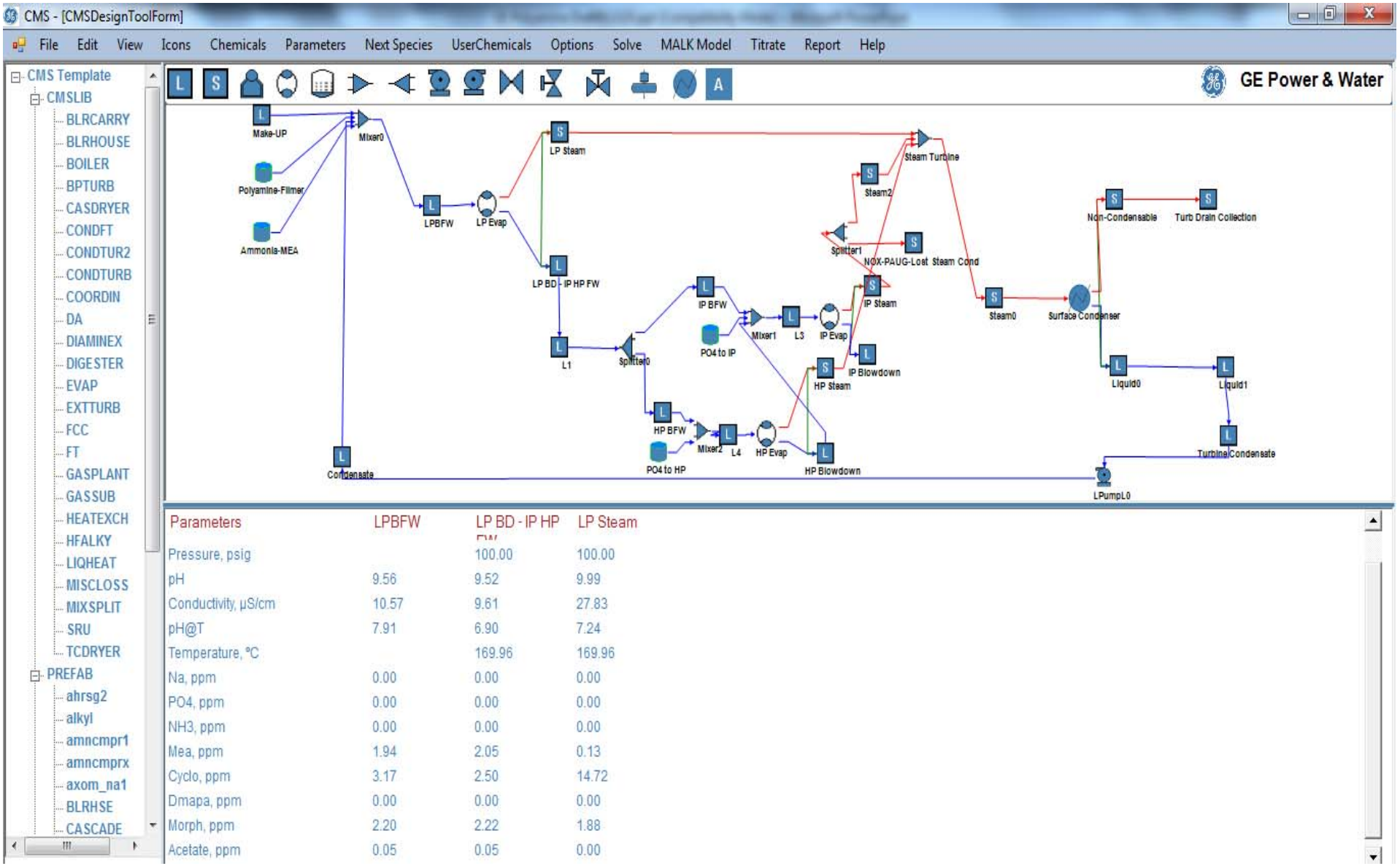
- Demin FW tests showed LCS corrosion mitigation
- AVT(O) treatment vs AVT(O) w/ filmer





