EPRI ELECTRIC POWER RESEARCH INSTITUTE

ACC Chemistry and the Use of Amines

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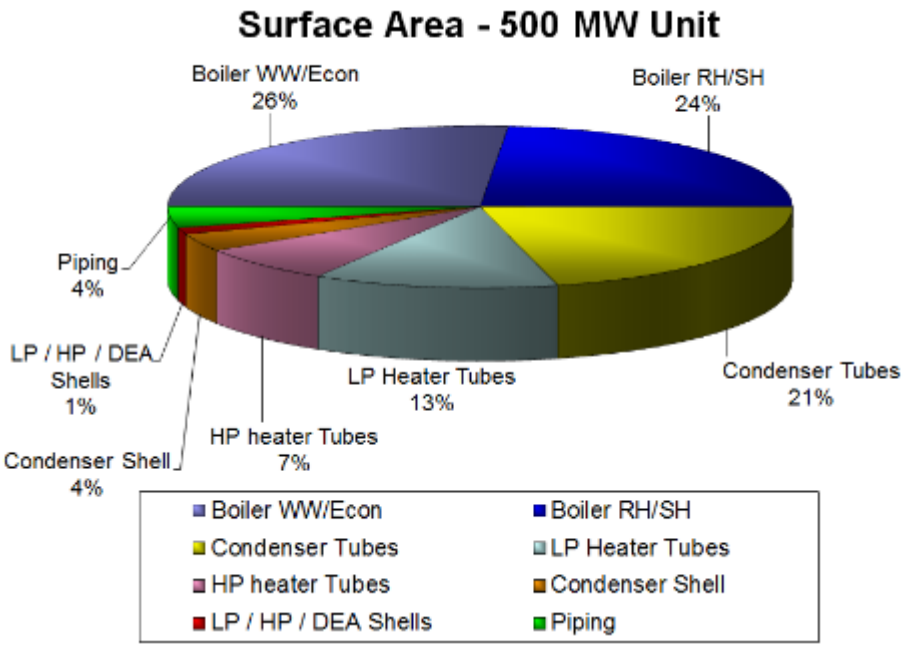
Agenda

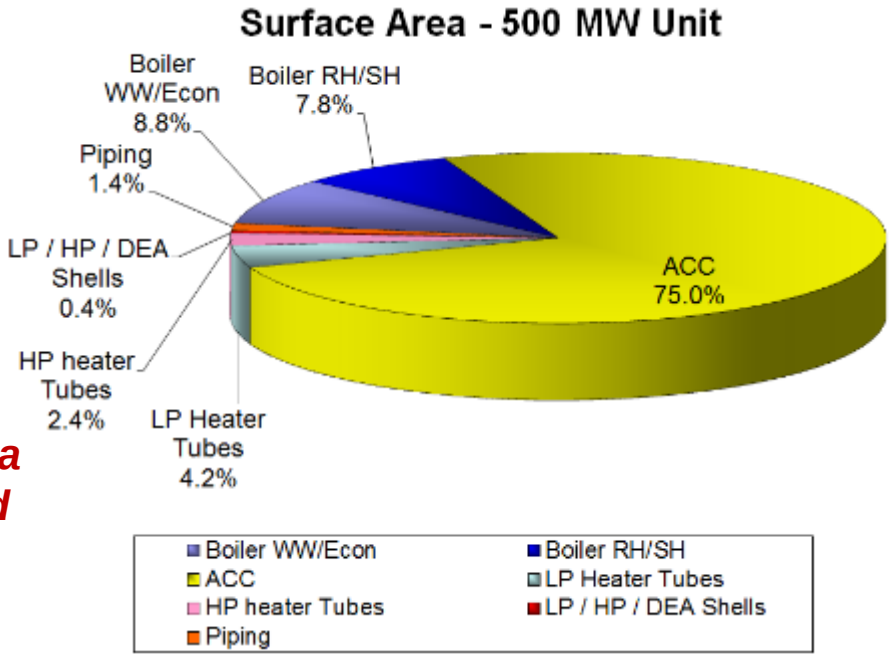
- Challenge of ACC Chemistry Control
  - Discussion of the fundamental problem
- Chemistry Control Options
  - Options without advanced amines
  - Neutralizing Amine use
  - Filming Amine use
- Path Forward

Chemistry Challenge

- Massive Surface Area
- Carbon Steel Construction
- Two-phase Environment
  - Significant Iron Corrosion Product Release
- Significant Air-in-leakage
  - Aggravated by operating at very high pH

