Fate of Ammonia in Refinery Amine Systems

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INTRODUCTION

Ammonia ingress and accumulation in refinery and bio-gas amine systems is not a new problem. However, increasing utilization of advantaged crudes with higher nitrogen content may present challenges in today's capital-constrained operating environment. Many refiners have instituted guidelines for purging amine regenerator reflux water for corrosion control. Historically, this has been done empirically based upon periodic lab analysis and adjustment of the purge water rate.

The true amount of ammonia ingress, and its material balance across refinery amine unit is not a topic that has been discussed in great detail, because until now, rate-based mass transfer models have not been available. Using the well-known ProTreat™ rate-based mass transfer process simulator, this paper addresses the following questions. Where available, comparisons to plant data measurements are provided.

1. How much ammonia can accumulate based upon choice of regenerator operating conditions?
2. How much ammonia rejection into the amine acid gas does this correspond to, and is this a significant concern to downstream (i.e., sulfur plant) operations?
3. Can ammonia build to levels that will cause additional H_2S to be trapped leading to higher lean loadings, reduced treating performance, or even regenerator flooding?
4. How much ammonia skates through refinery amine treaters?

Ultimately, we attempt to answer whether the ammonia balance on a refinery amine system can be fully characterized based upon the knowledge of a few simple parameters.

ProTreat™

Taking the Guesswork Out of Gas Treating

The Fate of Ammonia in Refinery Amine Systems

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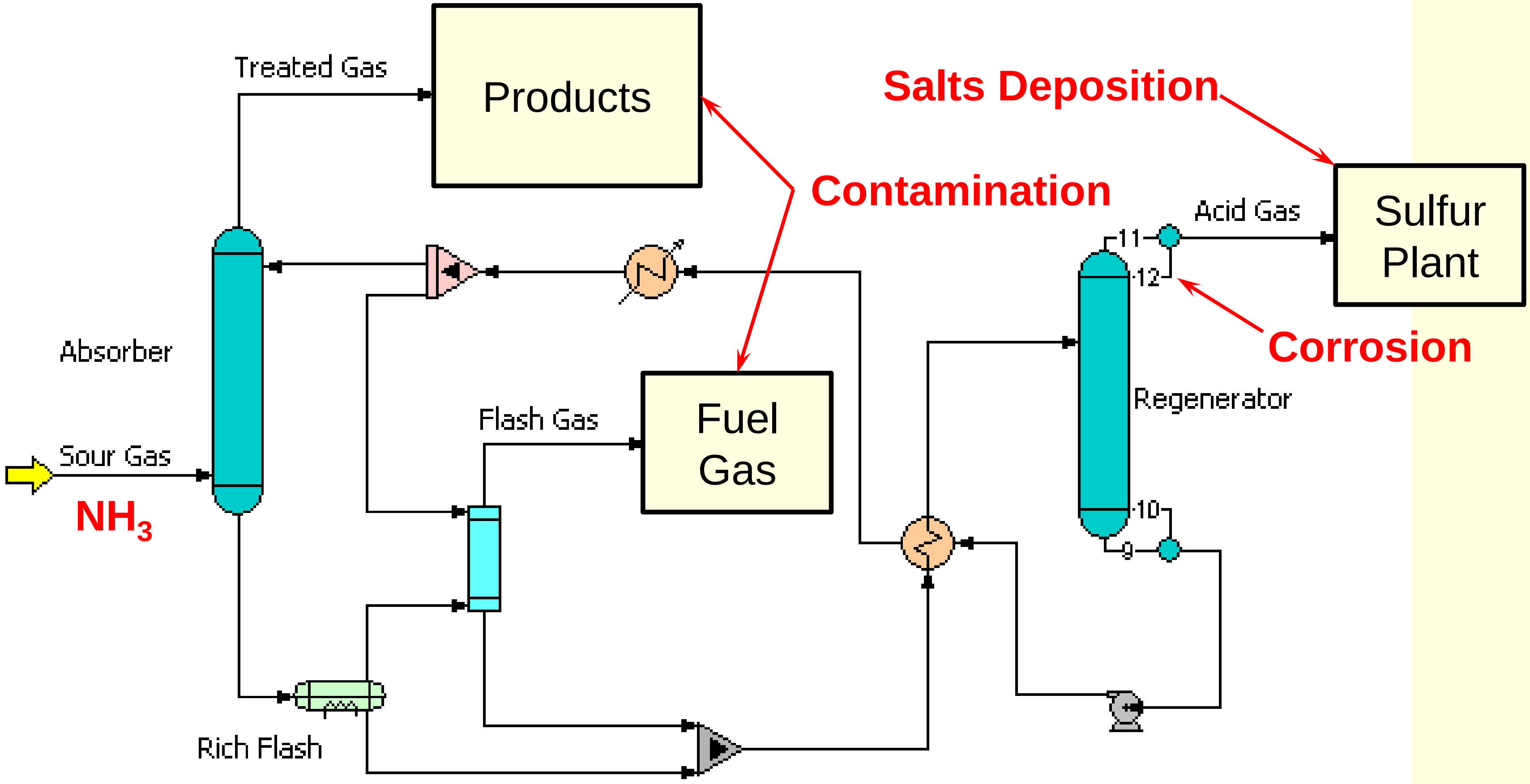
Objectives of Effort