Water beading on LCS coupons

How we apply: steam system modeling

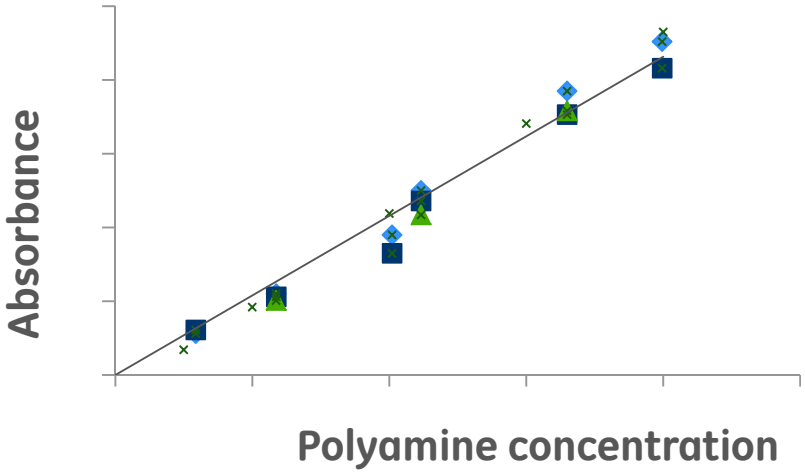


Parameters	LPBFW	LP BD - IP HP FW	LP Steam
Pressure, psig		100.00	100.00
pH	9.56	9.52	9.99
Conductivity, µS/cm	10.57	9.61	27.83
pH@T	7.91	6.90	7.24
Temperature, °C		169.96	169.96
Na, ppm	0.00	0.00	0.00
PO4, ppm	0.00	0.00	0.00
NH3, ppm	0.00	0.00	0.00
Mea, ppm	1.94	2.05	0.13
Cyclo, ppm	3.17	2.50	14.72
Dmapa, ppm	0.00	0.00	0.00
Morph, ppm	2.20	2.22	1.88
Acetate, ppm	0.05	0.05	0.00

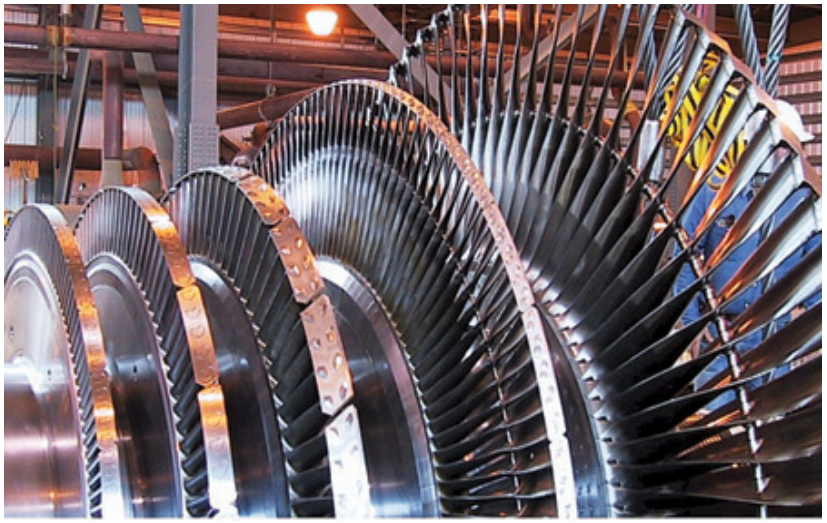
How we apply: bench top analytical test

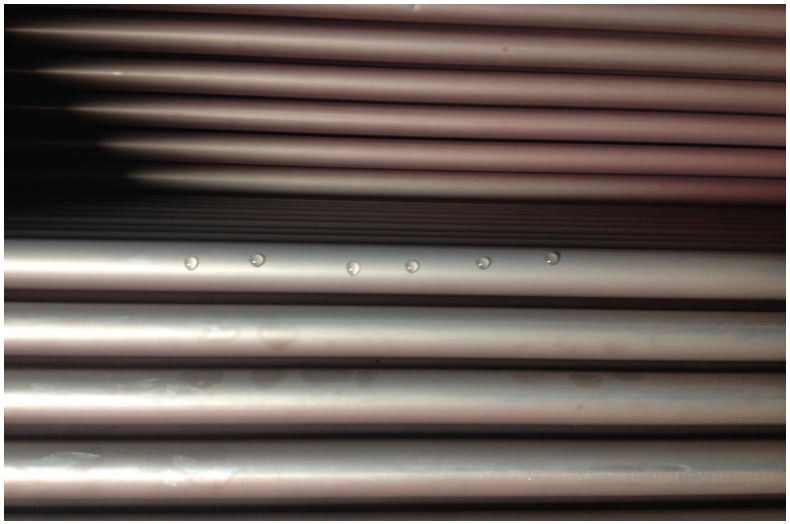
Bench analytical test can be used as needed

