Why Care About Chemistry Monitoring for Combined Cycle Plants?

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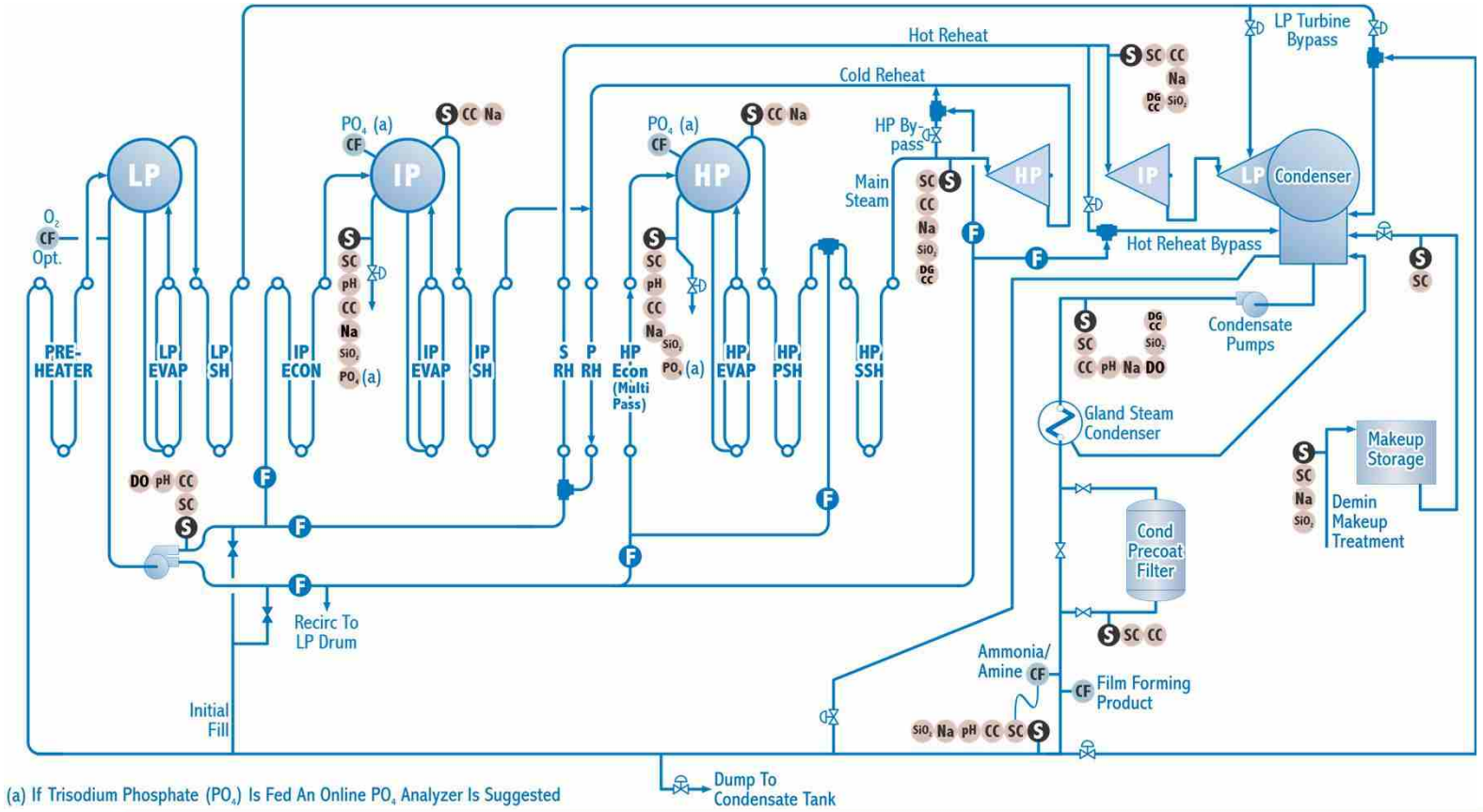
Online Monitoring in a Combined Cycle Unit



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Symbol List

- S: Sample Point.
- SC: Specific conductivity is a measure of total conductive ions
- CC: Conductivity after cation exchange, a measure of the conductive anions (often called cation conductivity)
- DGCC: Degassed CC, a measure of nonvolatile anions.
- pH: A measure of the balance of cations (alkaline ions) and anions (acidic ions).
- Na: Sodium.
- DO: Dissolved oxygen.
- SiO_2: Dissolved silica (slightly soluble form of sand).
- PO_4: Orthophosphate, a pH buffering agent applied to HP/IP evaporators.
- F: Flow meter. Calculate % Attemperation.

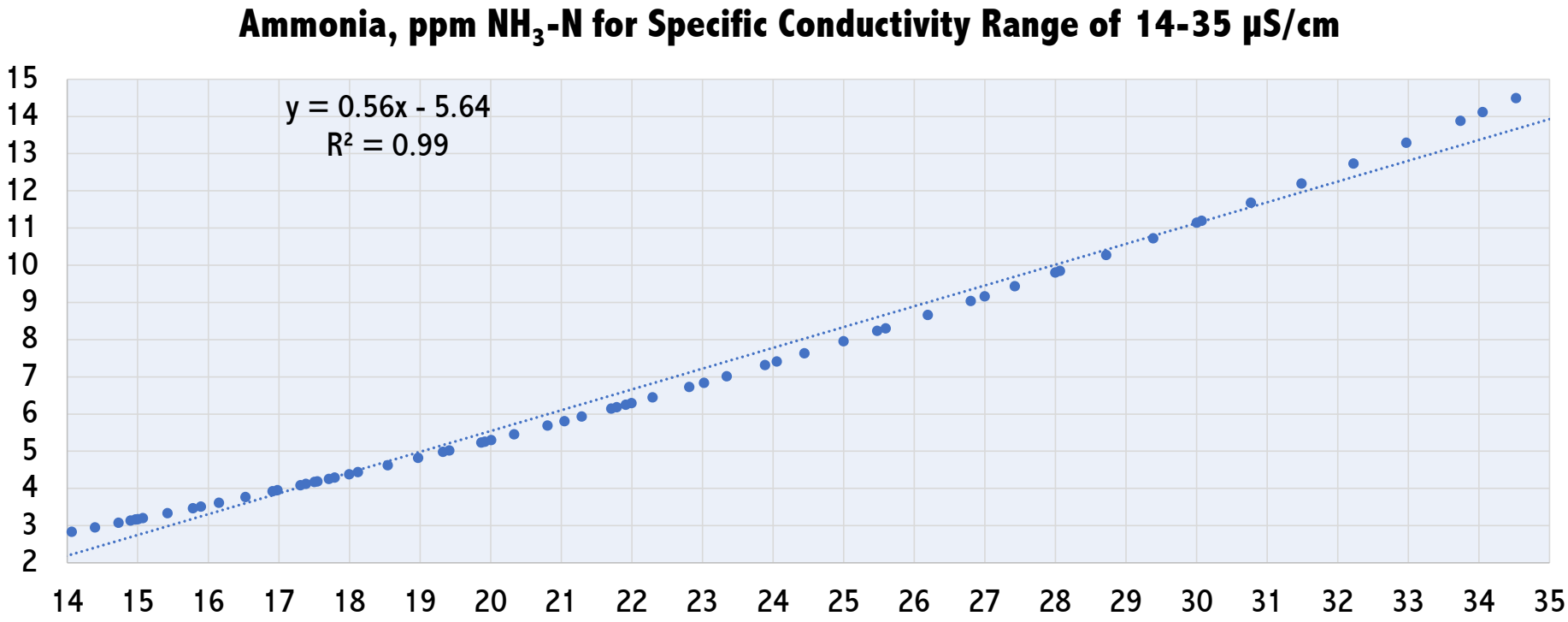
Recommended Monitoring on Inlet to Demineralized Water Tank

- A common limit for SC is <0.100 µS/cm at 25 °C for double pass RO with series mixed beds or EDI polishing. This limits salt to <20.9 ppb of NaCl (8.2 ppb as Na and 12.7 ppb as Cl), free alkali to <7.9 ppb as Na of NaOH, and free acid to <6.2 ppb as Cl of HCl in the makeup plant effluent. This limits the contaminants entering the unit from the makeup water supply. However, SC alone is not necessarily restrictive enough, and other online analyzers can be useful.
- A sodium monitor is recommended to ensure makeup sodium is <2-5 ppb Na.
- A silica monitor is recommended to document silica is <10 ppb SiO_2 because very high levels can pass through (e.g., >50 ppb SiO_2) with no SC increase.
- Sodium and silica monitors can help troubleshoot makeup system problems.

