

150 years



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Gas Treatment Technology

BASF, Intermediates Division

Solving the O₂ problem in Amine Units



OASE®

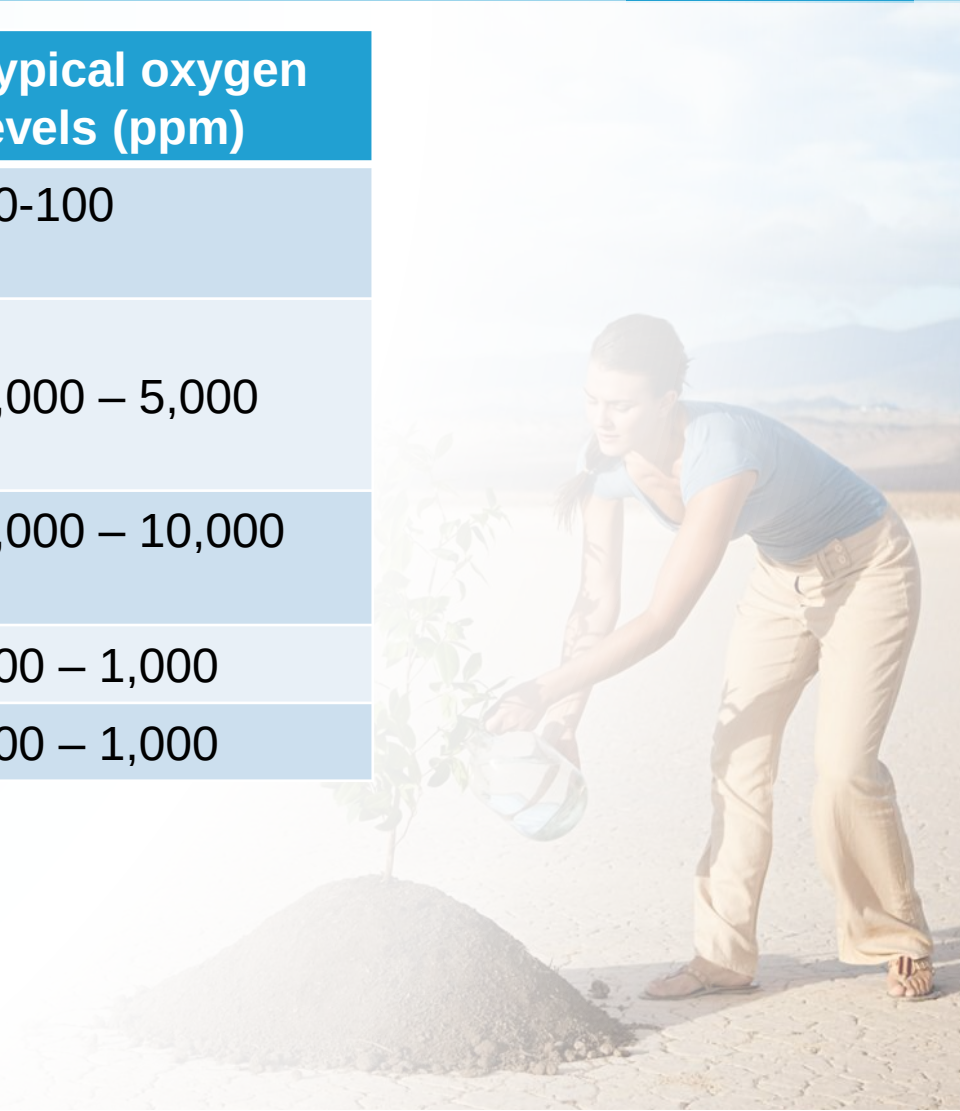
GAS TREATING EXCELLENCE BY BASF

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

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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 ?