Unit with ACC ~3x surface area of water cooled unit

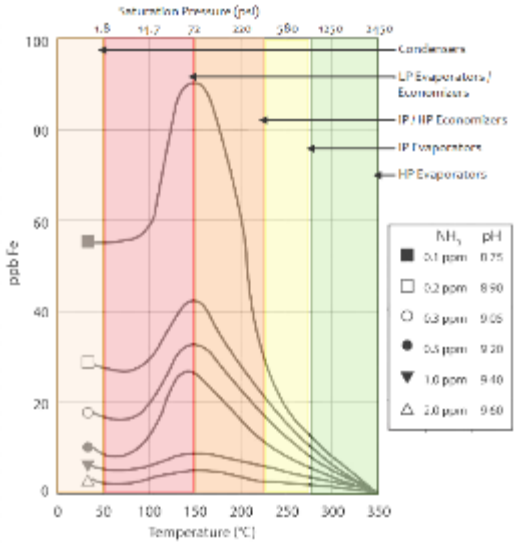




Air Cooled Condensers

Two Phase Lowered Liquid Phase pH

Fully Condensed	75% Steam
10	9.4
9.8	9.2
9.6	9.1
9.4	8.9
9.2	8.75



Elevated Iron is due to lowered two-phase pH in contact with tubing

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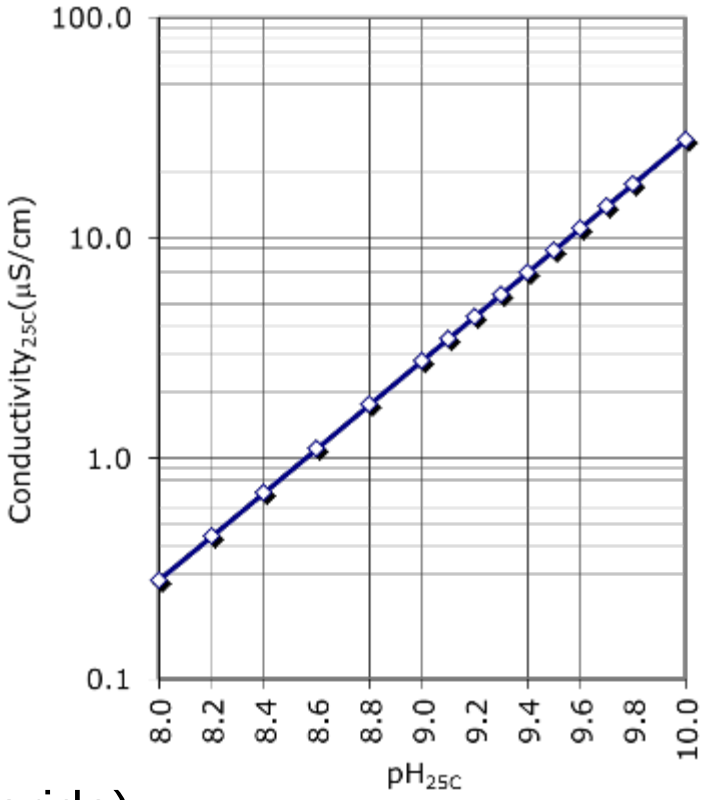
Chemistry Control with Ammonia

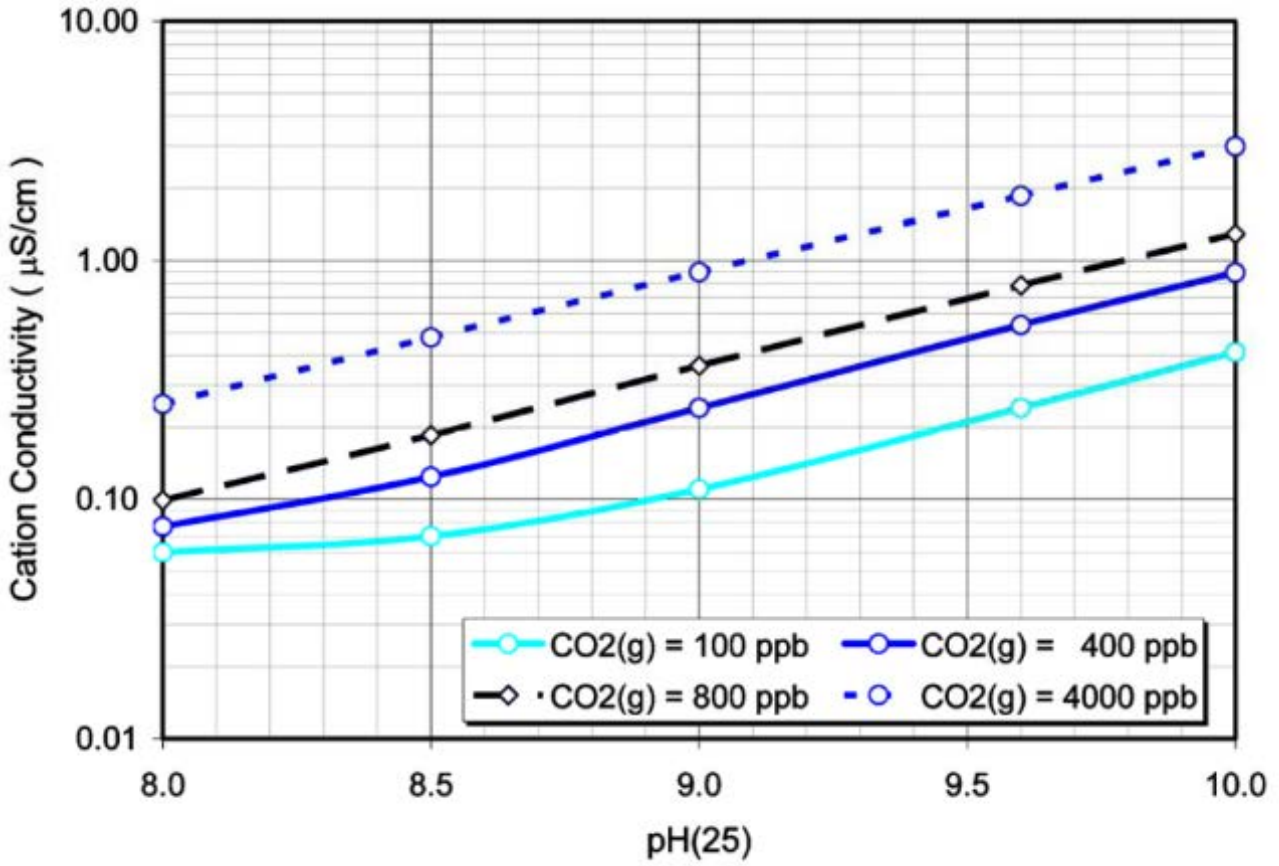
- Increase pH to 10 with ammonia
  - >10 ppm of Ammonia
  - Safety/Environmental issues
  - Large amount of chemical handling
- Deep bed polisher must be run in ammonia form
  - Increases leakage (chloride)
  - Can cause significant sodium throw
- Can significantly increase carbon dioxide ingress