- Understand NH_3 Ingress and Accumulation in Refinery Amine Systems
  - Quantify ingress and absorber pickup
  - How much can accumulate?
  - Impact of operating variables on accumulation
  - Accumulation effects on unit performance and reliability
  - Comparisons vs. real plant data

Background & Relevance

- NH_3 is an Amine
  - Simplest form possible
  - Volatile (lacks bulky alcohol chains)
  - Loves water
  - Reacts with and traps acid gases
- Acid Gases (H_2S + CO_2)
  - Toxic
  - Corrode steel in aqueous solution
  - Environmental concerns

Ammonia Volatility Ramifications



Salts Deposition

Contamination

Corrosion

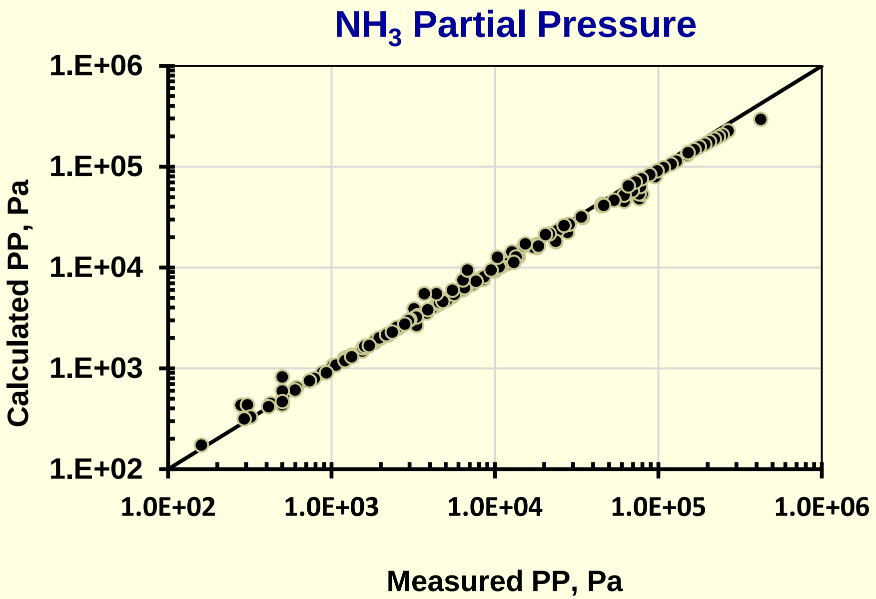
NH_3

About the Model

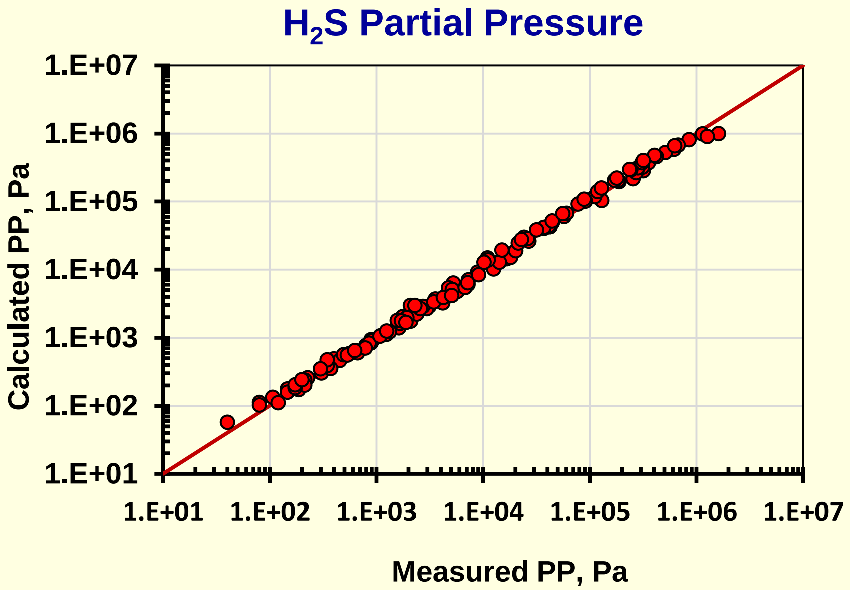
- Same basis as ProTreat™ for amines
- Mass transfer rate-based for H_2S, CO_2, NH_3, H_2O transport; equilibrium for inerts; includes kinetics
- All separations equipment characterized by individual phase mass transfer coefficient and interfacial area correlations – similar to HTXR calculations
- Fully predictive – NO GUESSWORK, no efficiencies, no HETPs, no ideal stages, don’t have to know the answer first!!! but…
- Can back efficiencies out if you want to see them
- Right answers out of the box without fitting – just data from P&IDs and internals vendor data sheets

ProTreat^{TM}

How good is the VLE model?