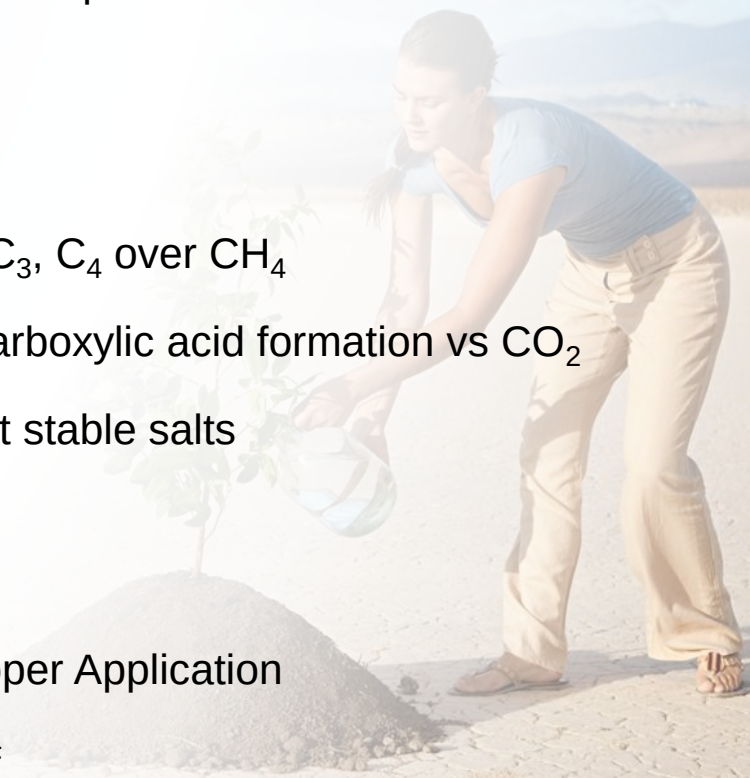
- Oxygen reacts with amines to in AGRUs to produce non-regenerable, corrosive amine salts and amino acids
 - Amine salts
 - Amine – Formate (HCOO^-)
 - Amine – Acetate (CH_3COO^-)
 - Amine – Oxalate ($\text{C}_2\text{O}_4^{2-}$)
 - Amine – Thiosulfate ($\text{S}_2\text{O}_3^{2-}$)
 - Amino Acids
 - Glycine ($\text{NH}_2\text{-CH}_2\text{-COOH}$)
 - 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-O₂TM, PuriStar[®] (regn)...etc
 - Solid Scavengers – Fe₂S₃ on wood chips → expired patent
- Issues with Catalytic Oxidation – X-O₂TM
 - Target Reaction
$$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2$$

At the reactor conditions, oxygen prefers C₂, C₃, C₄ over CH₄
 - Shale Basin Gas is not pure CH₄, resulting in Carboxylic acid formation vs CO₂
 - 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® or MEA) **[ABPG]**