SC and pH in Preheater Inlet

- Automatic Control of Ammonia Feed (next slide)
- Ammonia Feed Sets pH (subsequent slide)

Nearly Linear Relationship Between Ammonia and Specific Conductivity (Average Slope is ~0.58 for 20-30 µS/cm Range)



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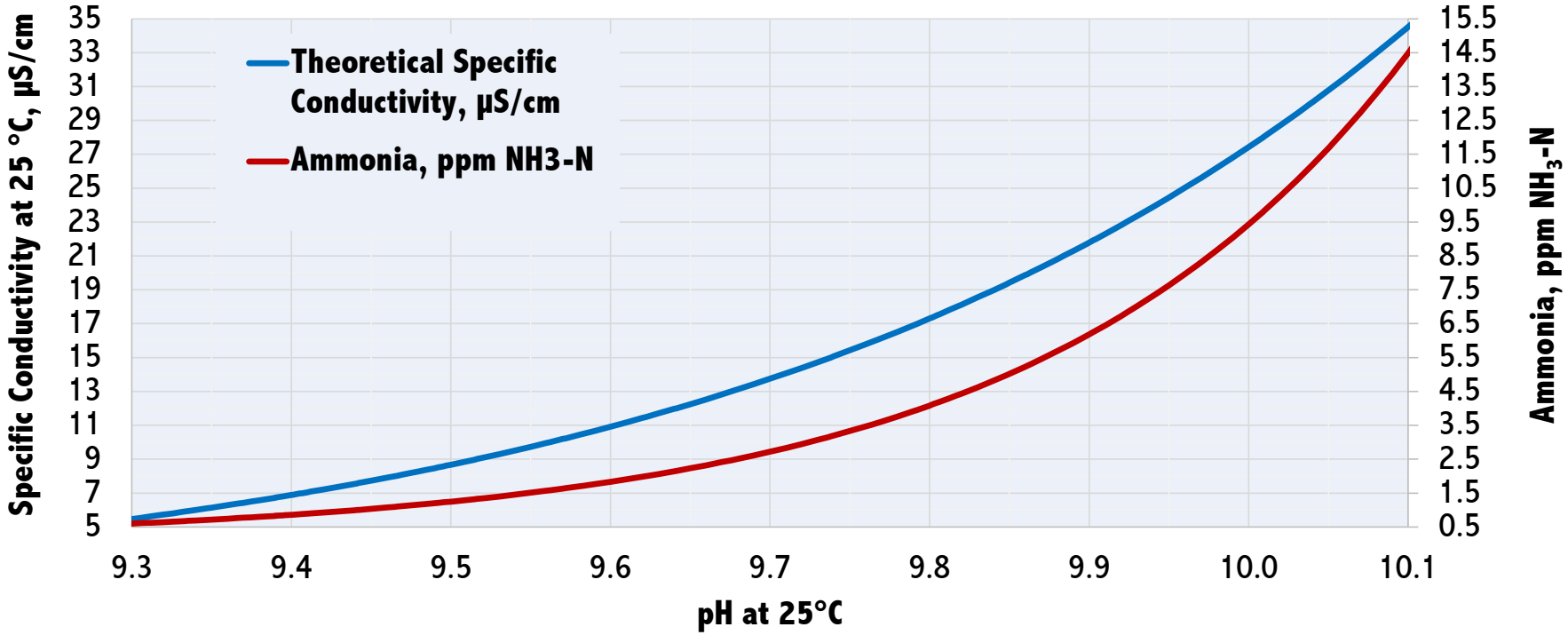
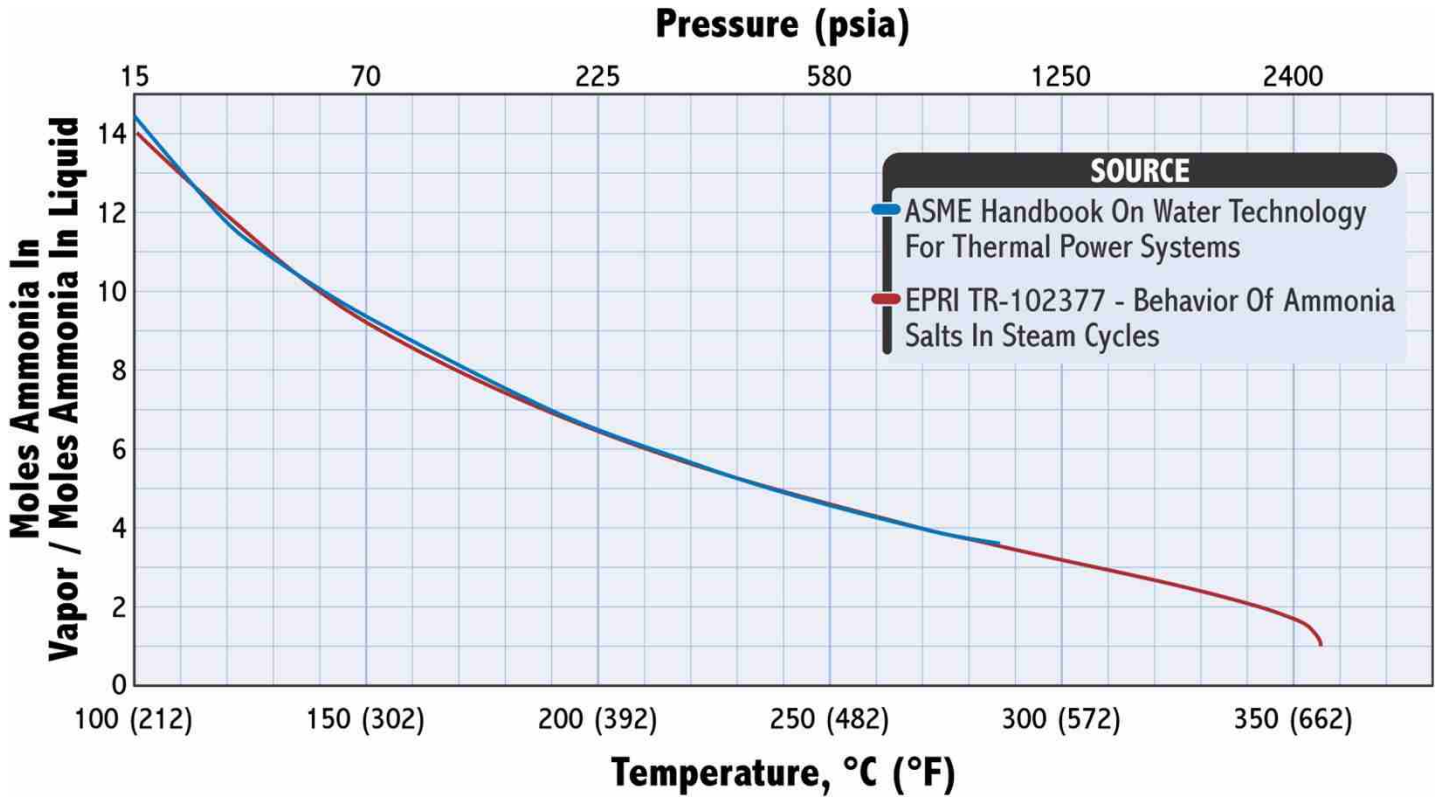
Conductivity and Ammonia (as NH_3-N) Vs. pH from Ammonia in Condensate, Feedwater, and Steam for All Steel Cycles



Ammonia is Volatile (Goes with Steam, Less Left in Water)



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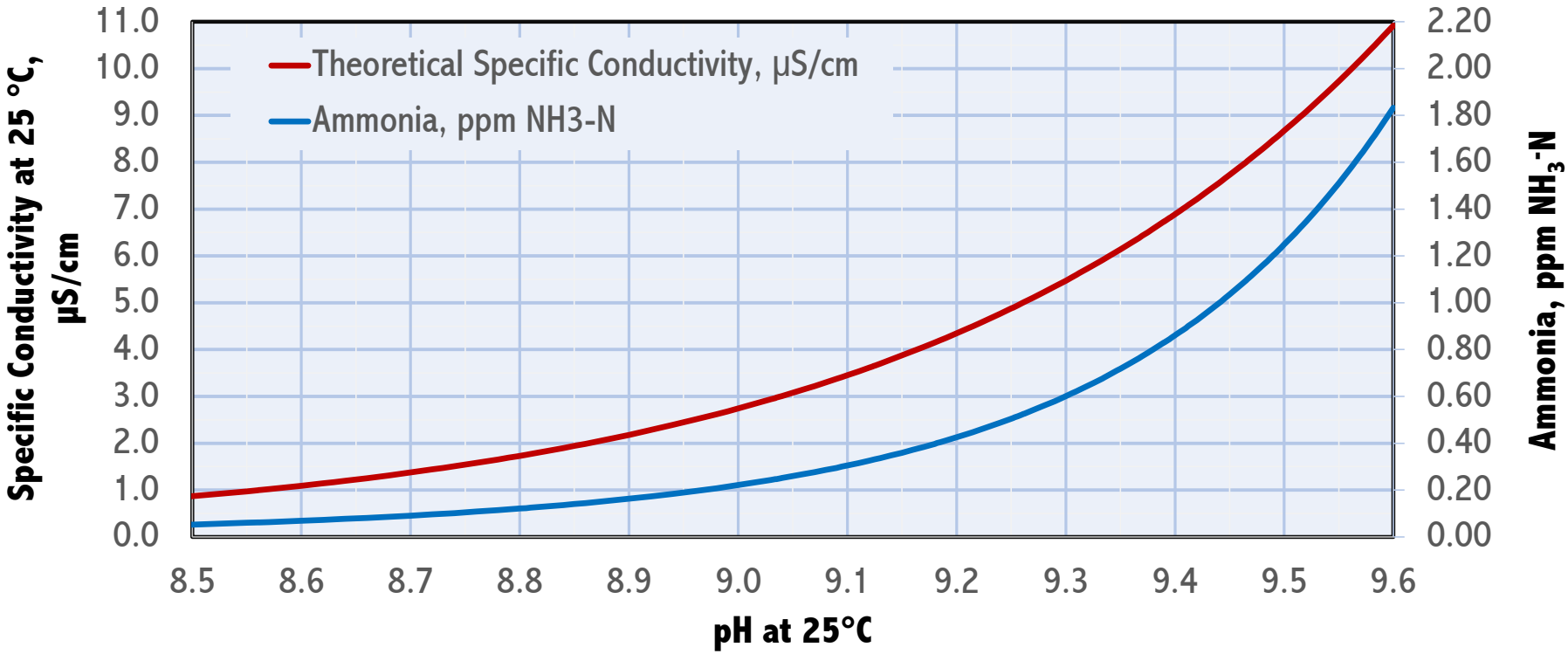
For AVT: Specific Conductivity and Ammonia (ppm NH_3-N) Vs. Measured pH Should be on or Below Red and Blue Lines