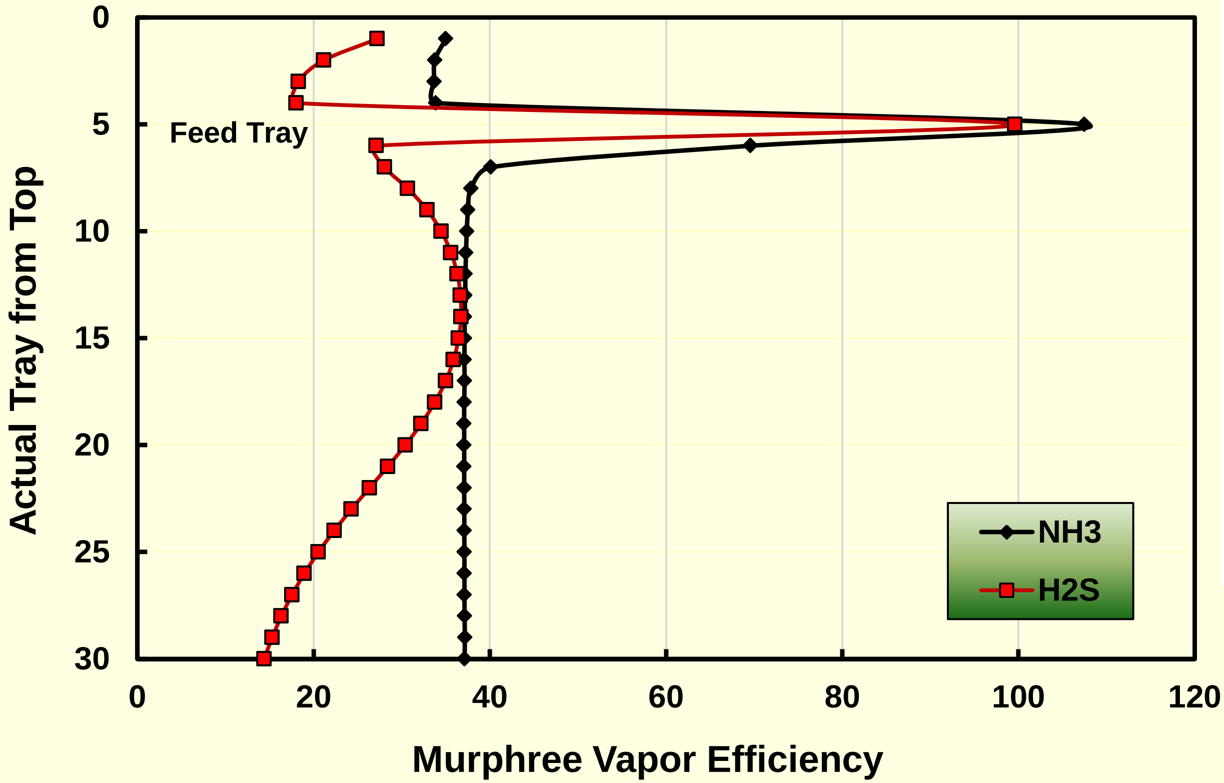
Data Sources: API 955, GPA RR-118 and Maurer (1999)

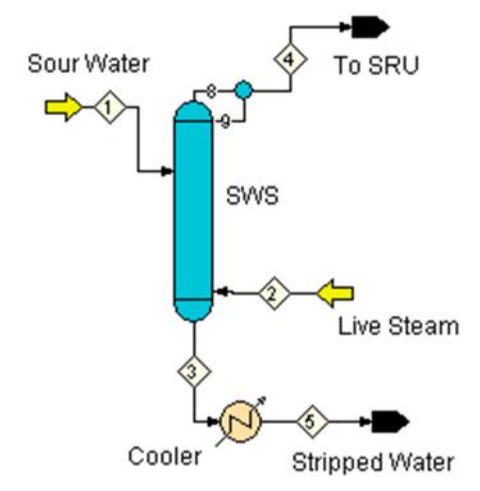


Partial Pressure (Calc/Meas)	**Avg.**	**Std. Dev.**
NH_3	1.004	0.149
H_2S	1.030	0.149
CO_2	1.043	0.185