pH	Conductivity (µS/cm)	Ammonia (ppm)
10.0	27.747	11.812
9.8	17.507	5.105
9.7	13.907	3.399
9.6	11.047	2.286
9.5	8.775	1.555
9.4	6.970	1.070
9.3	5.536	0.746
9.2	4.398	0.527
9.1	3.493	0.377
9.0	2.775	0.274
8.8	1.751	0.149
8.6	1.105	0.085
8.4	0.698	0.050
8.2	0.442	0.030
8.0	0.280	0.018

Carbon Dioxide Absorption and pH

- **If air enters cycle in steam phase the cation conductivity increases from CO_2** ***(dependant on pH of condensate and partial pressure of CO_2)***



Amine Treatment

- **Neutralizing Amine** (Generic Chemicals)
  - Similar to ammonia
    - adjust pH
    - minimize corrosion through solubility minimization
  - Generally short chain organic with an amine group (NH)

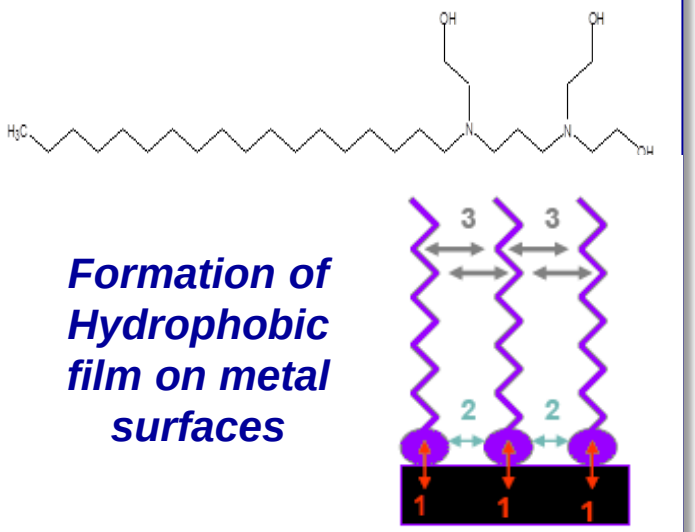
The 3D's

Dissociation: $NH_{3(aq)} + H_2O \Leftrightarrow NH_4^+ + OH^-$