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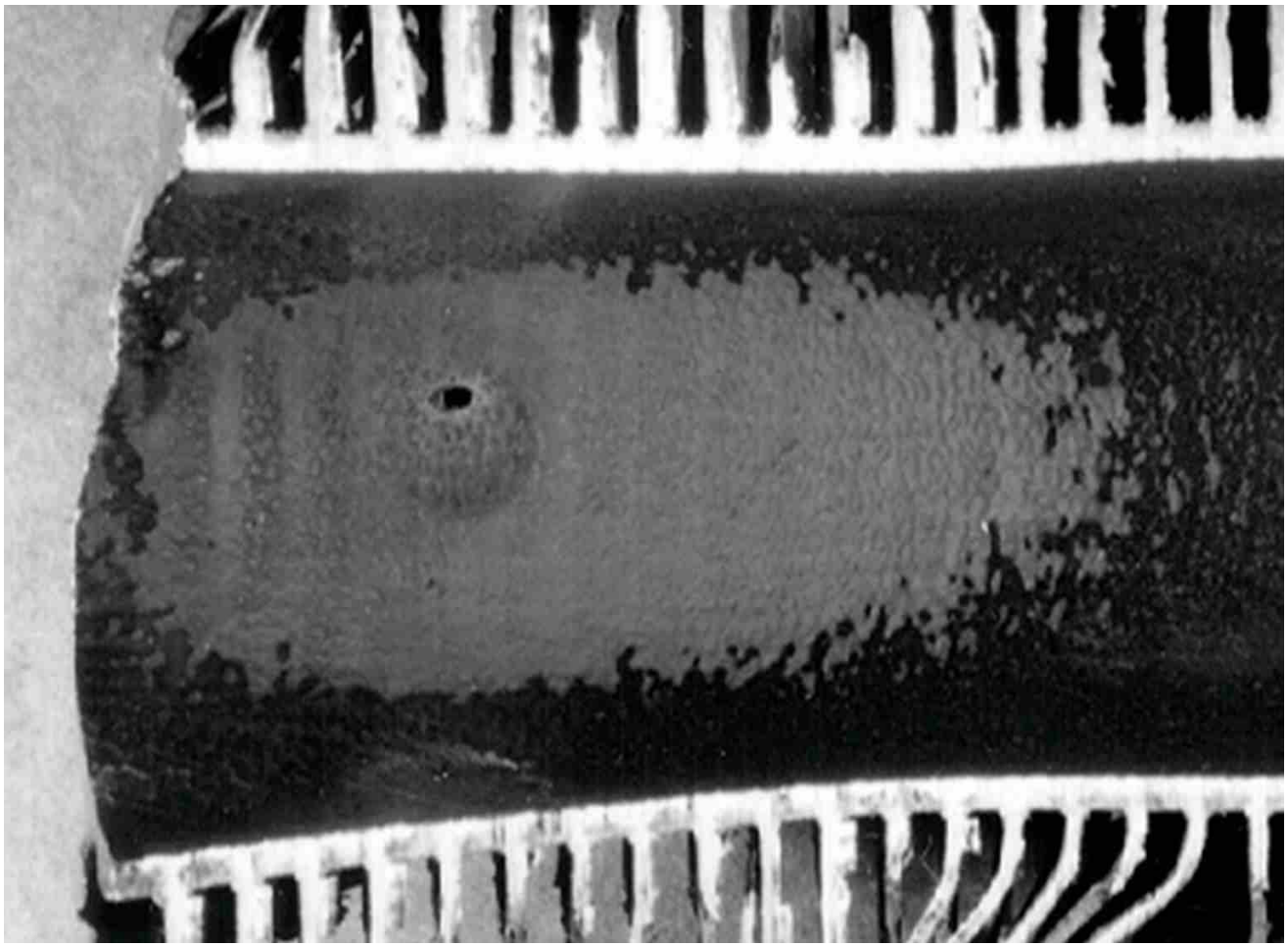
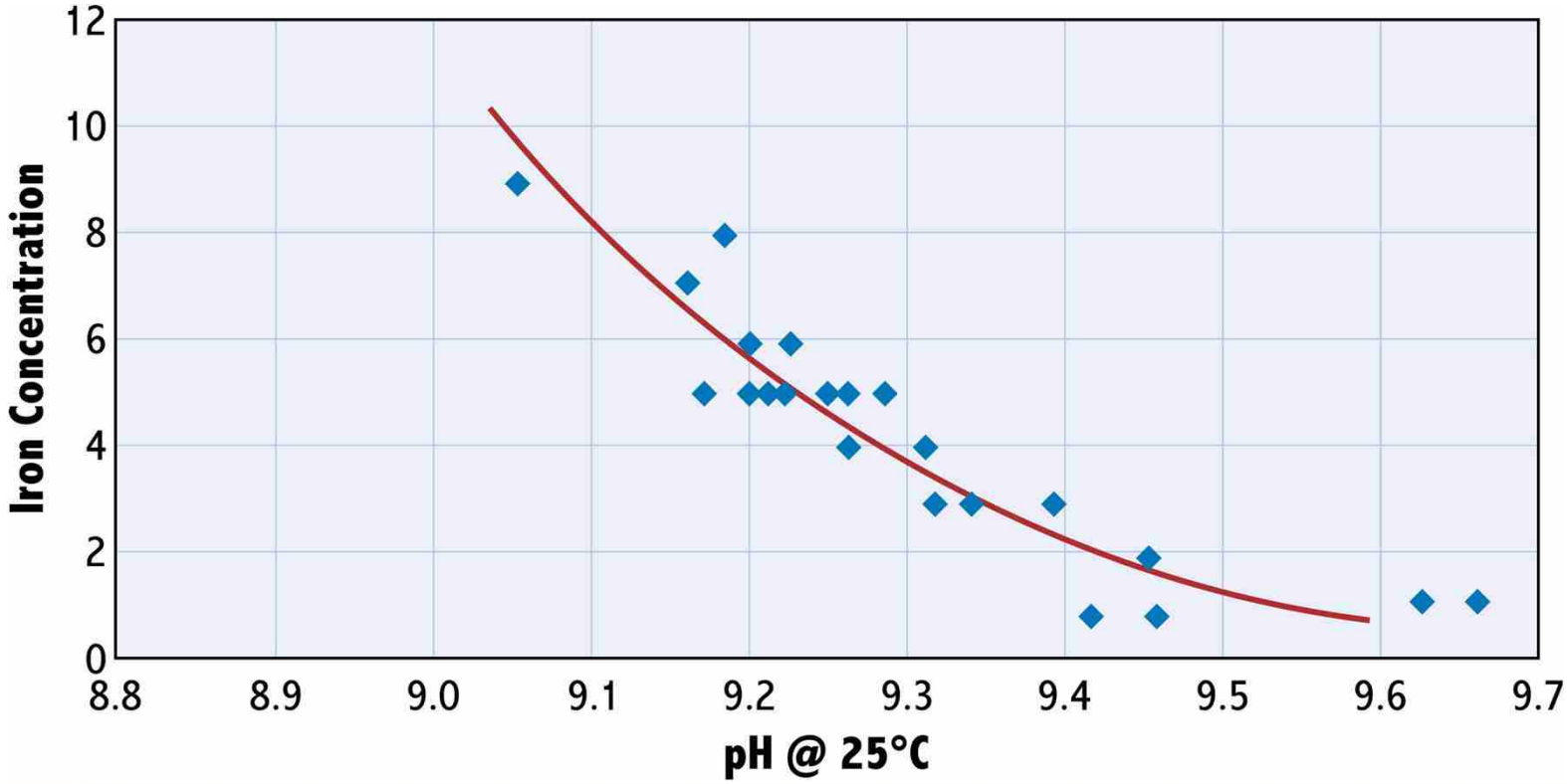
High pH Needed

- Reduces Flow Accelerated Corrosion (FAC) of steel surfaces (next slide)
- Reduces Iron Transport (subsequent slide)

