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# Gas Treatment Technology

BASF, Intermediates Division

## Solving the O<sub>2</sub> problem in Amine Units



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# But we don't have oxygen in our gas streams... Or do we?

Service	Source type	Typical oxygen levels (ppm)
Nat Gas Plants	Unconventional Drilling Basins	10-100
	Conventional Basins w/artificial lift (beam pump, vacuum systems)	1,000 – 5,000
	Coal Mine Methane & GOB Piles	5,000 – 10,000
Oil Refineries	FCC Off-Gas	300 – 1,000
	Delayed Coker	500 – 1,000



# Any why is it a problem ?

- Oxygen reacts with amines to in AGRUs to produce non-regenerable, corrosive amine salts and amino acids
  - Amine salts
    - Amine – Formate ( $\text{HCOO}^-$ )
    - Amine – Acetate ( $\text{CH}_3\text{COO}^-$ )
    - Amine – Oxalate ( $\text{C}_2\text{O}_4^{2-}$ )
    - Amine – Thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ )
  - Amino Acids
    - Glycine ( $\text{NH}_2\text{-CH}_2\text{-COOH}$ )
    - Bicine – (aka: N,N-Bis(2-hydroxyethyl)glycine)

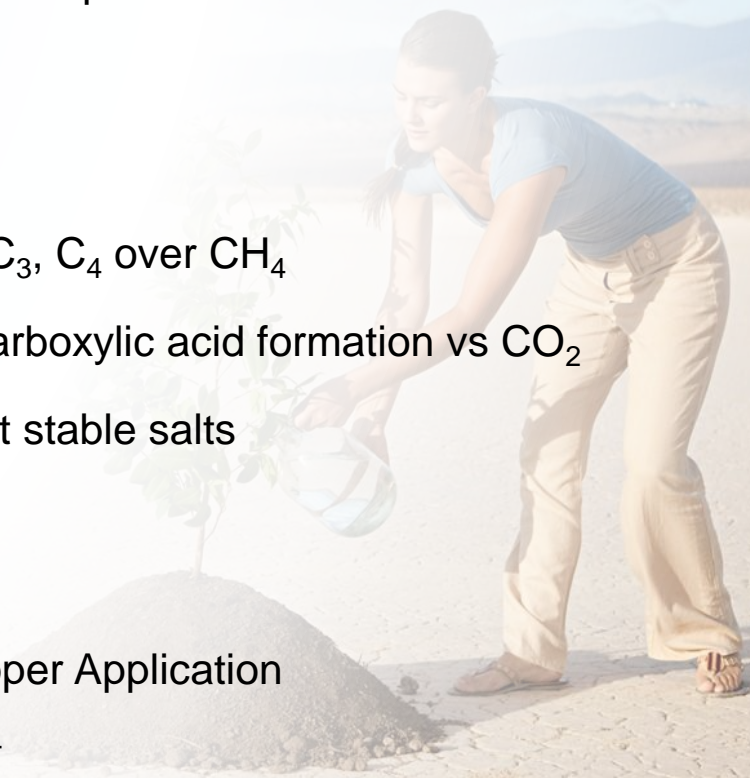




# Technologies for removing Oxygen from Transmission Gas and Refinery Off-Gases

- Trimeric Corporation paper (2011 LRGCC)
  - Catalytic Oxidation - Deoxo-Catalyst (Non-regn), X-O<sub>2</sub><sup>TM</sup>, PuriStar<sup>®</sup> (regn)...etc
  - Solid Scavengers – Fe<sub>2</sub>S<sub>3</sub> on wood chips → expired patent
- Issues with Catalytic Oxidation – X-O<sub>2</sub><sup>TM</sup>
  - Target Reaction 
$$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2$$

At the reactor conditions, oxygen prefers C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> over CH<sub>4</sub>
  - Shale Basin Gas is not pure CH<sub>4</sub>, resulting in Carboxylic acid formation vs CO<sub>2</sub>
    - Carboxylic Acids + Amine → Corrosive heat stable salts (formates, acetates, oxalates)
- Challenges with current technologies
  - CapEx, Available Space for Equipment or Improper Application



# Technologies for removing or reducing corrosivity of degradation products

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- Removal of degradation products after they reach intolerable levels

- Thermal Reclaimer (limited to ADEG<sup>®</sup> or MEA) **[ABPG]**

- Increases amine losses, if not monitored (another unit to monitor)