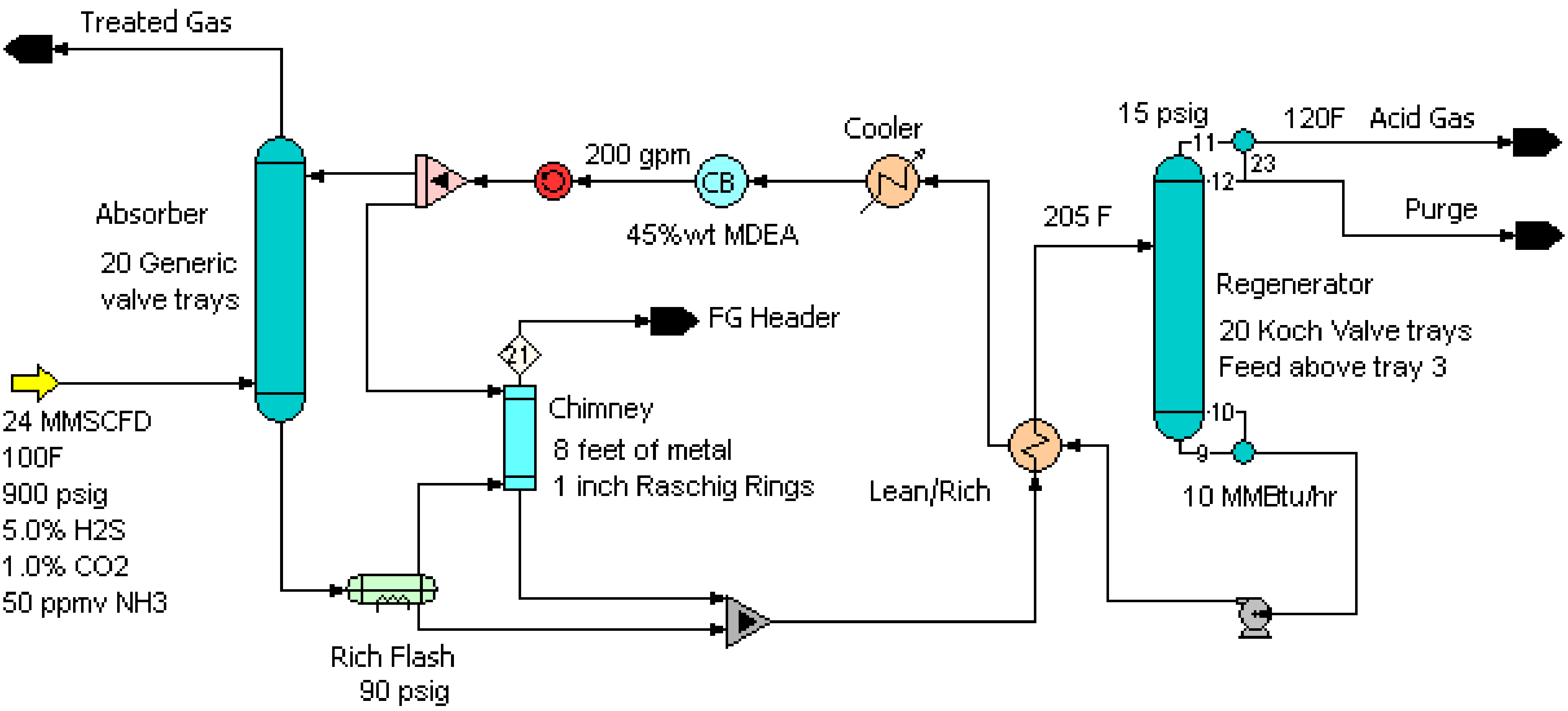
ProTreat™

Efficiencies for H_2S and NH_3 Stripping





Basis for Parametric Studies



Parametric Study

- Absorber Pickup
  - Sour gas temperature: 100ºF, 120ºF, 140ºF
  - Lean amine temperature: Sour gas + 10F ΔT
  - Feed Pressure: 900 psig, 450 psig, 125 psig
  - NH_3 in Feed: 50, 150, 500 ppmv (dry)
- Accumulation Studies
  - Condenser temperature: 120ºF, 140ºF, 160ºF
  - Purge reflux water