Distribution: $NH_{3(aq)} \Leftrightarrow NH_{3(g)}$

Decomposition: $Amine \Rightarrow NH_3 + TOC + CO_2$

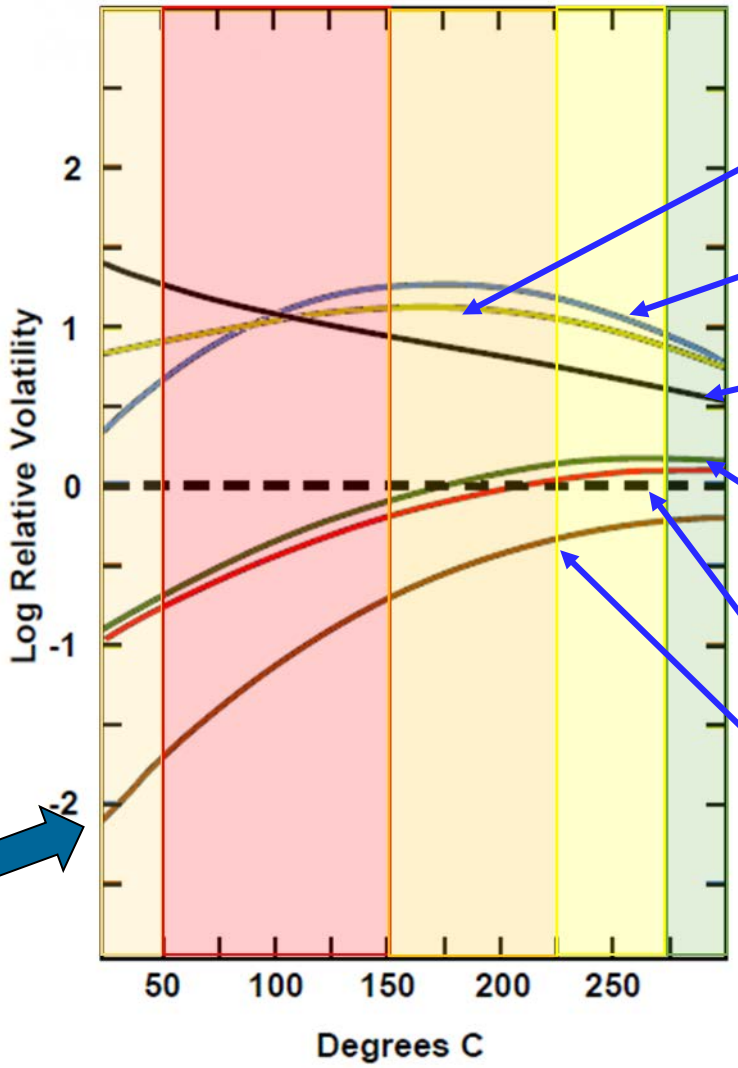
- **Filming Amine** (Proprietary Chemicals)
  - Longer chain organic not like ammonia
    - Hydrophilic and hydrophobic end
    - Film metallic surface
    - Minimize corrosion through breaking the corrosion cell (requires metal + water + oxygen)

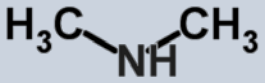
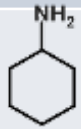
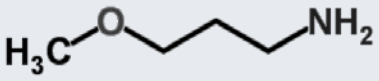
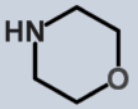


Formation of Hydrophobic film on metal surfaces

Neutralizing Amines – 3D's: Distribution

- Lower Volatility is Stronger affinity for Liquid Phase



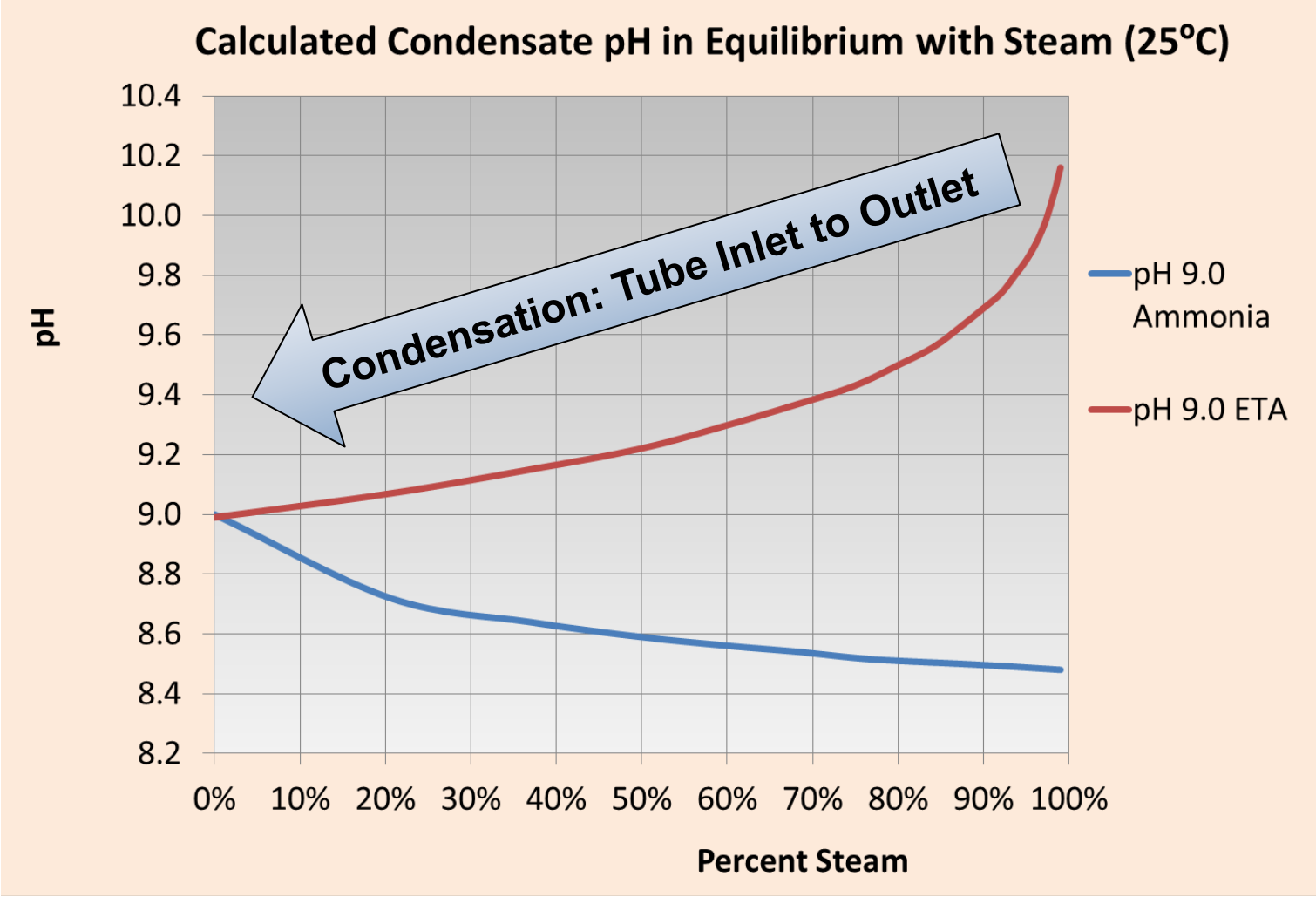
Abbrev.	Structure
DMA	
CHA	
NH3	NH_3
MOPA	
Morph	
ETA	