- Ion-Exchange or Vacuum distillation (all other amines)

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- Neutralization with stronger acids

- Converts Amine-Salts to

- May reduce corrosivity of



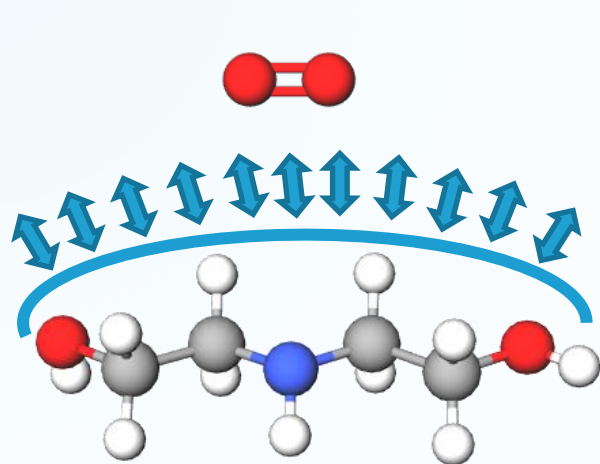
$\text{CO}_3$



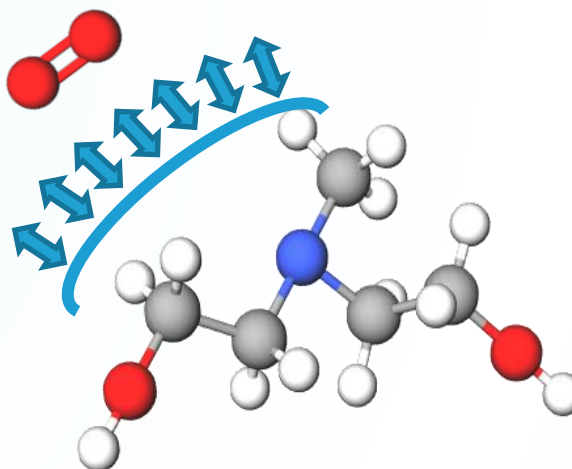
Shield of protection between the amine and free radical oxygen → mitigates the degradation reaction

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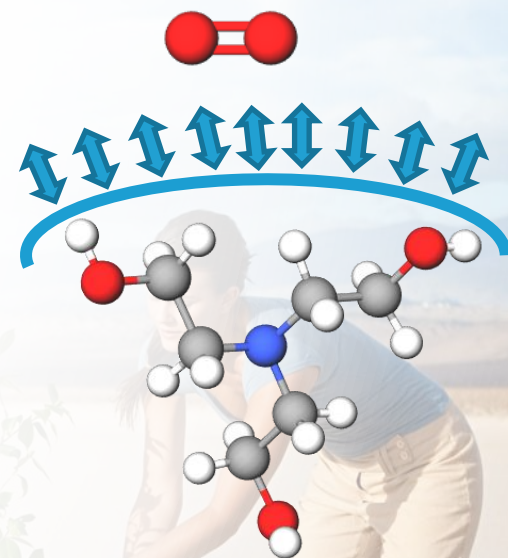
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Diethanolamine  
(DEA)



Methyl diethanolamine  
(MDEA)



Triethanolamine  
(TEA)

“Amine Stabilizer”