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

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

- Neutralization with stronger acids

- Converts Amine-Salts to

- May reduce corrosivity of



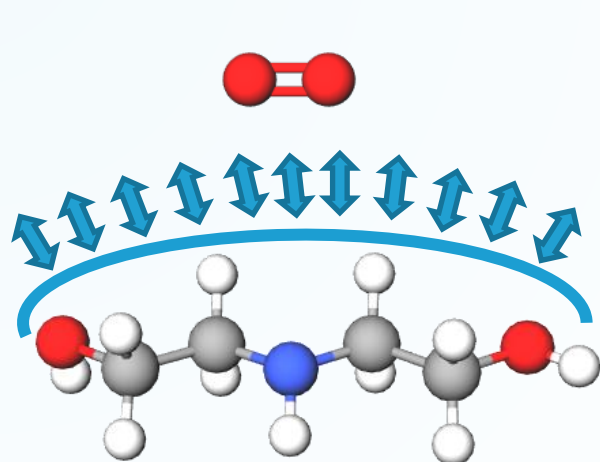
CO_3 **[ABPG]**



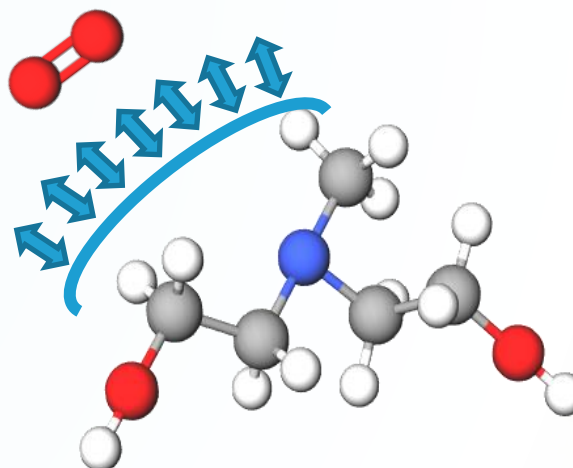
Shield of protection between the amine and free radical oxygen → mitigates the degradation reaction

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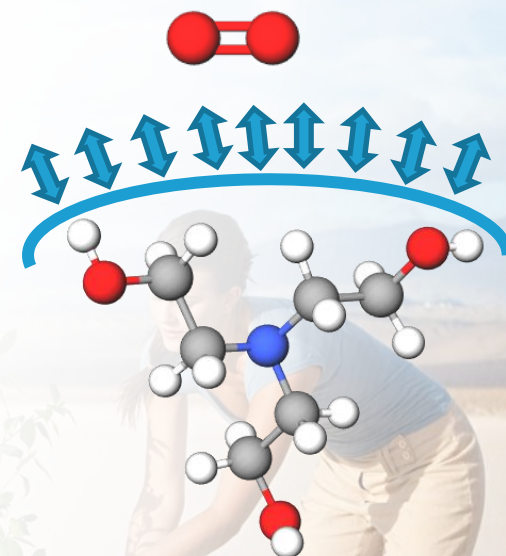
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Diethanolamine
(DEA)



Methyl diethanolamine
(MDEA)



Triethanolamine
(TEA)

“Amine Stabilizer”

BASF Amine Stabilizer

Application

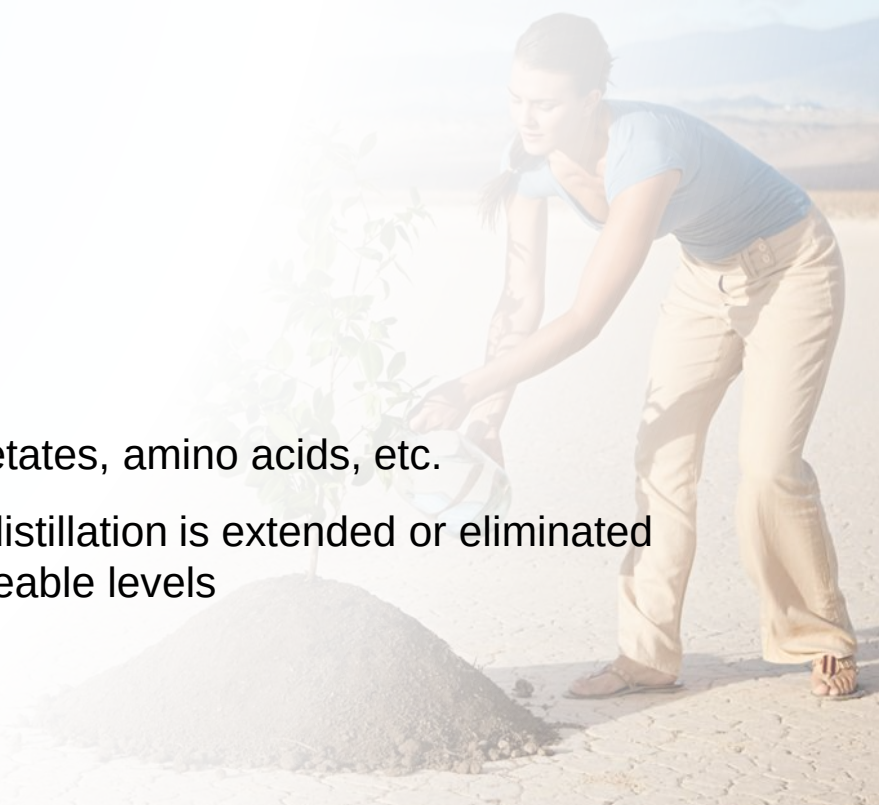
- Single charge by drum pump or chemical pump
- Incorporated into amine formulation to maintain protection level