Ethanolamine potentially can significantly improve ACC corrosion

ACC Two Phase Flow

With neutralizing amines possible to have higher pH in the condensing tubes than in the fully condensed solution

(800 ppb ETA)



Neutralizing Amine Application

Combined Cycle Plant with ACC

2009 Treatment

- *All Ammonia*
- *pH Target Value 9.1-9.2*
- *Condensate Iron >100 ppb*

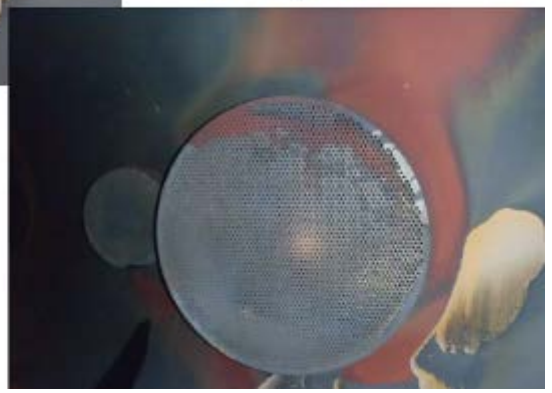
2011 Treatment

- *Ammonia / Ethanolamine*
  Applied 4:1 Blend
- *pH Target Value 9.1-9.2*
- *Condensate Iron <10-20 ppb*