# BASF Amine Stabilizer

## Application

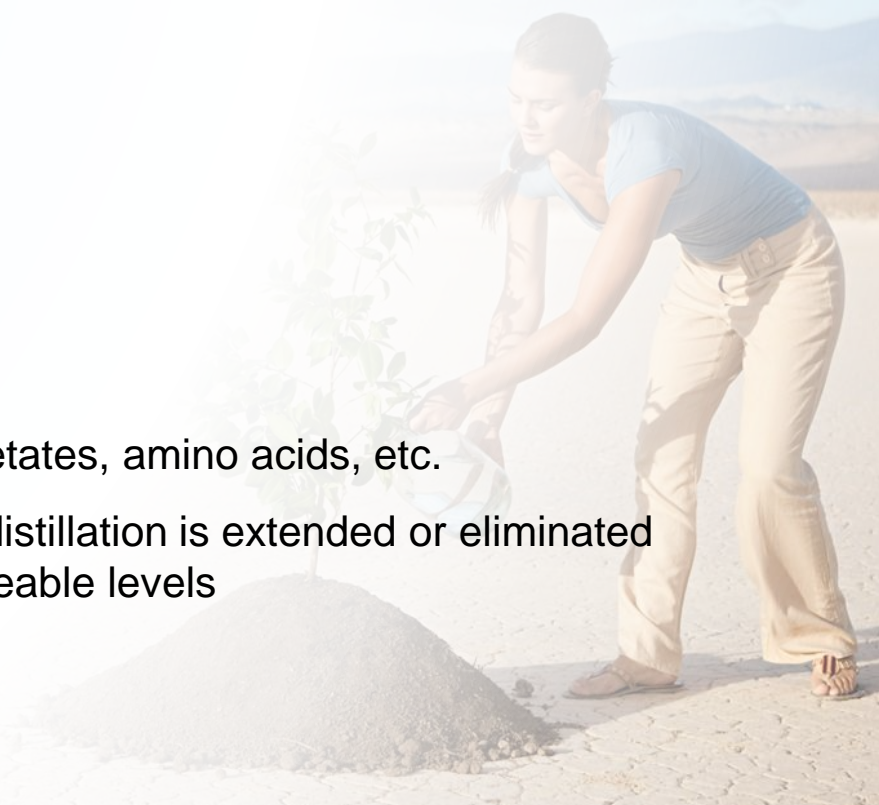
- Single charge by drum pump or chemical pump
- Incorporated into amine formulation to maintain protection level

## Function

- Protects amine from free radical oxygen attack
- Not consumed by oxygen, not a scavenger

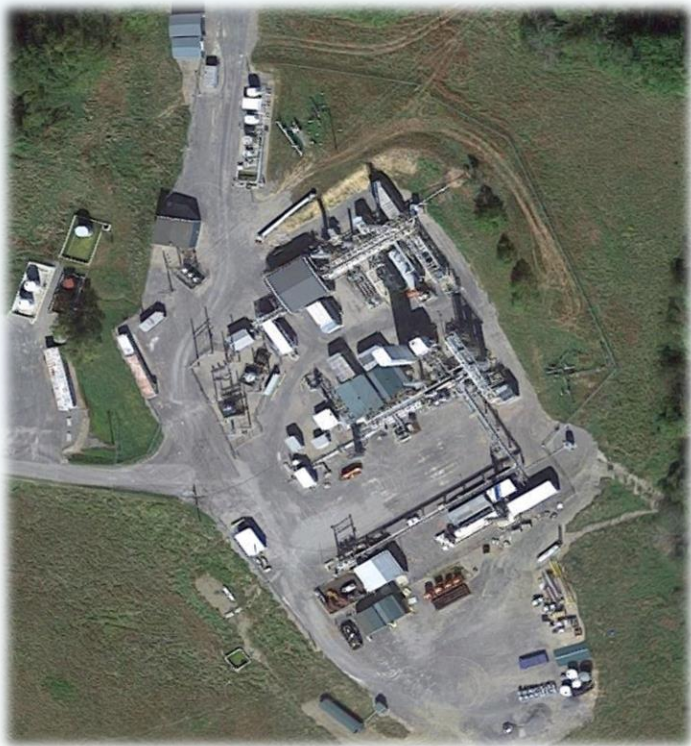
## Results

- Mitigates development of formates, oxalates, acetates, amino acids, etc.
- Reclamation cycle by Ion Exchange or Vacuum distillation is extended or eliminated  
→ degradation is significantly reduced to manageable levels





# CNX Resources – Pine Bank Gas Plant



- 5 -7 ½ MMSCFD
- 830-920 Psig / 40°-77° F
- Coal Mine Methane & GOB Gas
- 10% CO<sub>2</sub>, 80% CH<sub>4</sub>, 1% O<sub>2</sub>