Function

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

Results

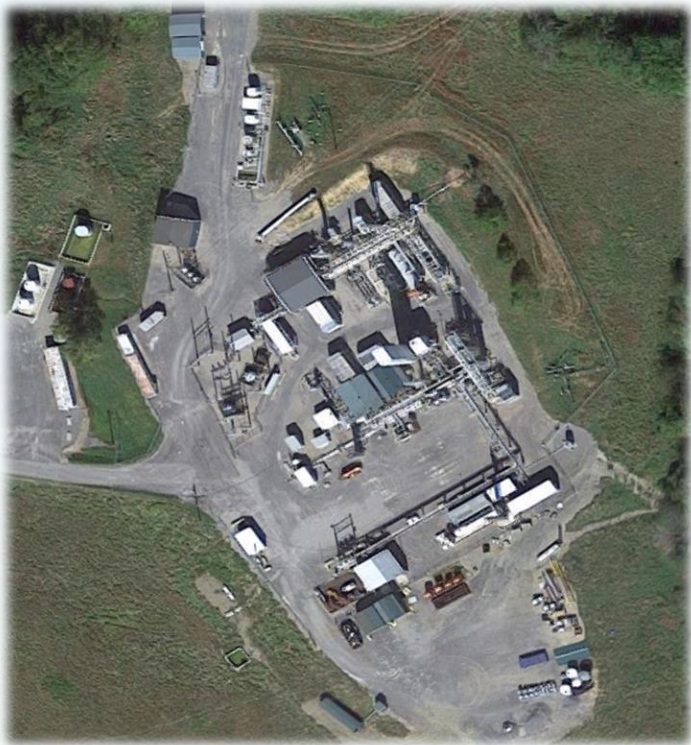
- Mitigates development of formates, oxalates, acetates, amino acids, etc.
- Reclamation cycle by Ion Exchange or Vacuum distillation is extended or eliminated
➔ degradation is significantly reduced to manageable levels



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CNX Resources – Pine Bank Gas Plant