- ✓ modification of published Rose Bengal test
- ✓ measures active filmer concentration in system
- ✓ no relevant interference of neutralizing amines
- ✓ detection limit ~50 ppb of Polyamine



Case Studies





Case Study #1 background

Plant Overview

- 3-on-1 Combined Cycle Gas Turbine Plant
- 3 multi-drum HRSG units
  - ✓ HP = 2000 psig, IP = 500 psig, LP = 100 psig
  - ✓ LP provides feedwater for IP/HP
  - ✓ Superheat/Reheat of 1050 °F
- Cycling operation dependent on demand for power

Pre-trial Chemistry

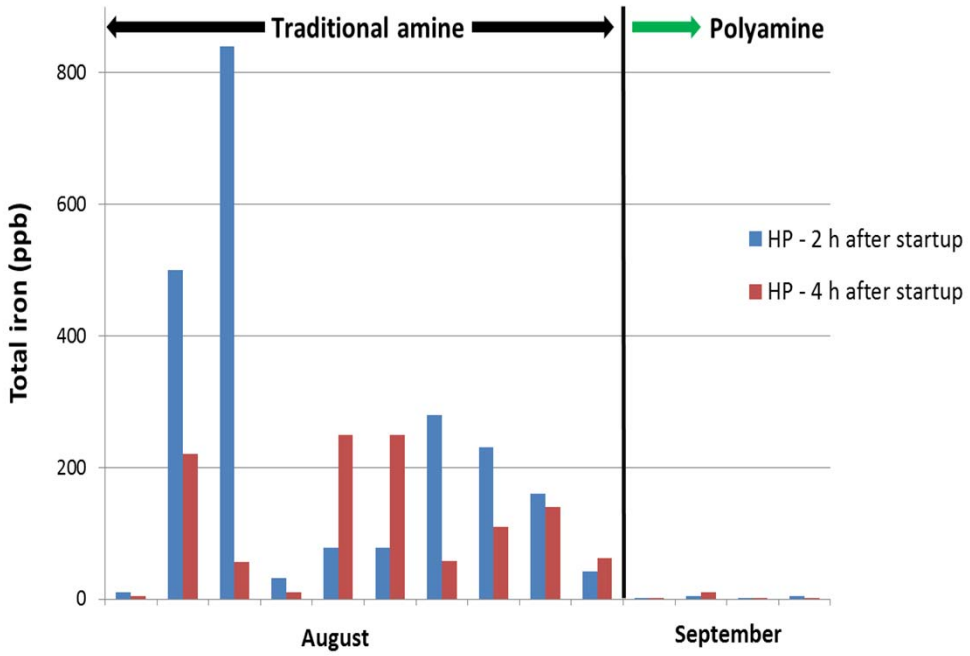
- PO_4 (O)
- Ammonia:MEA in 4:1 ratio
- Target pH of 9.4-9.8 in FW (including LP evap)
  - ✓ pH of CPD often >9.75
- PO_4 chemistry utilized in HP/IP
- All-ferrous metallurgy – no reducing agent