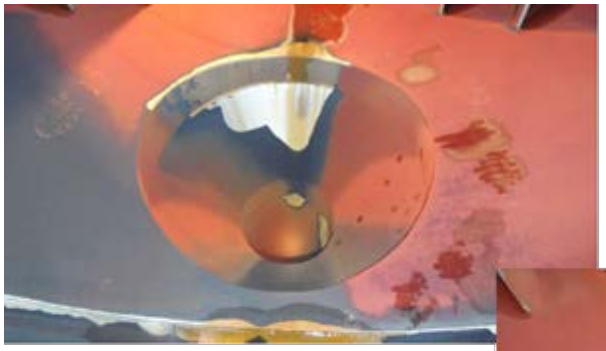
2009 inspection

Source Bill Stroman / Neil Hawkins

2011 inspection



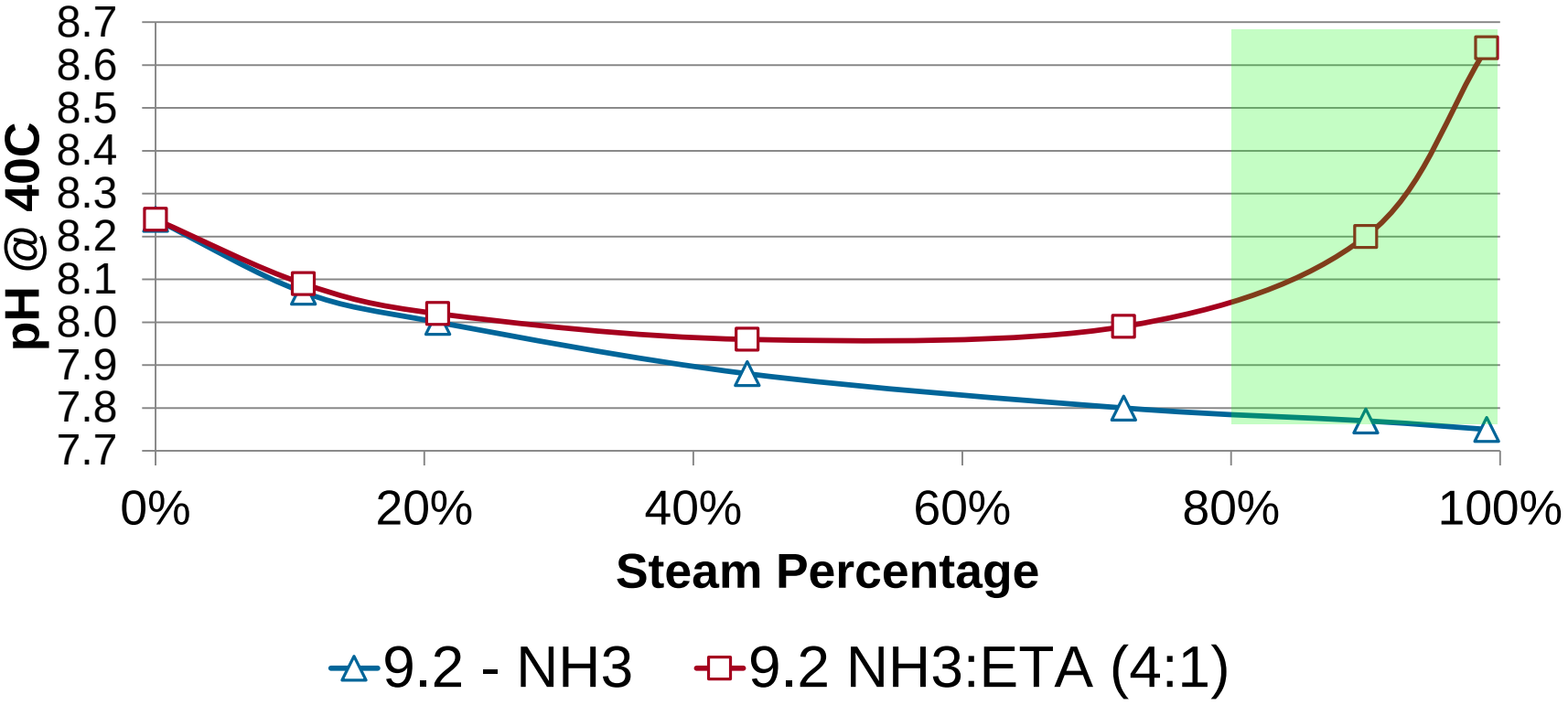
2011 inspection



2009 steam turbine condensate Duct drain.

Amine	Abbreviation	Chemical Formula	Molecular Weight (g/mol)	Structure
Ethanolamine	ETA	C_2H_7NO	61.08	HO—⟍—NH_2

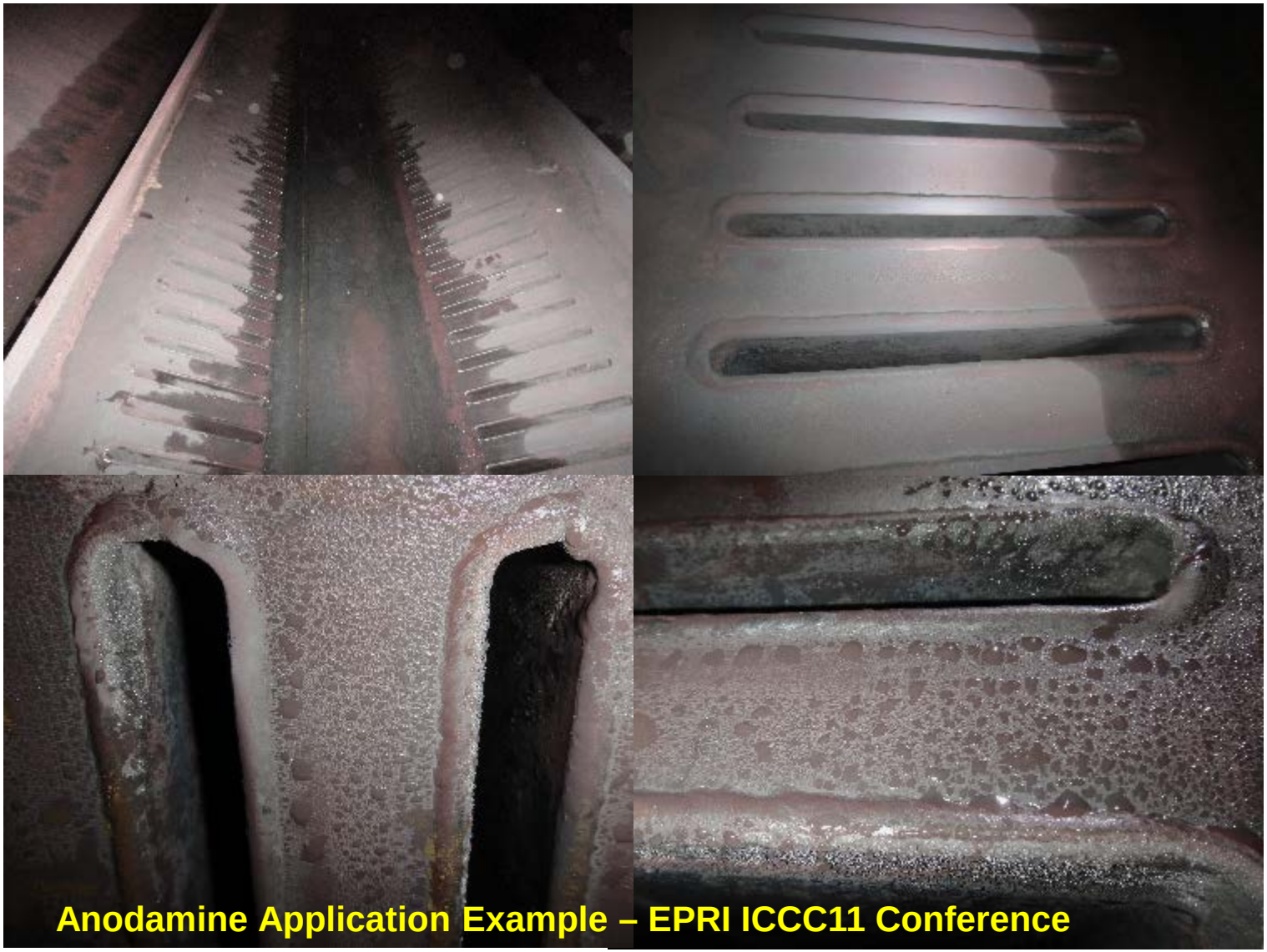
Modeling of Ammonia : Ethanolamine pH in ACC