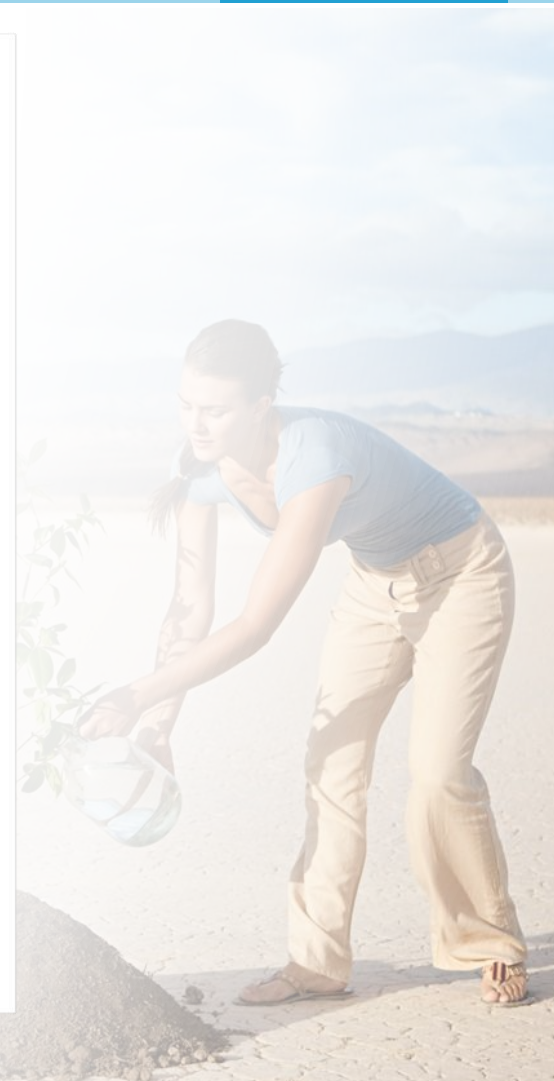
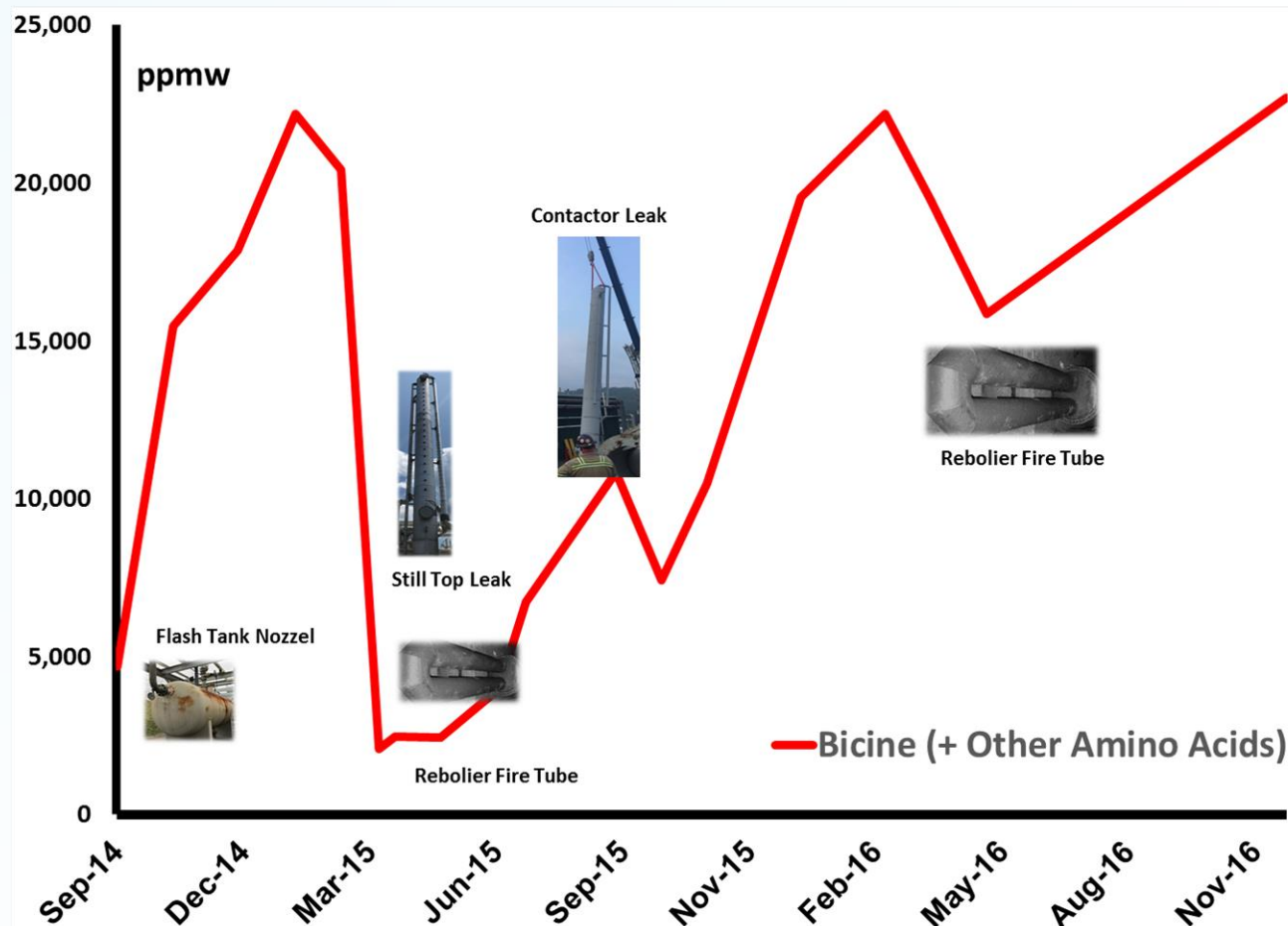