Absorber NH_3 Pickup

Parameter	Base Case	Elevated Temperature		Lower Absorber Pressure	
Inlet Gas Temperature °F	100	120	140	100	100
Lean Amine Temp, °F	110	130	150	110	110
Absorber Pressure, psig	900	900	900	450	125
NH_3 Conc. In Feed, ppmv	50	50	50	50	50
% NH_3 pickup in Absorber	97.5	96.9	96.2	96.5	91.5
ppmv NH3 in Treated Gas	1.3	1.6	2.0	1.9	4.4
wt % NH_3 in reflux water	1.35	1.35	1.36	1.37	1.35
Lean H_2S loading	0.0084	0.0082	0.0080	0.0083	0.0081
Lean CO_2 loading	0.0003	0.0003	0.0003	0.0003	0.0003
Treated Gas, ppmv H_2S	7.9	11.6	17.7	12.8	96
ppmw NH_3 in lean amine	16.2	13.7	11.9	14.5	10.1
% CO_2 pickup in Absorber	80.5	75.3	68.7	63.1	21.1
NH_3 in Acid Gas, %vol (wet)	0.072	0.072	0.074	0.074	0.073

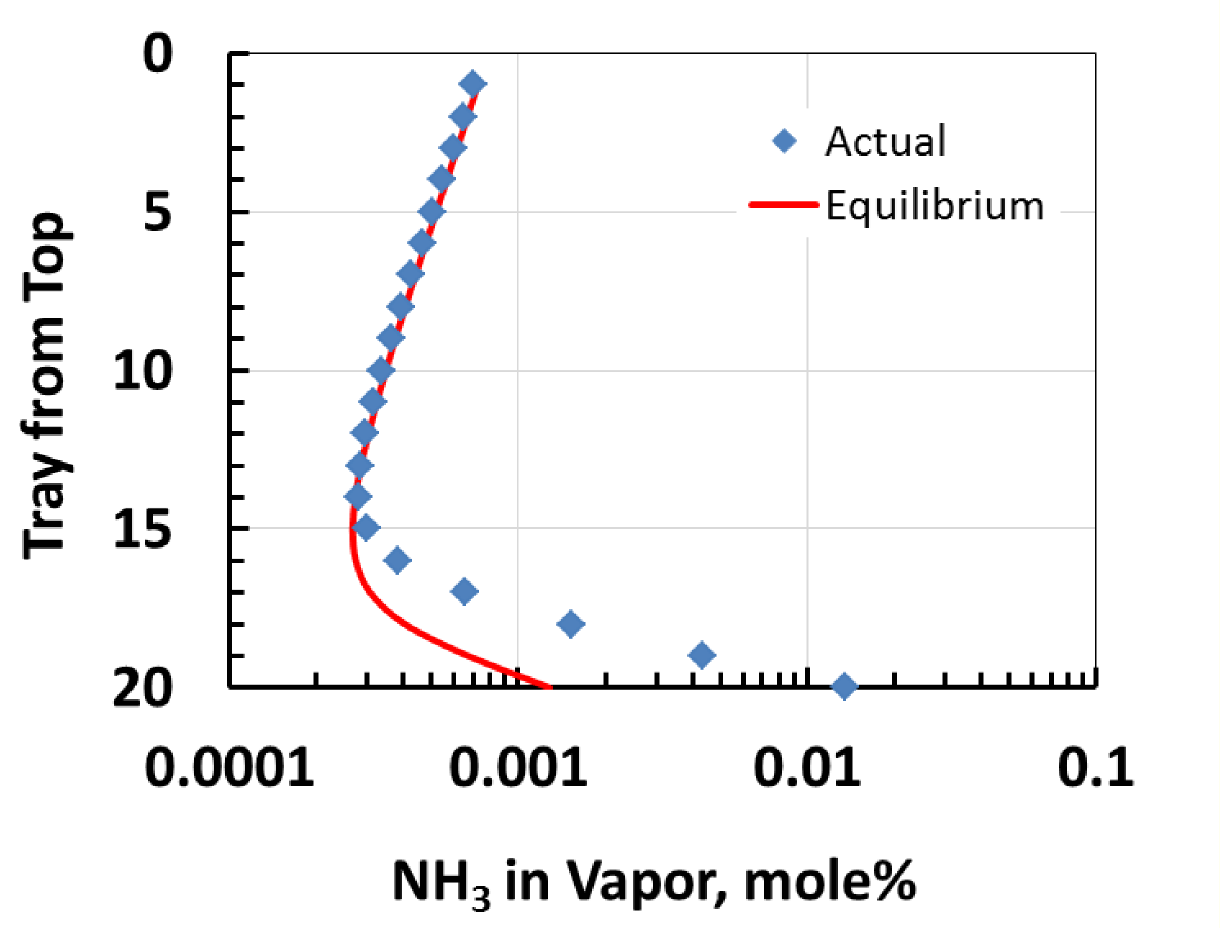
Effect of NH_3 Concentration

Parameter	Base Case	Higher NH_3 Feed Content	
Inlet Gas Temperature °F	100	100	100
Lean Amine Temp, °F	110	110	110
Absorber Pressure, psig	900	900	900
NH_3 Conc. In Feed, ppmv	50	150	500
% NH_3 pickup in Absorber	97.5	98.3	98.7
ppmv NH3 in Treated Gas	1.3	2.8	7.0
wt % NH_3 in reflux water	1.35	2.60	5.21
Lean H_2S loading	0.0084	0.0085	0.0086
Lean CO_2 loading	0.0003	0.0003	0.0004
Treated Gas, ppmv H_2S	7.9	8.0	8.2
ppmw NH_3 in lean amine	16.2	33.8	85.4
% CO_2 pickup in Absorber	80.5	80.6	80.8
NH_3 in Acid Gas, %vol (wet)	0.072	0.23	0.77