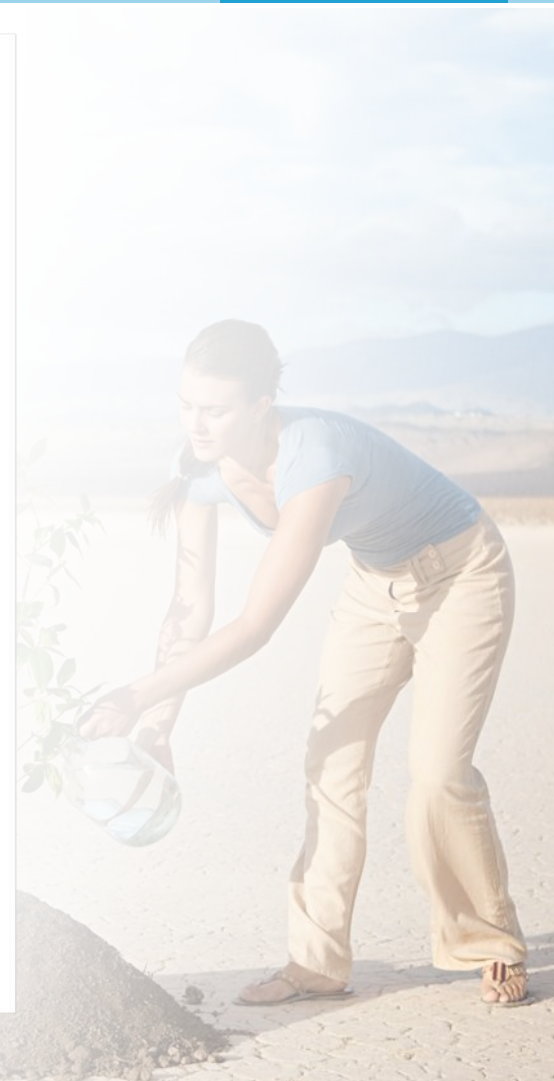
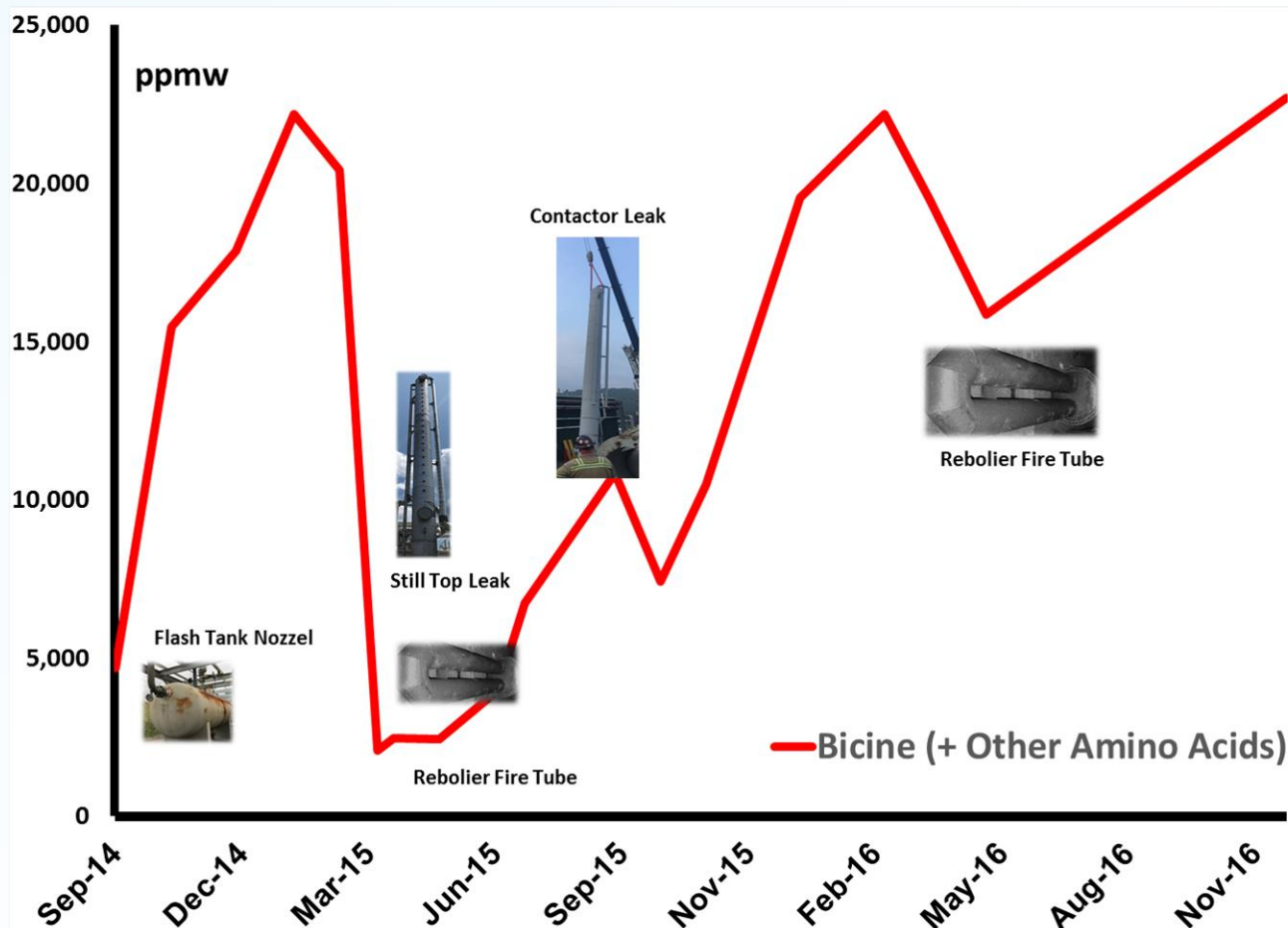
- 5 -7 ½ MMSCFD
- 830-920 Psig / 40°-77° F
- Coal Mine Methane & GOB Gas
- 10% CO₂, 80% CH₄, 1% O₂