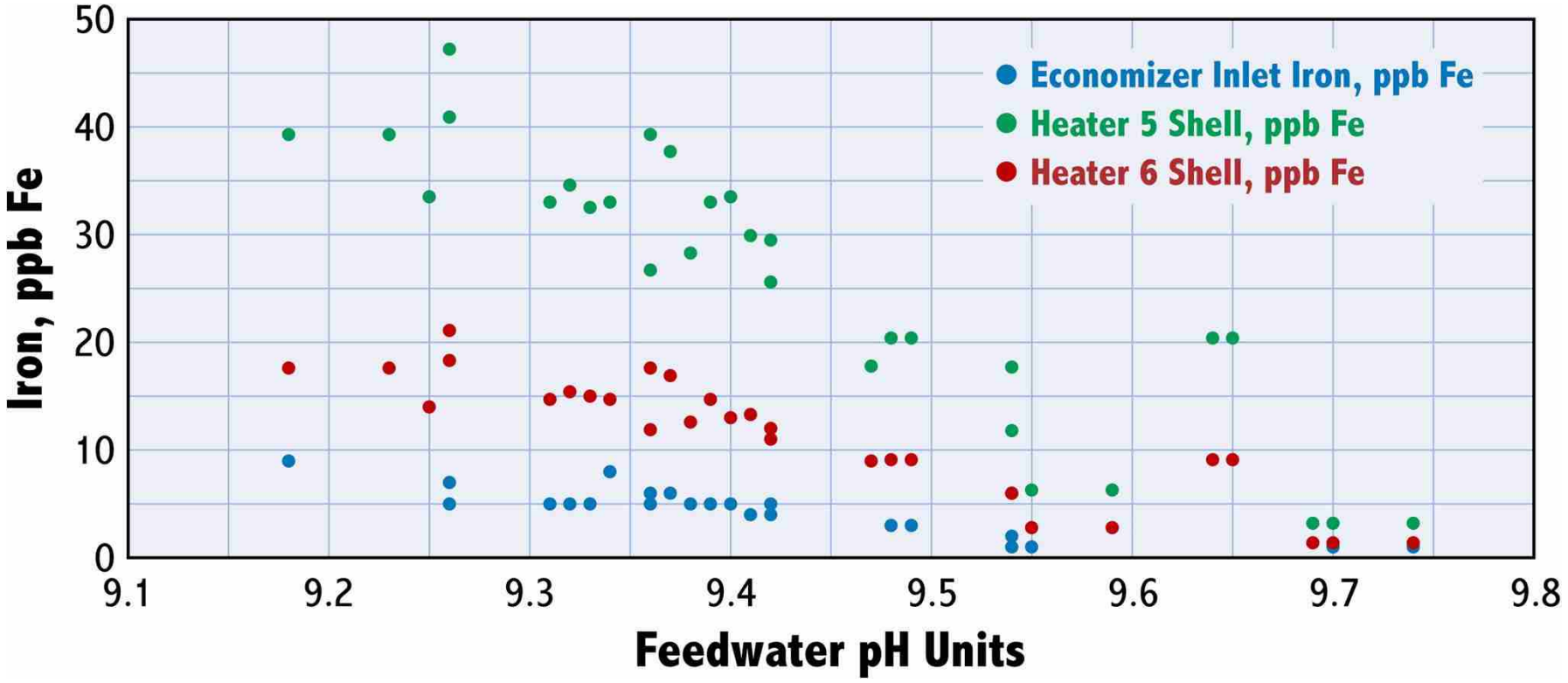
Flow Accelerated Corrosion (FAC) Failure in LP Evaporator Tube



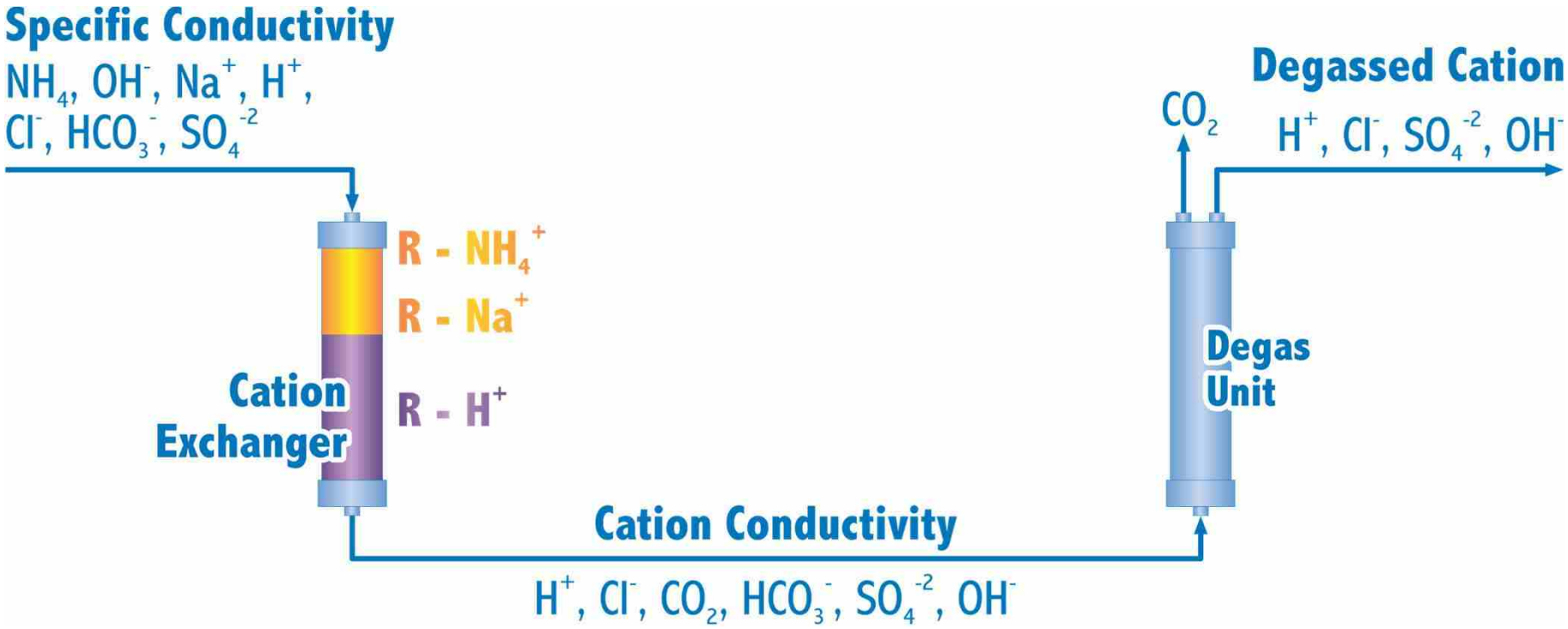
Corrosion Product Release for Carbon Steels as a Function of Feedwater pH



FAC is Greater With 2-Phase Flow (Iron in Water from Shell Sides of FW Heaters 5 (234 psig) and 6 (552 psig)



Cation and Degassed Conductivity



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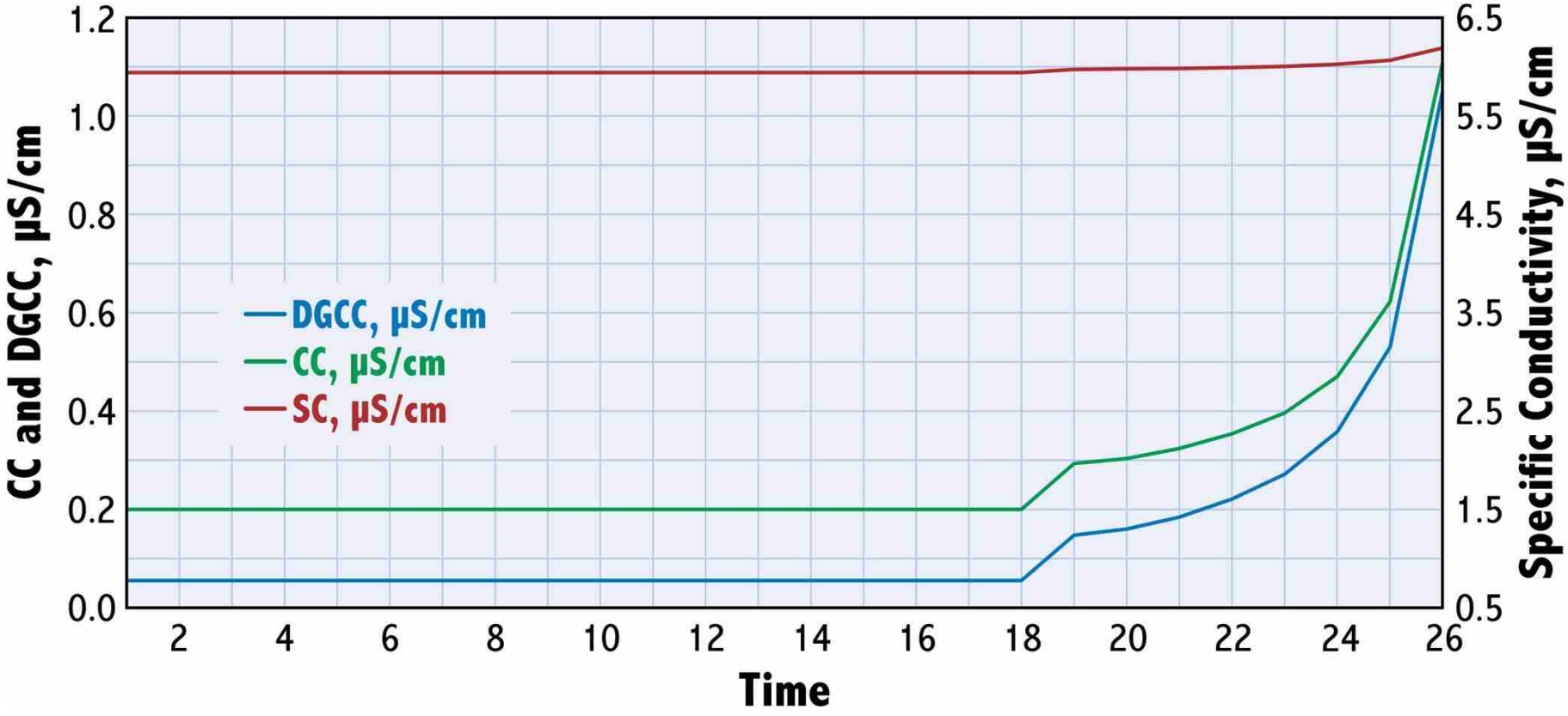
Compare Measured/Calculated pH