- Only 120 ppb of Ethanolamine!
- Accomplished with ~500 ppb Ammonia

Filming Amine Application

- 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 °F / 568 °C. Total generation capacity is 530 MW with two 134 MW Alstom Turbines.



Anodamine Application Example – EPRI ICCC11 Conference

Condensate pump discharge total iron < 3 ppb with frequent startups

Condensate pH 9.6-9.8, 10 on startup with ammonia

Consistent 500 ppb Filming Amine Residual

Control with Ammonia Alone

2015: 11th International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with HRSG: Olszewski

Nov 2011

Nov. 2014

Before pH Increase – Riser Duct Inlet Louvers

- Extensive white (bare metal) areas
- Serious risk “4” based on DHACI

After pH Increase – Riser Duct Inlet Louvers

- After ~16,500 hours of operation
- Few white (bare metal) areas
- Surfaces re-passivating
- No shiny surfaces
- Mild corrosion “3” based on DHACI

Control with Ammonia Only

2015: 11th International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with HRSG: Olszewski

Nov 2011

Nov 2014

Before pH increase

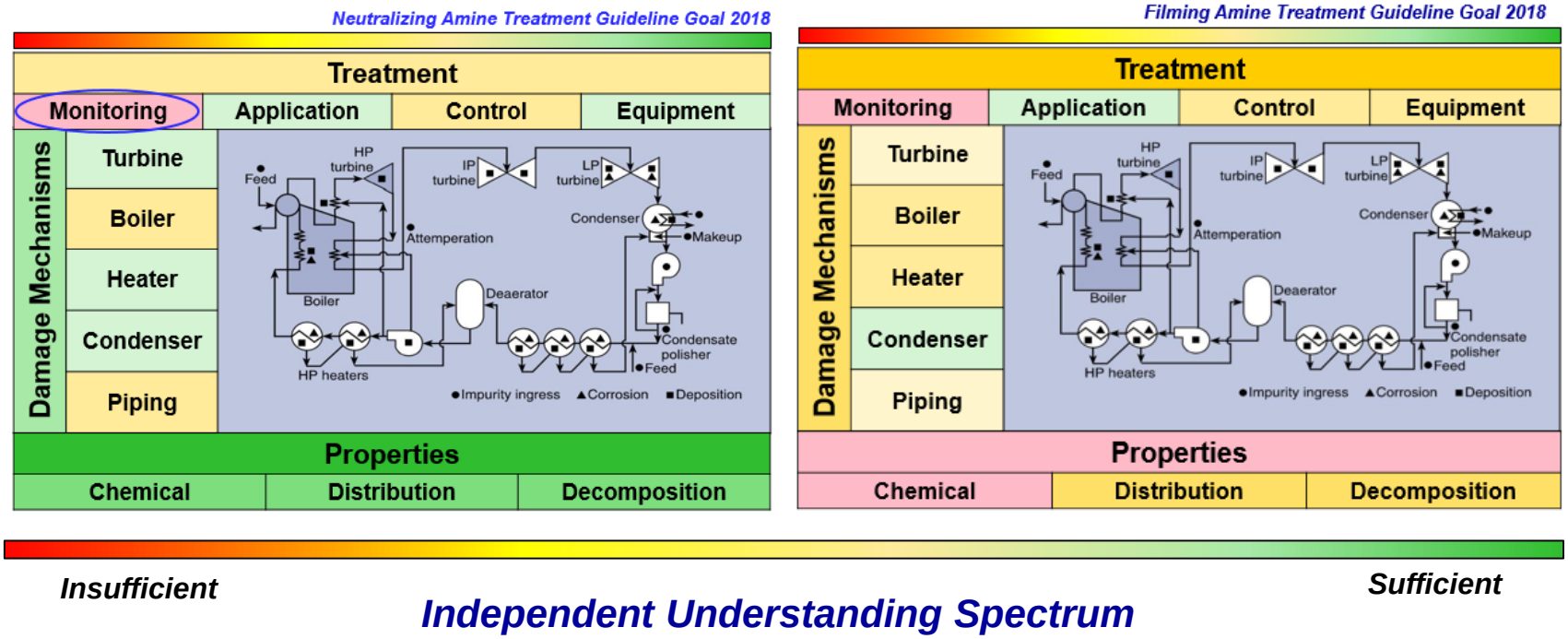
- pH of 9.2 in condensate
- FAC observed on
  - o Cross beams
  - o Exterior & Inside tube entries
- Serious risk “4” based on DHACI