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History of Equipment Failures with High Bicine Levels



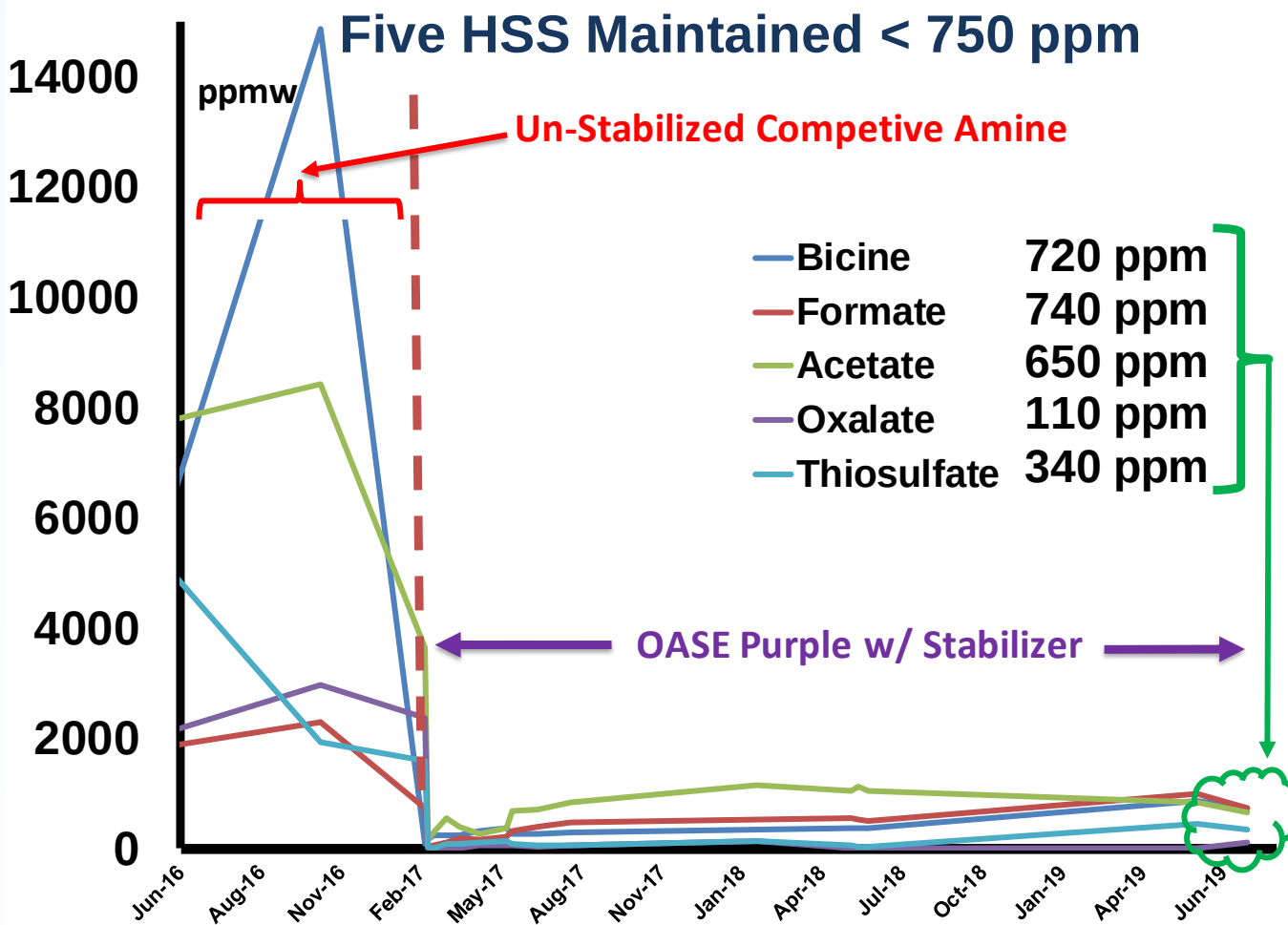
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Pin-hole Leak through High Pressure Contactor