- Use SC and CC to cross-check online Preheater Inlet (PI) measured pH against the calculated pH: $pH = 8.55 + LOG(SC - CC/4)$
- Caution. If you have a bad intrusion of acidic material (acid regenerant, glycol, anion exhaustion, contaminated process condensate, etc.) CC will be very high, the SC controller for ammonia may shut down, but **the calculated pH formula fails (will indicate it is alkaline when it is acidic).**

Projected Seawater Contamination Effect on SC, CC and DGCC



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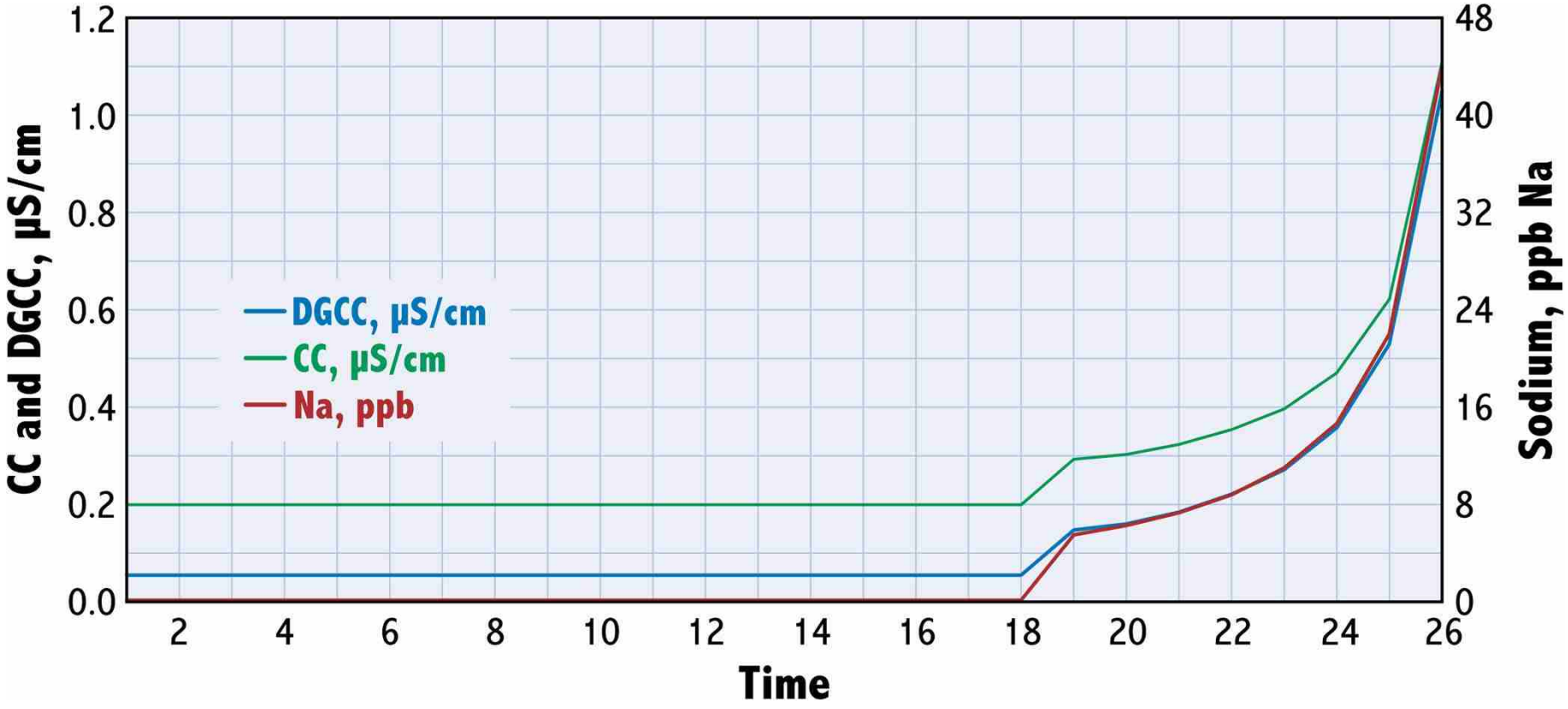
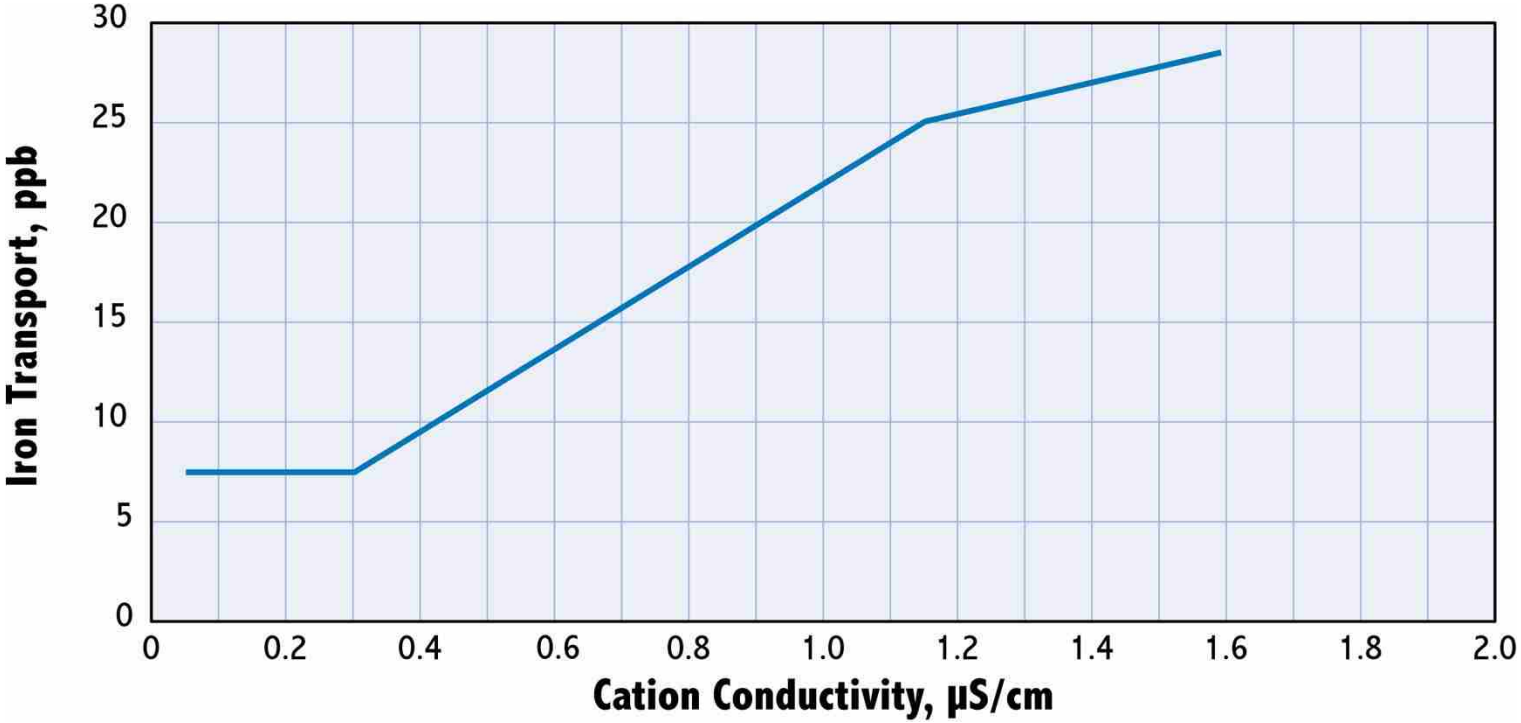
Effect of Seawater on CC, DGCC, and Sodium (Na)