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# History of Equipment Failures with High Bicine Levels



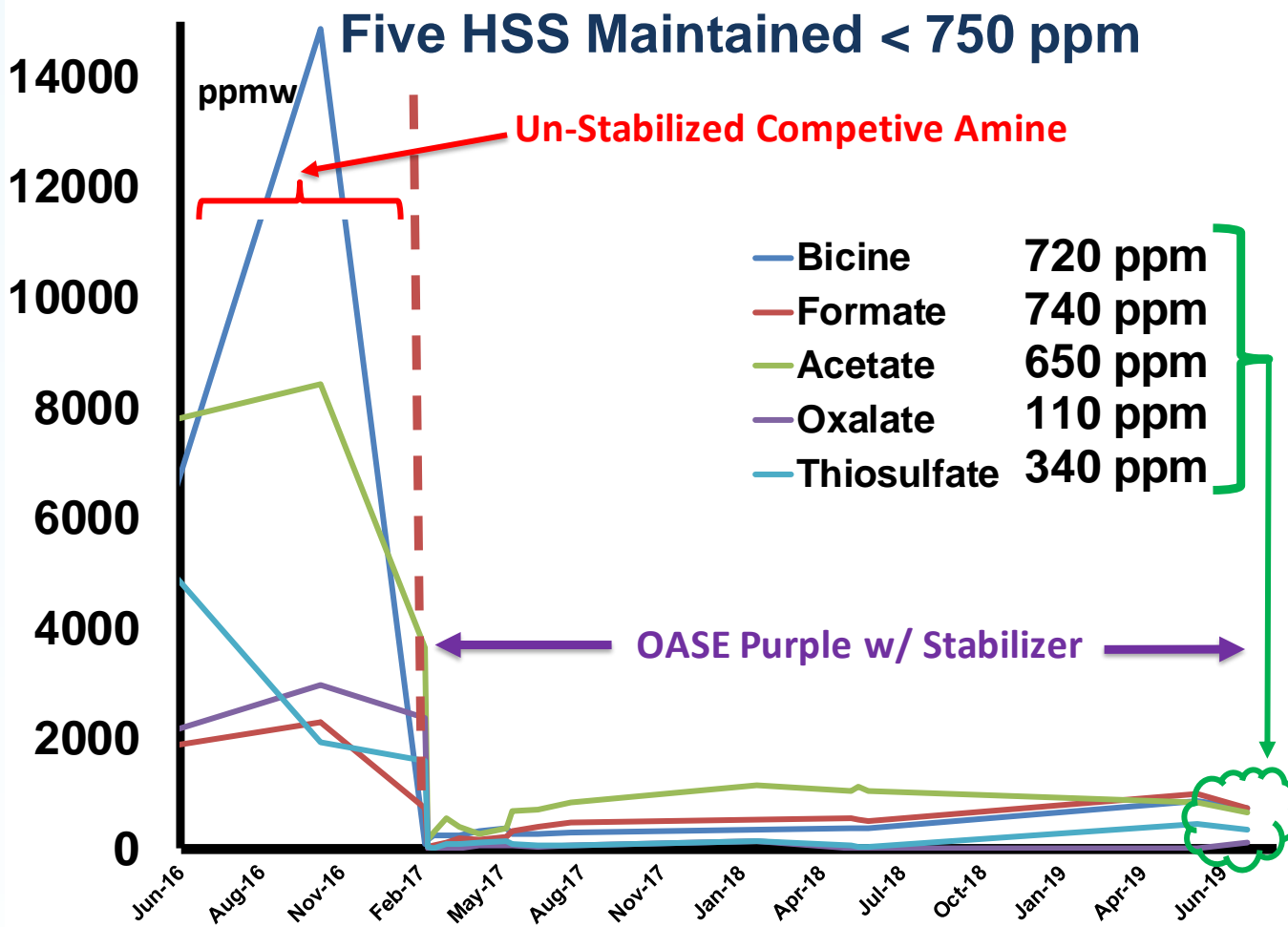
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# Pin-hole Leak through High Pressure Contactor