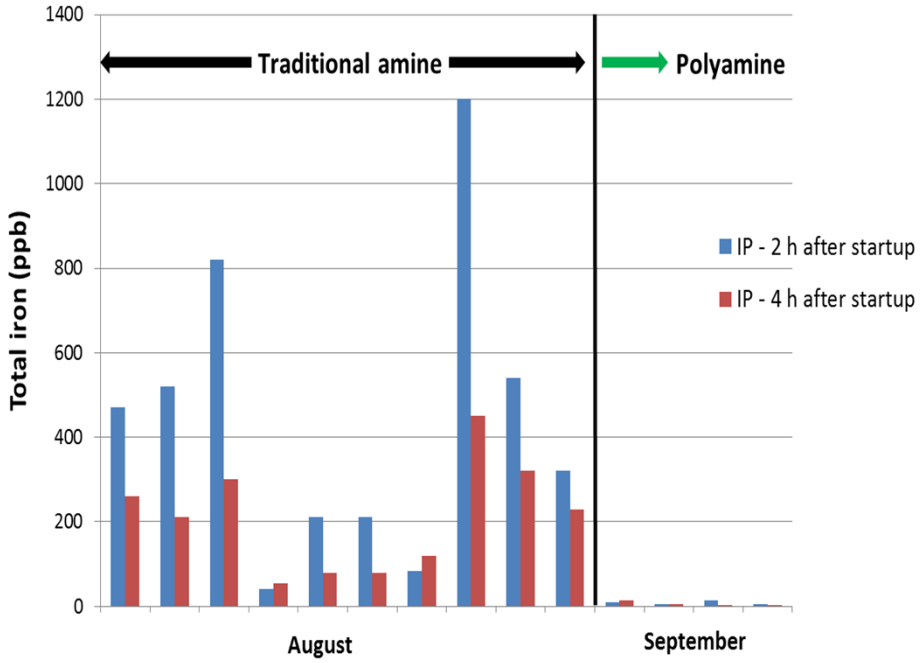
HRSG comparison over time

Plant observed significant corrosion inhibition in both continuous and cycling operation

Combined startup data for 3 units: total iron

- Sampled 2 & 4 hours after startup





Case Study #2 background

Plant Overview

- Coal-fired 2600 psig boiler
- 630 MW power output
- Base-loaded with periodic shutdown
- Large ACC with air in-leakage & corrosion concerns incl. FAC

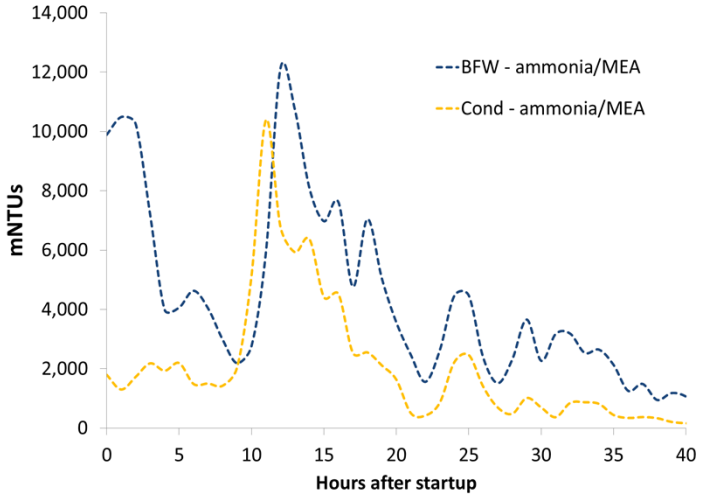
Pre-trial Chemistry

- AVT (O)
- Ammonia:MEA Target pH of 9.4-9.6 in BFW & condensate
- All-ferrous metallurgy – no reducing agent
- Corrosion monitoring on-line via Hach FT-660 laser nephelometer in BFW & Condensate
  - 5 mNTU ~ 1 ppb Fe oxide particulate

Cold start w/ ammonia:MEA AVT

Turbidity peaked ~12K mNTU

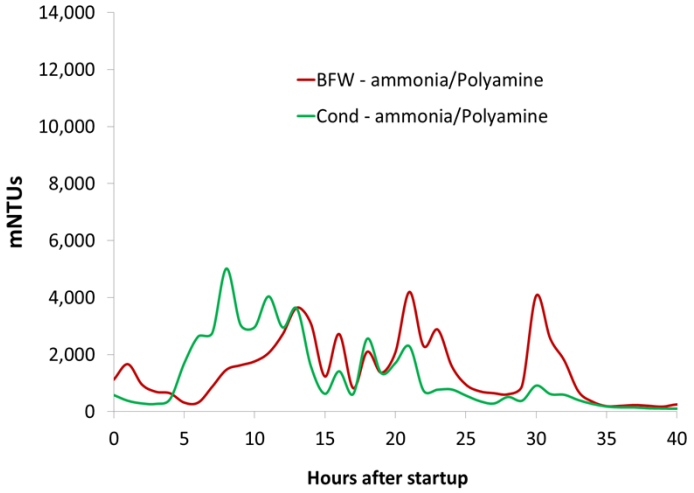
Condensate turbidity in 2-10K mNTU range