Conductivity Vs Corrosion Product Transport



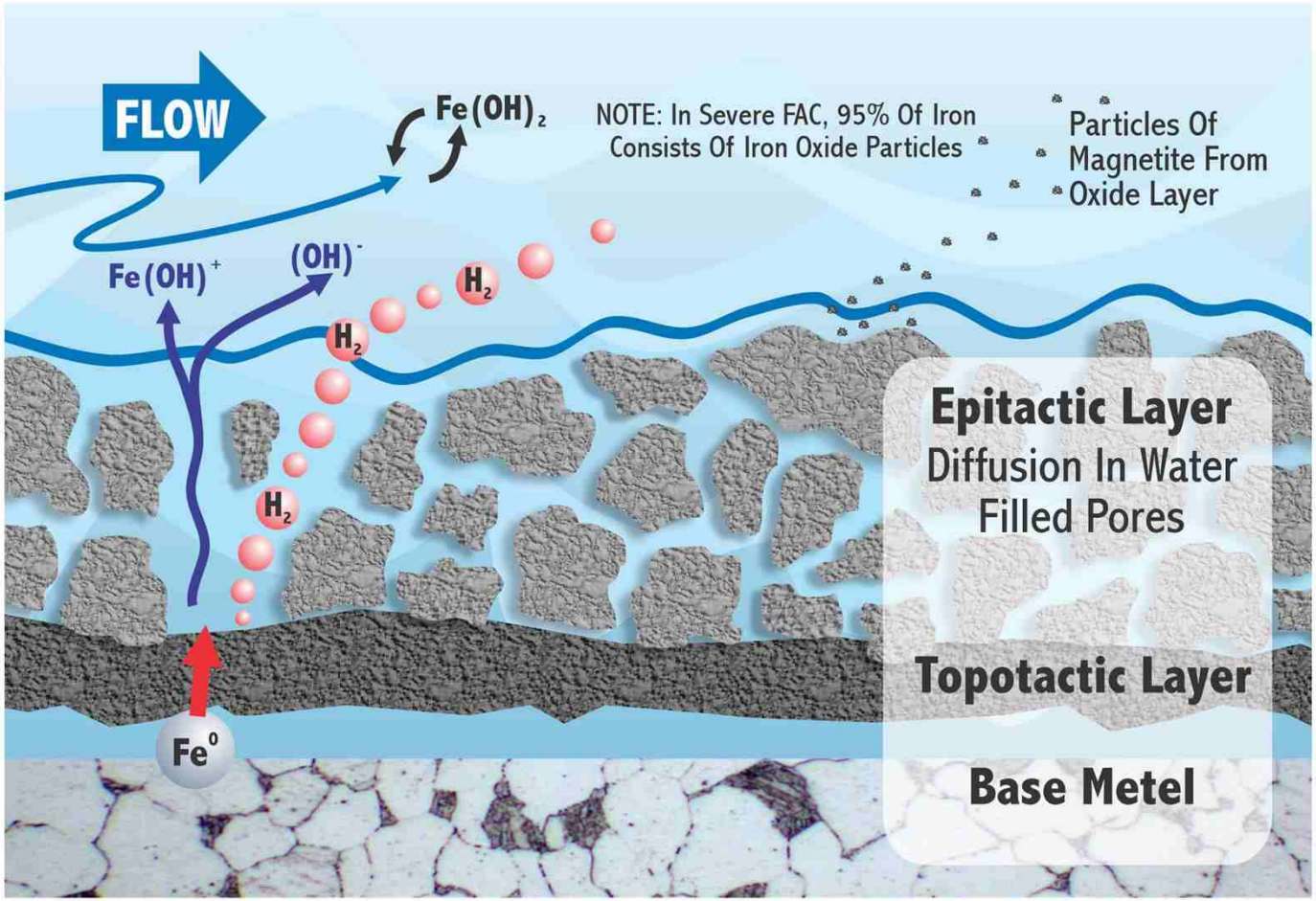
SOURCE: G. V. Vasillenko. "Quality Guidelines and Water Chemistry Control in Supercritical Pressure Units." Proceedings of the Third International Conference on Improved Coal-Fired Power Plants, EPRI Report TR-100848

Dissolved Oxygen (DO)

- OT (Oxygenated treatment): If CC <0.15 µS/cm & single phase (no boiling), you can maximize FW DO (target 30-50 ppb) to form a mixed oxide - greatly reducing single phase flow accelerated corrosion (FAC).
- AVT (O) – Goal of most all steel combined cycle plants because less restrictive CC limit (<0.2 µS/cm). A lesser amount of feedwater DO (e.g., 5-10 ppb) is used, because it often is enough for a significant reduction in FAC.
- Note: The former EPRI target of 5-10 ppb is suggested to start as a compromise of potentially competing concerns [Although EPRI now allows an AVT(O) DO range to 5-30 ppb DO as of 2020].

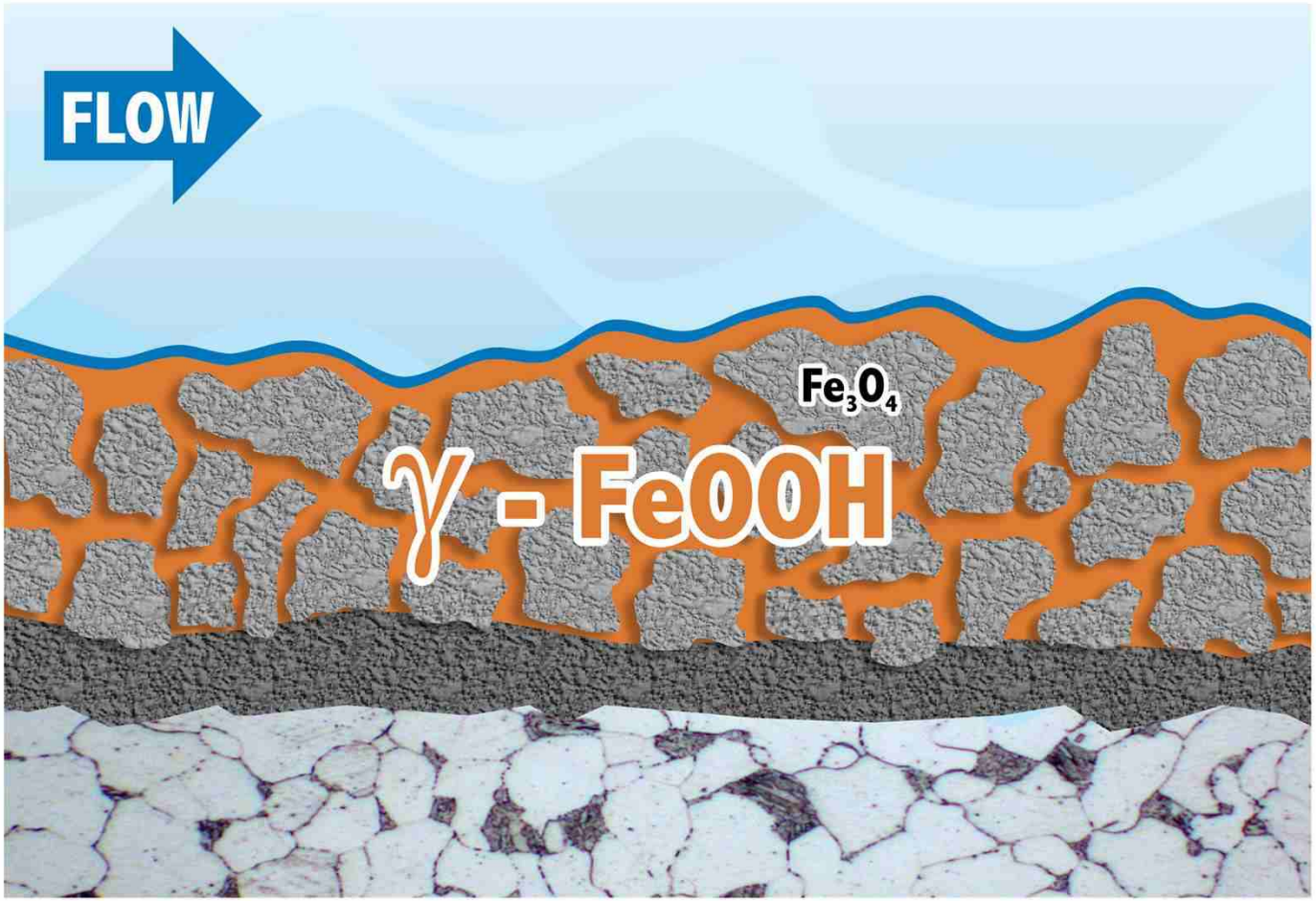
FAC - Direct Dissolution Of Iron

- Passive (Topotactic) Layer Protective, but Allows Some Dissolution to Continue

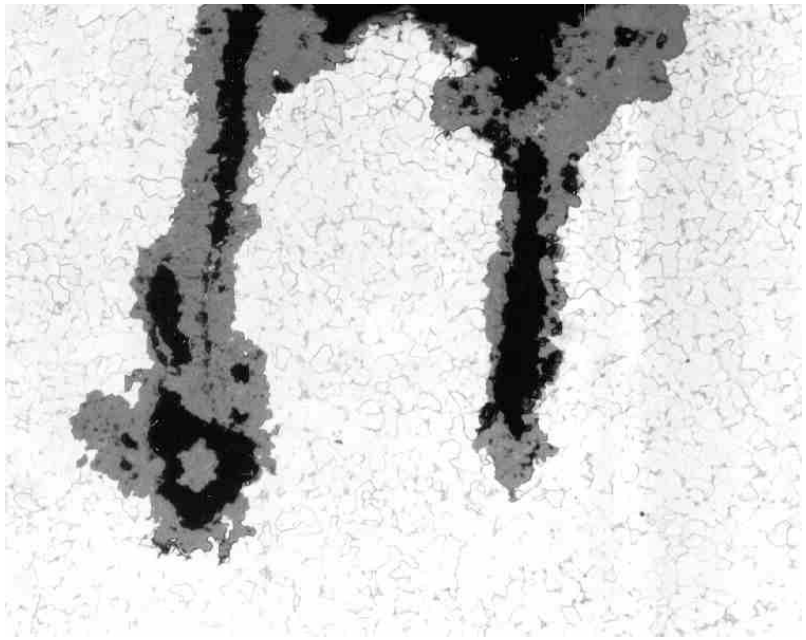


FAC - Mixed Oxide Fully Developed

- With oxygenated treatment all pores in magnetite are filled in with the lower solubility ferric oxide, which slows corrosion.