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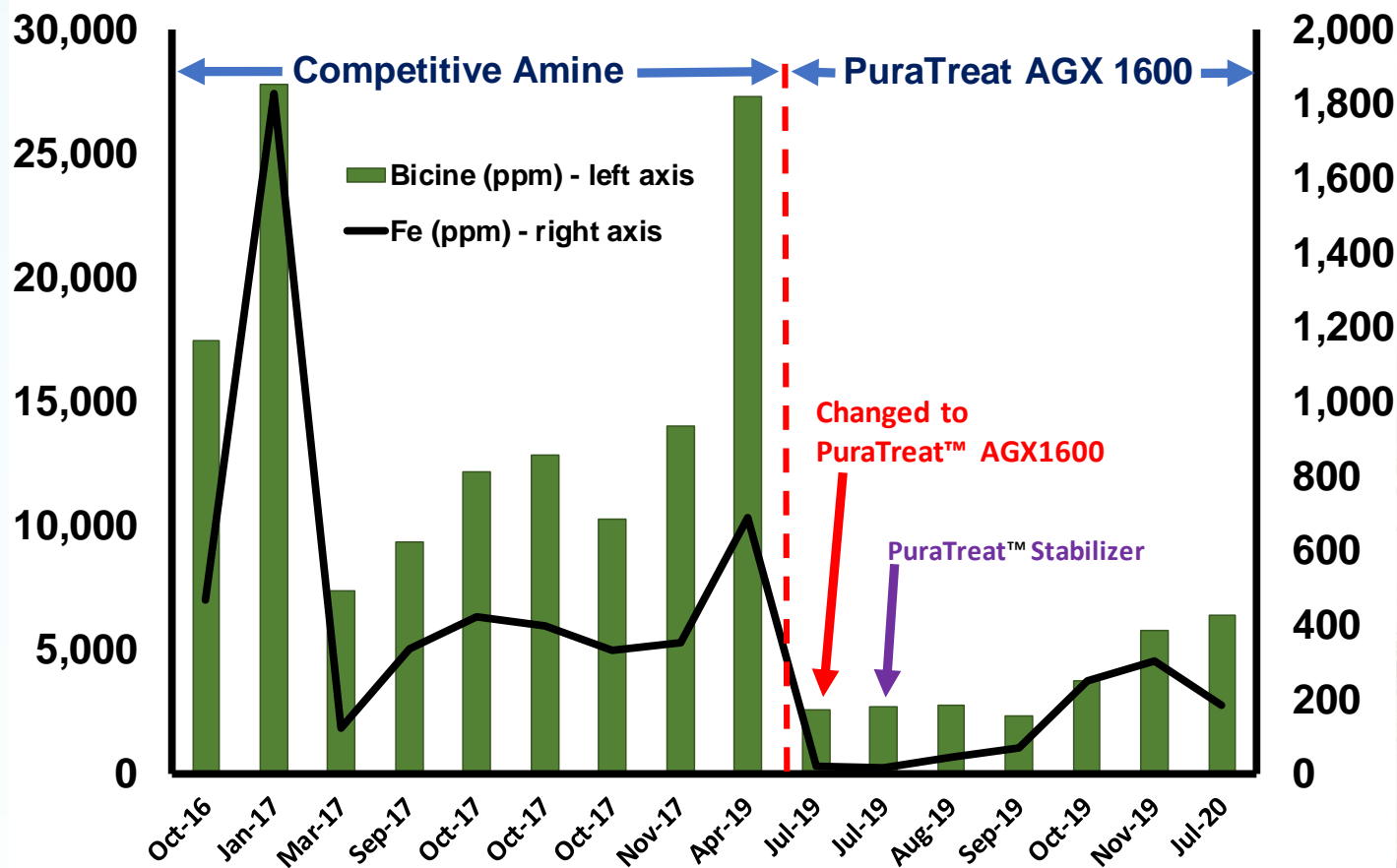