Absorber Pickup Conclusions

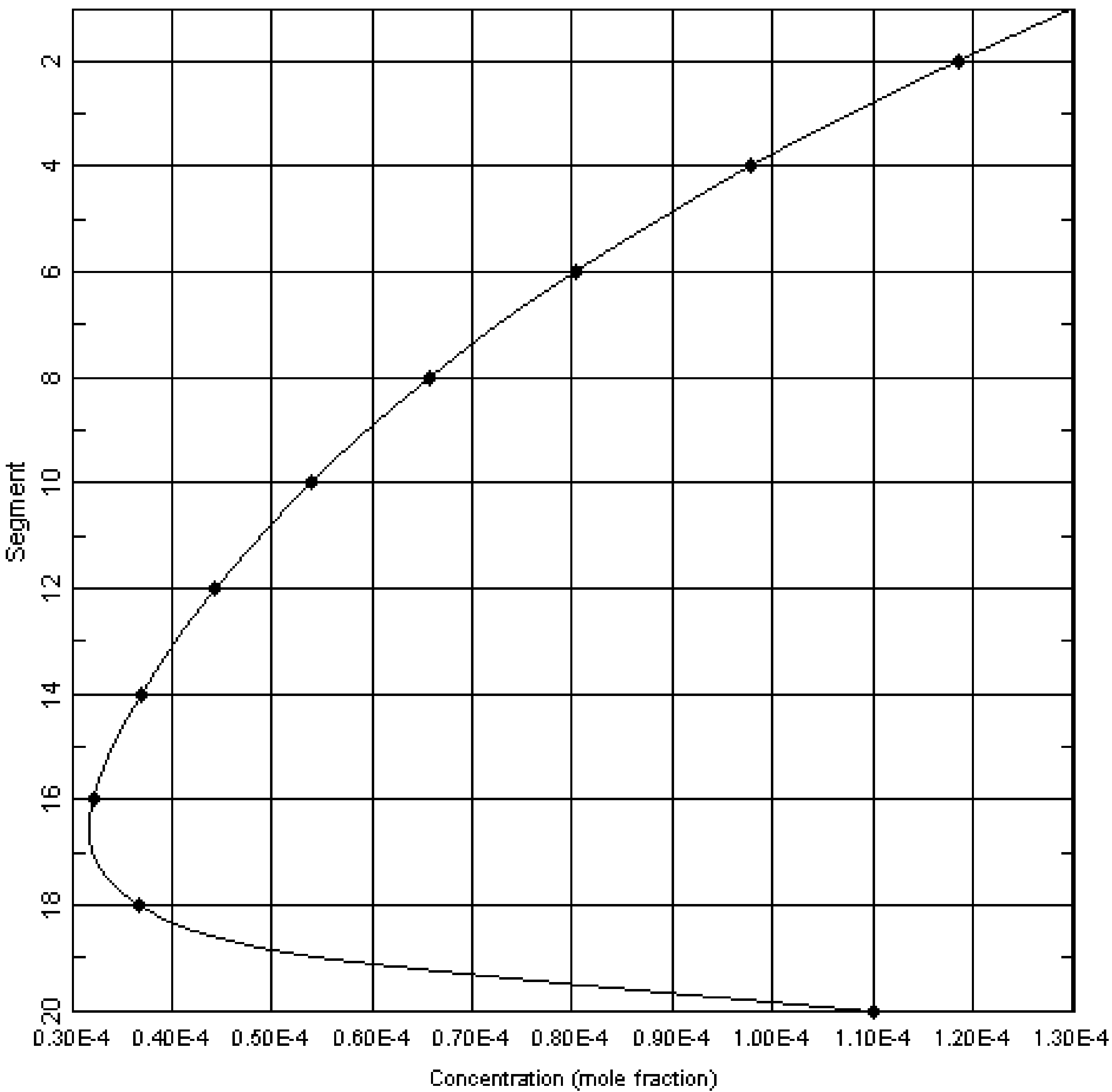
- Higher temperature and lower pressure reduce NH_3 pickup
- NH_3 pickup efficiency increases with partial pressure in the feed
- NH_3 slip into treated gas is controlled by residual NH_3 levels in the lean amine
- CO_2 pickup is only marginally increased so the presence of NH_3 does not significantly “activate” the MDEA at these low levels.