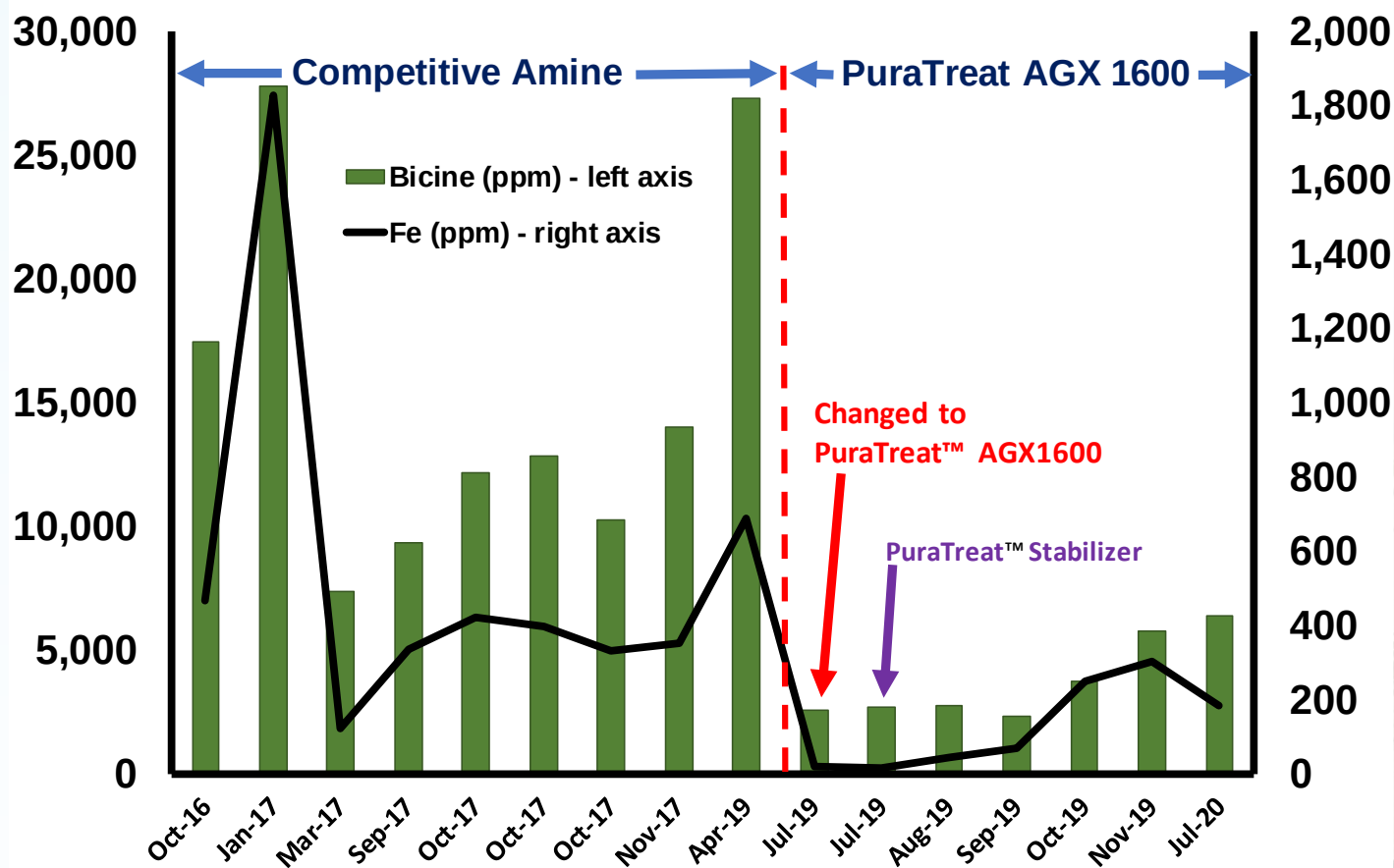
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CNX Resources Results