After pH increase from 9.2 to 9.8

- After ~16,500 hours of operation
- Surfaces re-passivating (even on crossbeam)
- No shiny surfaces
- Minimal corrosion “2” based on DHACI

Present Conclusions

- Neutralizing Amine Properties demonstrate strong potential for use to mitigate FAC and improve pH in the PTZ and early condensate of Air Cooled Condensers (ACC).
  - Field data supports this using Ethanolamine
- Filming Amines (Anodamine) been demonstrated to improve surface appearance and reduce iron transport in ACC



Path Forward

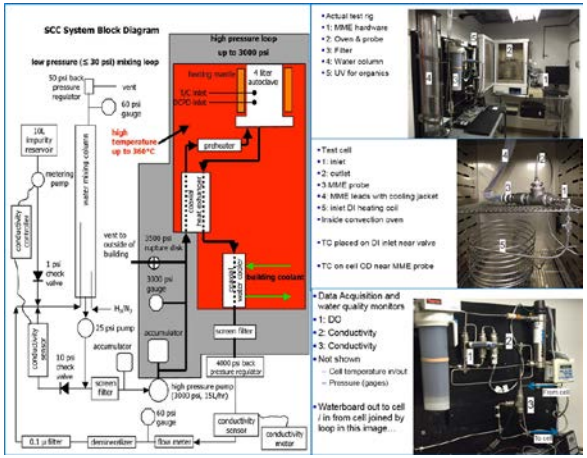
- EPRI has a goal for fully developed / research guidance for both Neutralizing and Filming Amine Treatments for all cycles by 2018

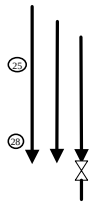
EPRI Has many corrosion testing rigs in the field looking to develop our knowledge further on amine treatments

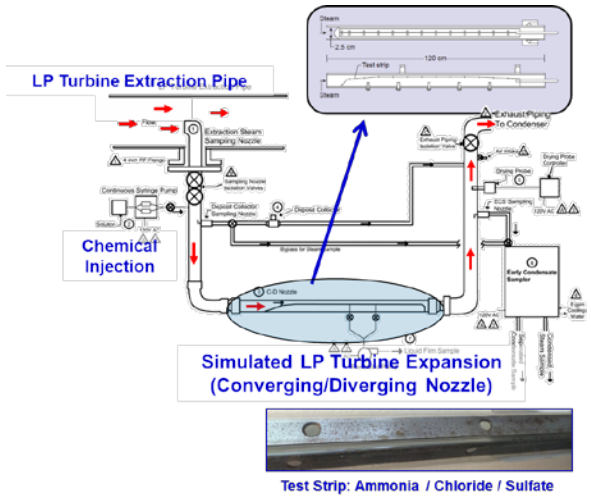
Filming Amine Treatment: P64 Research High Level Summary

- Monitoring 2015-2017
  - Working on methods for monitoring techniques Filming amines in water and for filming on internal components
- Damage mechanisms 2013-2017
  - Phase transition zone side loop testing (Marshall Steam Station) evaluating turbine corrosion
  - Planned Penn State online/offline corrosion testing rigs for boiler tubing
  - Ongoing feedwater system corrosion testing at DNV testing laboratories (Columbus Ohio)
  - Continuing work on evaluating impact on Flow-Accelerated Corrosion
- Equipment 2014-2017
  - Evaluating impact of filming amines on condensate polishing resin
- Application 2010-2017
  - Continuing to work with members applying filming amines to develop case histories
- Additional Benefits? 2016 forward
  - Evaluating projects to examine impact of filming amines on performance:
    - Dropwise condensation?
    - LP turbine efficiency?

Program 64 has a goal of developing a Filming Amine Treatment Guideline for Fossil Plants by Year end 2018







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