NH_3 Vapor Profile in Absorber



- Above tray 15, NH_3 is stripped from the solvent by "lean gas"
- Below tray 15, H_2S and CO_2 pickup are significant, which binds NH_3 into solution as NH_4^+ and NH_3COO^-

Absorber: NH3 Ionic Concentration



Accumulation vs. Condenser Temperature

NH_3 Conc. In Feed, ppmv	150	150	150	500	500	500
Condenser Temperature ^oF	120	**140**	**160**	120	**140**	**160**
% NH_3 pickup in Absorber	98.3	99.0	99.4	98.7	99.2	99.5
ppmv NH3 in Treated Gas	2.8	1.7	1.0	7.0	4.3	2.9
wt % NH_3 in reflux water	2.60	1.42	0.76	5.21	2.90	1.59
Lean H_2S loading	0.0085	0.0084	0.0083	0.0086	0.0085	0.0084
Lean CO_2 loading	0.0003	0.0003	0.0003	0.0004	0.0003	0.0003
Treated Gas, ppmv H_2S	8.0	7.8	7.7	8.2	8.0	7.8
ppmw NH_3 in lean amine	33.8	20.3	12.6	85.4	52.5	35.4
% CO_2 pickup in Absorber	80.6	80.6	80.5	80.8	80.7	80.7
NH_3 in Acid Gas, %vol (wet)	0.23	0.22	0.21	0.77	0.75	0.70

Condenser Temperature Conclusions

- Effective at driving NH_3 into the acid gas.
  - Helps to remove more NH_3 in the absorber
  - H_2S treat marginally improved due to lower lean loading (less reflux and NH_3 + trapped H_2S to restrip)
  - Reflux circuit corrosion may not be reduced due to the higher temperature offset
- Bad for the sulfur plant