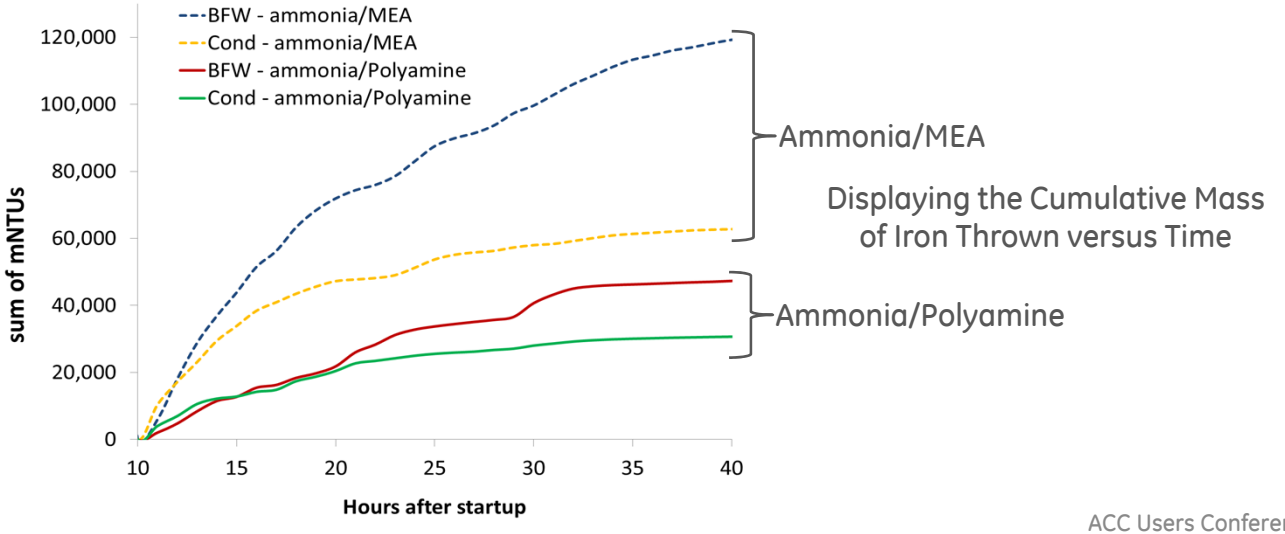


Cold start after Polyamine addition

Turbidity peaked ~5K mNTU

Condensate turbidity in 1-5K mNTU range



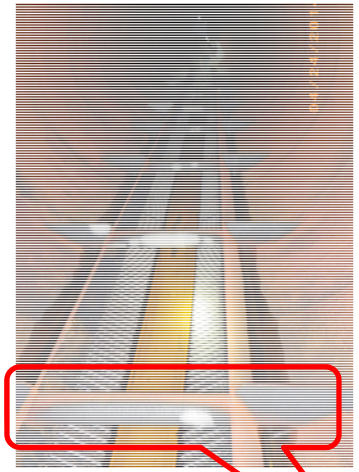


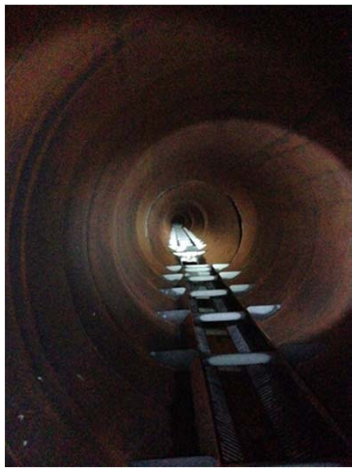
Turbine Exhaust

Clear evidence of hydrophobic film

ACC Street

Progression of inspections





Fall 2013

Spring 2014

Pre-Polyamine

Fall 2014

Spring 2015

DHACI rating of 2 and moving slowly to a DHACI rating of 1

ACC inlet
100+ Days on Polyamine

Inspection video

Case Study #3 background

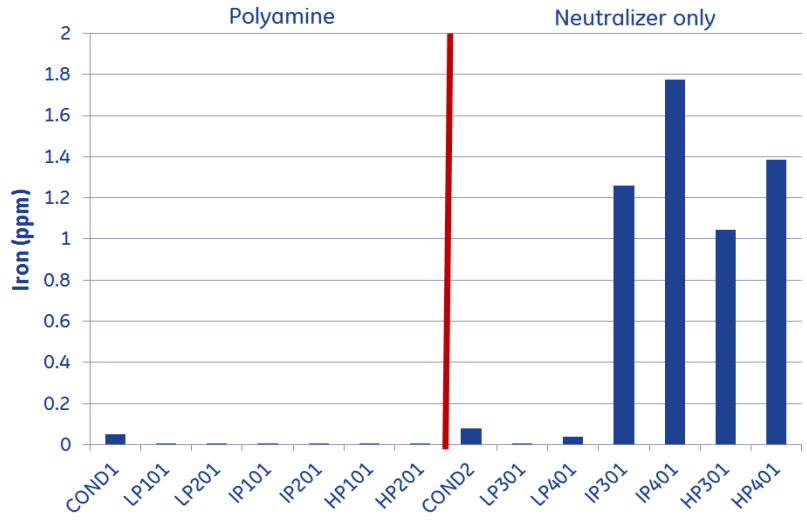
Plant Overview

- 2 x (2x1) Combined Cycle Gas Turbine Plant
- 4 multi-drum HRSG units
  - ✓ HP = 1800 psig, IP = 450 psig, LP = 70 psig
  - ✓ LP provides feedwater for IP/HP
  - ✓ Superheat/Reheat of 1050 °F
- Cycling operation dependent on demand for power

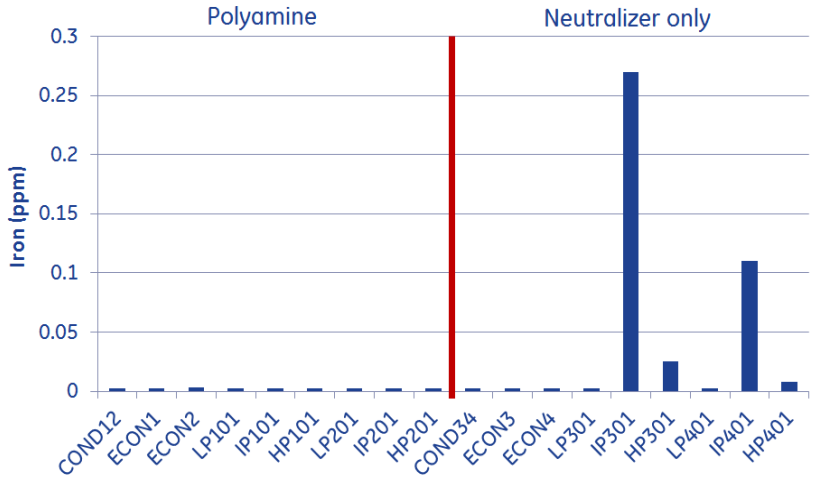
Pre-trial Chemistry

- PO_4 (R) -> PO_4 (O)
- Neutralizing amine blend (methoxypropylamine & cyclohexylamine)
- Target pH of 9.4-9.5 in FW/Cond
- PO_4 chemistry utilized in HP/IP
- All-ferrous metallurgy – prior reducing agent use

HRSG comparison side-by-side



Startup – sampled after 4 hours (2 starts averaged)



Continuous operation (4 months after treatment changed)

Inspection pictures

Clear evidence of hydrophobic film on LP belly pan

Polyamine

Neutralizing amine

Conclusions

Steam cycle treatment continues to evolve

- Continued study by organizations such as EPRI
- Traditional and Power filmer applications are growing
  - ✓ Continuous feed application
  - ✓ Layup –feed only prior to an outage
- Chemistry evolving to keep up with evolving power plant operation
- Application expertise continues to expand and improve

Future work

- ❑ impact on heat transfer
- ❑ impact on polishers
- ❑ thermal stability & breakdown pathways