# CNX Resources Results





# Associated Gas from Vacuum to 980 Psig (0.1% - 0.5% O<sub>2</sub>)



# Review of mitigation successes (5 operating years of results)

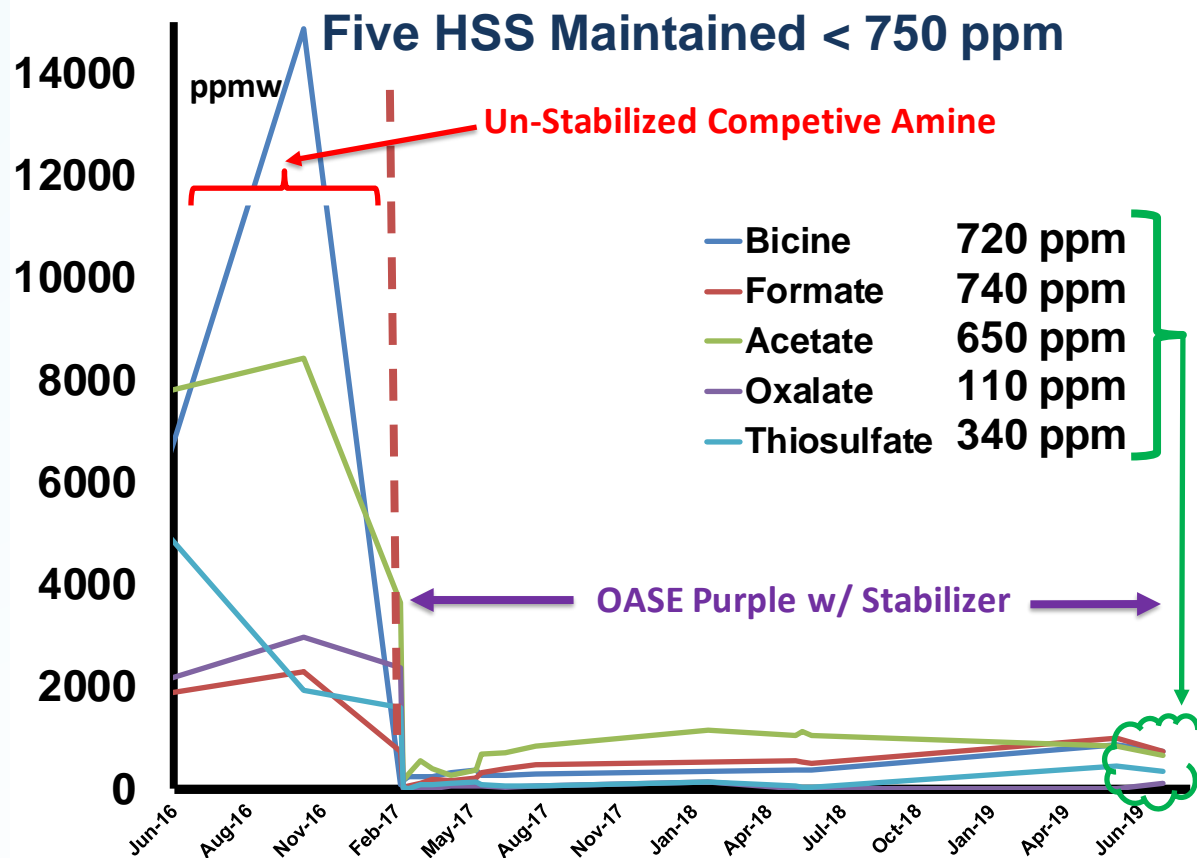
- Coal Mine Methane & GOB Pile Gas (1% O<sub>2</sub>)
- Associated Gas - Vacuum to 980 Psig (0.1-0.5% O<sub>2</sub>)
- Two West Texas Plants – 250 MMSCFD (20 ppm O<sub>2</sub>)
- Western Canada Gas Plant – 60 MMCFD



# Questions and Answers

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