Corrosion Fatigue (CF) and Stress Assisted Corrosion (SAC)

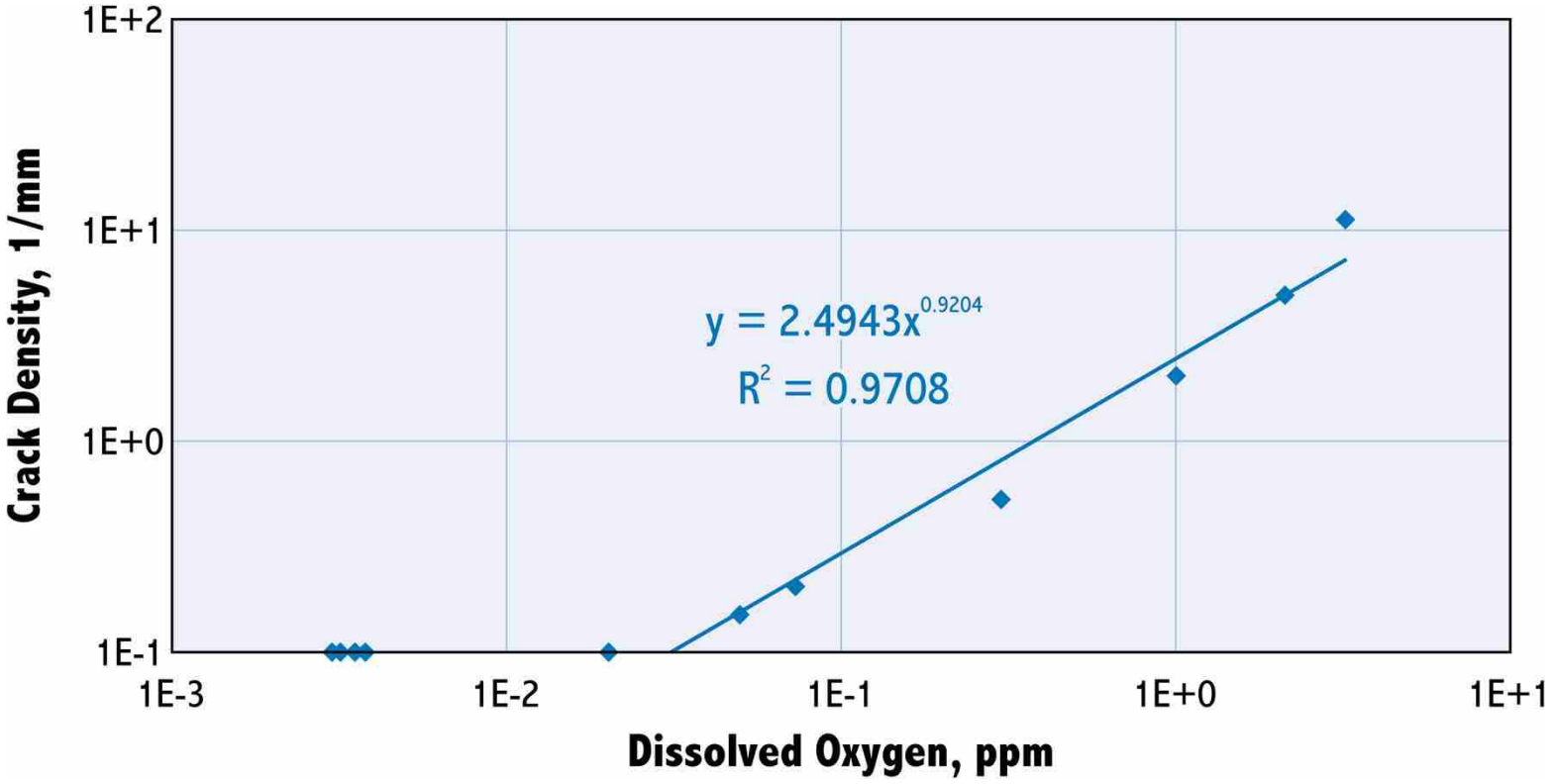


- CF and SAC both increase with increasing stress level, stress cycles, and DO, and with decreasing pH.
- Metallograph at left is SAC on the waterside surface of an economizer tube that received 300°F (149°C) feedwater and had excessive DO (fluctuated from 40 to 800 ppb) due to problems with the feedwater pump seals. [Labuda 2005]

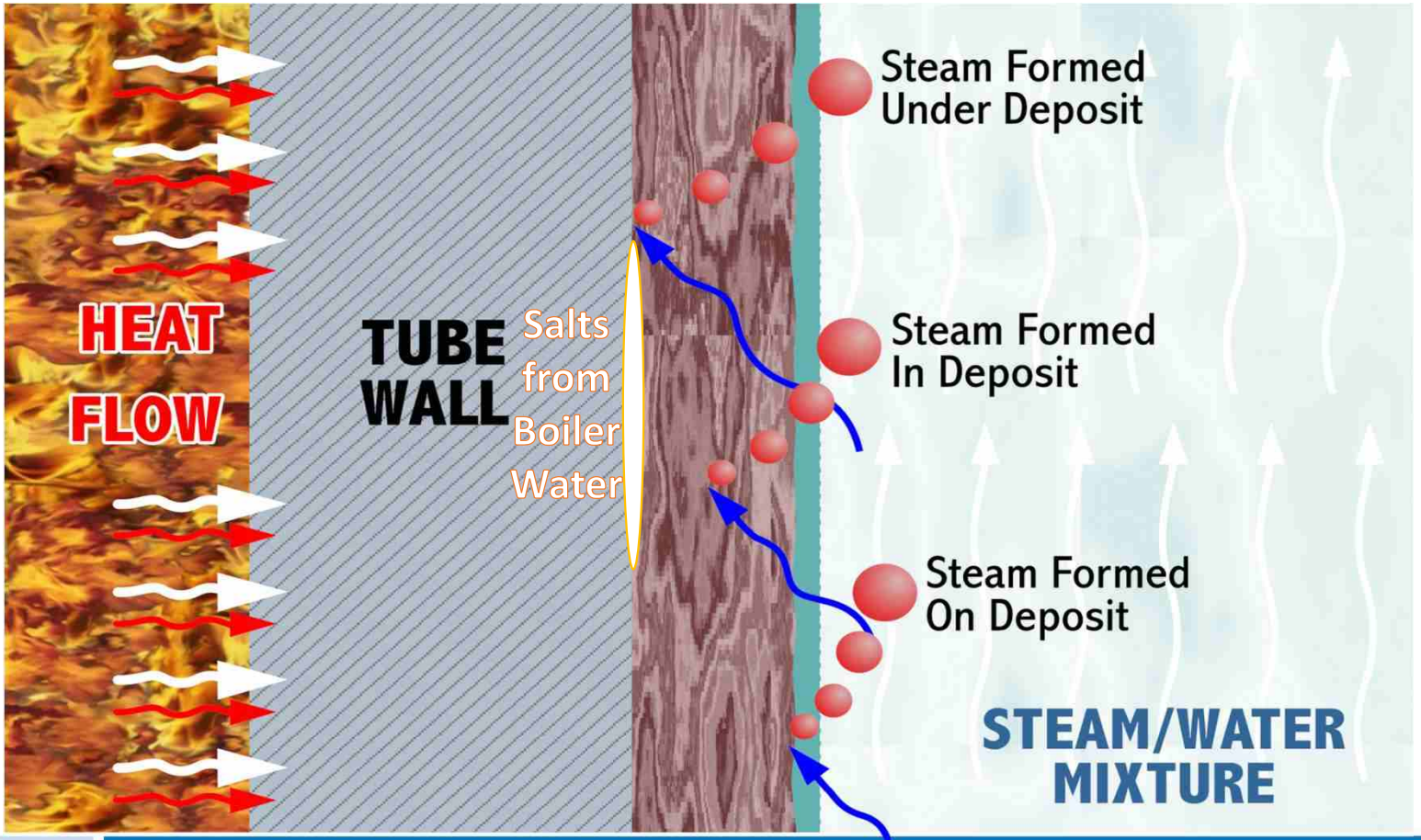
Stress Assisted Corrosion

- High FW DO levels may contribute to stress assisted corrosion (SAC) or corrosion fatigue (CF) of HP/IP Economizers or Evaporators. Dong Yang reported that stress assisted corrosion (SAC) initiation and propagation can occur in SA210C steel at and above 20 ppb of DO at 572 °F (300°C). (While DGCC not reported, I estimated DGCC of 0.35 µS/cm and a pH of ~7 at 25°C due to sodium sulfate resulting from trace sodium sulfite addition present during the testing).