Associated Gas from Vacuum to 980 Psig (0.1% - 0.5% O₂)



Review of mitigation successes (5 operating years of results)

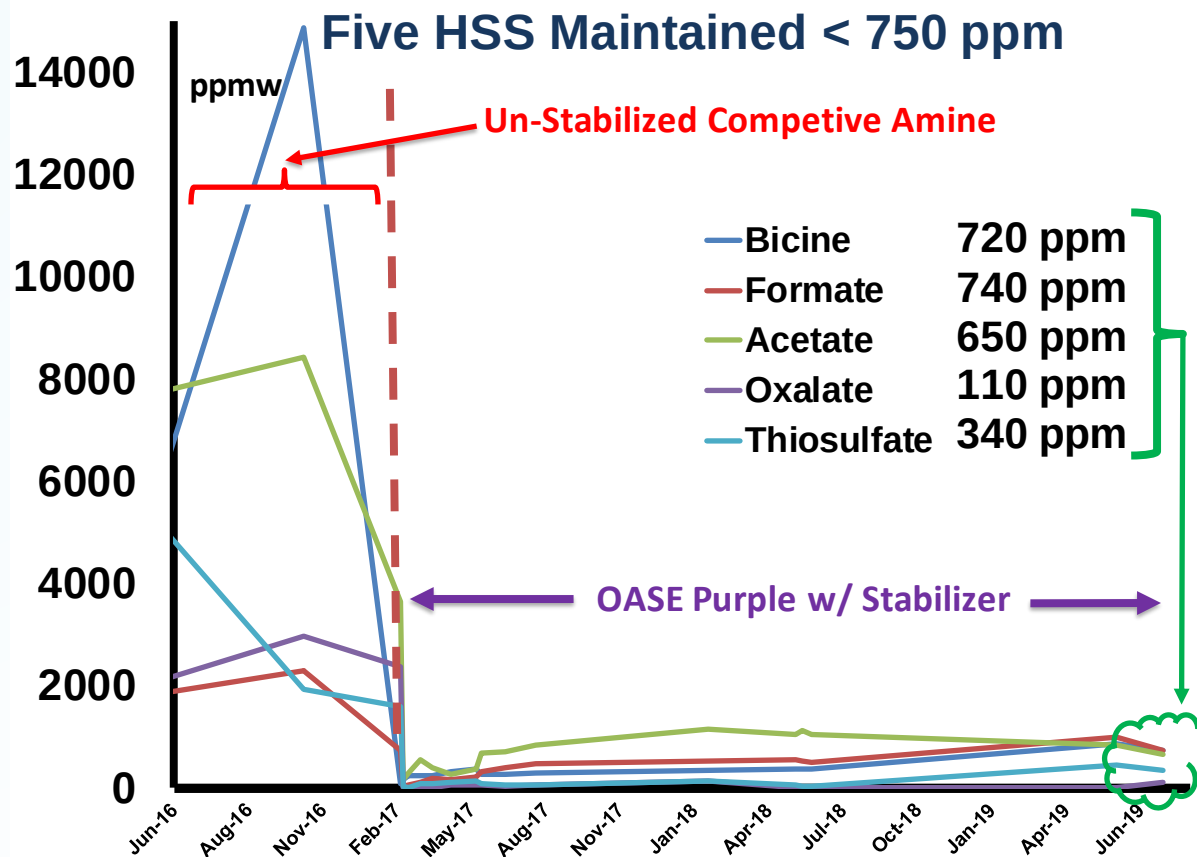
- Coal Mine Methane & GOB Pile Gas (1% O₂)
- Associated Gas - Vacuum to 980 Psig (0.1-0.5% O₂)
- Two West Texas Plants – 250 MMSCFD (20 ppm O₂)
- Western Canada Gas Plant – 60 MMCFD



Questions and Answers

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