Effect of Dissolved Oxygen on SAC at 300 °C (572°F)



Evaporative Concentration Under Deposits



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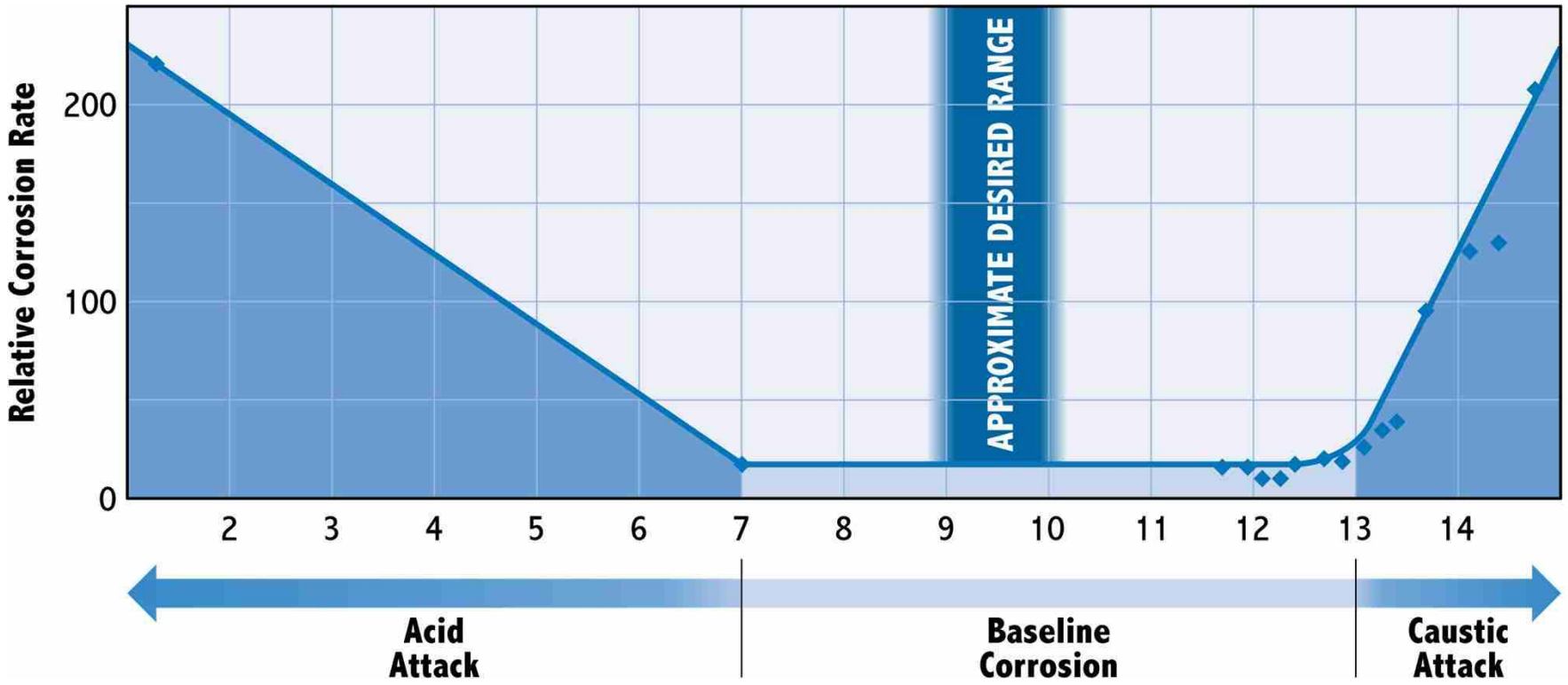
Effect of pH on Corrosion Rate of Steel by Water



Evaporator & Underdeposit Evaporative-Concentration and pH

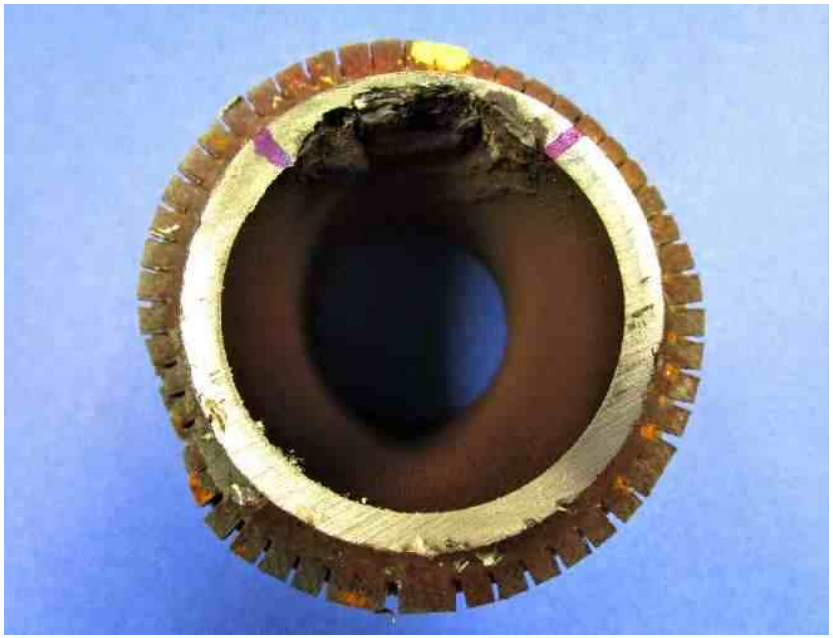
- Feedwater Concentrated 1000X in Evaporator at 0.1% Blowdown
- Evaporator Water Concentrates at Tube Surface (e.g., by 1000 Times) as Compared to Bulk Evaporator Water.
- Feedwater Could be Concentrated 1,000,000 X at Evaporator Tube Surface
- **Caustic Attack:** pH↑ – (e.g., pH at Tube Surface can be 3 pH Units Higher than in Bulk Evaporator Water Sample).
- **Acid Attack:** pH↓ – (e.g., pH at the Tube Surface can be 3 pH Units Lower than in Bulk Evaporator Water Sample).

Comparison of Acid and Caustic Attack Rates

- **New HP Evaporator Tubes Typically Are 0.12-0.20 inch Thick**
- **Acid Attack**
  - Max literature reference from acid attack >0.39 inch/year.
  - Causes Pitting-Type Corrosion.
  - Can Rapidly Lead to Hydrogen (H_2) Damage (For example in a 2100 psig HP Evaporator: 0.008 Inch Affected in 35 hours <8.0 + **4.25 hours <7**, Min. pH 4.75 with 165 g/ft^2 Deposit).
- **Caustic Attack and Phosphate (PO_4) Gouging (Acid Phosphate Corrosion)**
  - Max Observed Caustic Gouging Rate: 0.08 inch/year
  - Previous Max Observed Phosphate Gouging Rate: 0.073 inch/year
  - **New PO_4 Gouging Incident: Average 0.167 inch/year thinning where chloride was present along with the PO_4.** 952 hours HPE online pH < 9.0 (likely acidic nonvolatile pH), and 143 hours HPE online pH >10.0 (free caustic – although no residual signs of caustic attack were noted in the failure). The tube failed 415 days after installation. No H_2 damage at the point of failure (wall thickness at lip was 0.001 inch). The H_2 damage noted above was in a gouge, but away from the failure.

2100 psig Evaporator Failed in 415 Days of Tube Installation

Cross-cut of Failed Tube Before Fin Removal



Cut through point of failure prior to mounting

Danger of Bad Evaporator Water pH

- **Immediately Remove Boiler from Service** if Boiler Water **pH <8.0**.
- Corrosion May Occur in Minutes from Very Low pH.
- pH <4.0 - 4.5 is Free Mineral Acid Range.
- pH Under Deposits.
  - If Concentrates 1000-Fold.
  - If Inorganic Anions (e.g. Chloride) pH can be 3 Units Lower than Bulk Solution.
- You also should set a maximum pH and very tight pH control range for your system based on your normal ammonia/amine concentrations and other treatment chemicals.

Salt Deposition and Corrosion[a]

- All Turbines can be Contaminated with Sodium Chloride Based on Low Solubilities.
- Even with Oxygenated Treatment (100 ppb O_2), Oxygen During Operation will be Very Low (<0.0014 ppb O_2). Therefore, **Operational Corrosion is Unlikely.**
- **Corrosion is Expected on Shutdown** in a Moist, Aerated Environment.
- **Nitrogen Padding (99.9% Pure) can** Keep Oxygen Below 40 ppb and **Control Corrosion**.
- **Dry Air can Protect Against Chloride Attack** Below RH <64%, But <1.4% RH is Needed for Caustic. (RH = Relative humidity)

(a) Bellows, Power Plant Chemistry, 2008, 10(2), p. 121.

Estimated from Bellows,
2018 International Cycle Chemistry Conference EPRI

Condition	Approximate Deposition Rate, g/m²/year			
	HP	IP	LP	Sum
FULL LOAD, 0.5 ppb NaCl	--	0.0-1.3	0.5-1.1	0.5-2.4
60% LOAD, 0.5 ppb NaCl	--	0.0-0.4	0.4-1.0	0.4-1.4
14% LOAD, 0.5 ppb NaCl	0.0-0.3	0.4-1.1	1.0-2.1	1.4-3.2
FULL LOAD, 10 ppb NaCl	0-13	13-30	9-23	22-66
60% LOAD, 10 ppb NaCl	0-3	3-11	11-21	14-35
14% LOAD, 10 ppb NaCl	4-7	8-22	21-43	33-72

Silica Deposition on Steam Turbines

- **At 100 ppb Silica**, Can Get 80 µm Deposits/Year in LP Turbine From Silica, But Actual Deposition is Much Greater due to Iron Going Down with the Silica.(b)
- At Very Low Loads (14%) and High Silica (**100 ppb**), Silica can Deposit in the HP Turbine due to Low Pressures.(a)
- A 87-mW Turbine had **20-100 ppb Silica for 3000 Hours**. Passed 2-3 kg Silica through the Turbine, But Only 145 Grams of Silica was Found on the Turbine. This corresponds to **deposition of 5-7% of Inlet Silica**.(a)
- **"Older Turbine Blades** with Rough Surfaces Tend to **Collect Deposits More than Smooth New Blades."**(a)

(a) Power Plant Chemistry, 2006, 8(5), p. 271.

(b) Power Plant Chemistry, 2008, 10(2), p. 122.