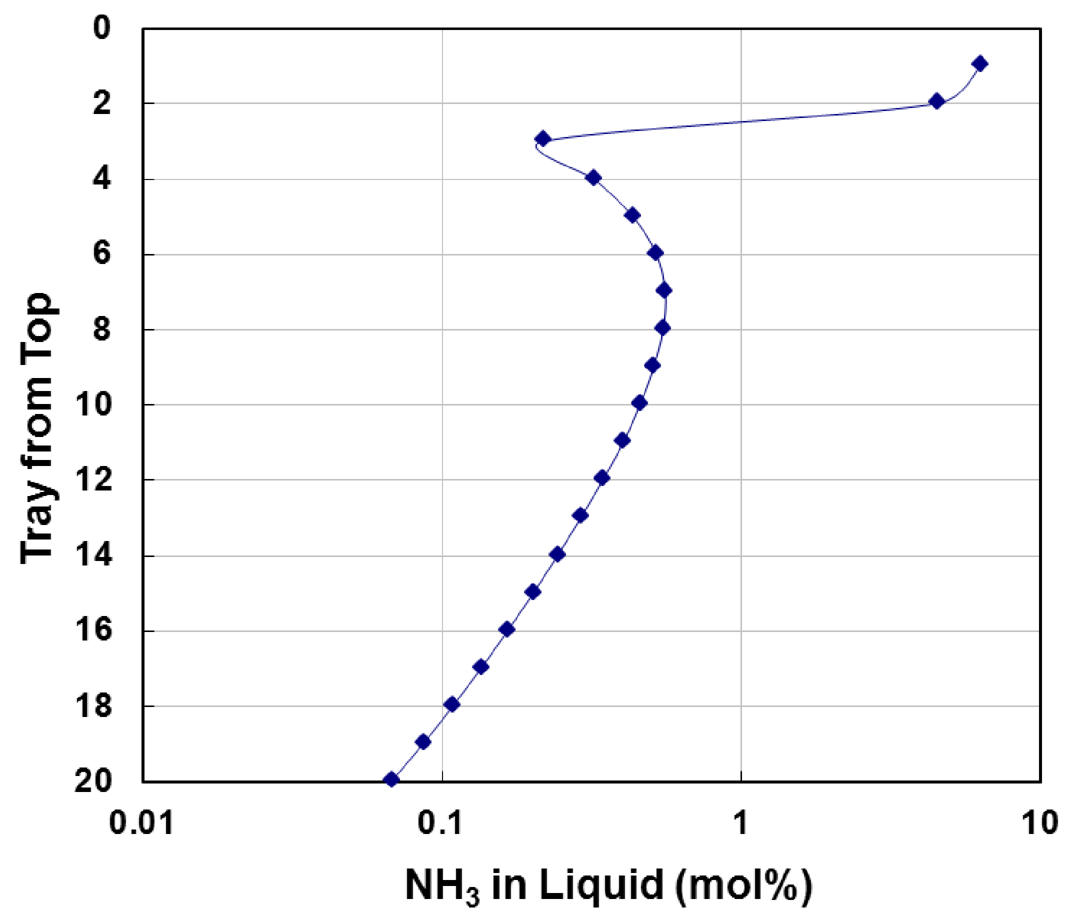
Effect of Reflux Purging

NH_3 Conc. In Feed, ppmv	500	500	500	500
% Reflux Water Purged	0	**15**	**75**	**51***
% NH_3 pickup in Absorber	98.7	99.1	99.7	99.3
ppmv NH3 in Treated Gas	7.0	4.7	1.8	3.5
wt % NH_3 in reflux water	5.21	3.87	1.6	0.99
Lean H_2S loading	0.0086	0.0085	0.0081	0.0086
Lean CO_2 loading	0.0004	0.0003	0.0003	0.0003
Treated Gas, ppmv H_2S	8.2	8.0	7.4	8.1
ppmw NH_3 in lean amine	85.4	57.4	21.7	42.9
% CO_2 pickup in Absorber	80.8	80.8	80.7	80.7
NH_3 in Acid Gas, %vol (wet)	0.77	0.46	0.10	0.17

Reflux Purging Conclusions

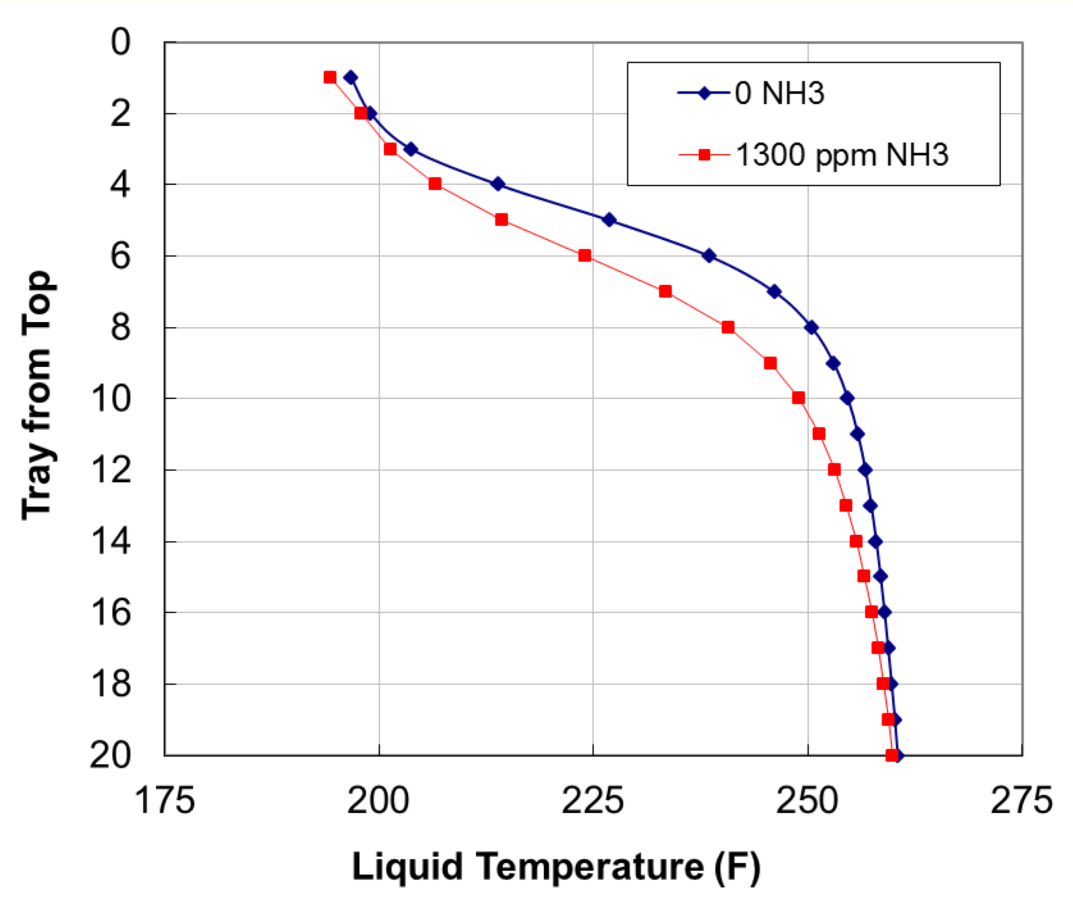
- Effective at removing NH_3 from the amine system
- Minimizes NH_3 slip into acid gas
- Reduces corrosion in the reflux system
- Fresh water make-up into the reflux amplifies benefits

Regenerator Profile (Unpurged)



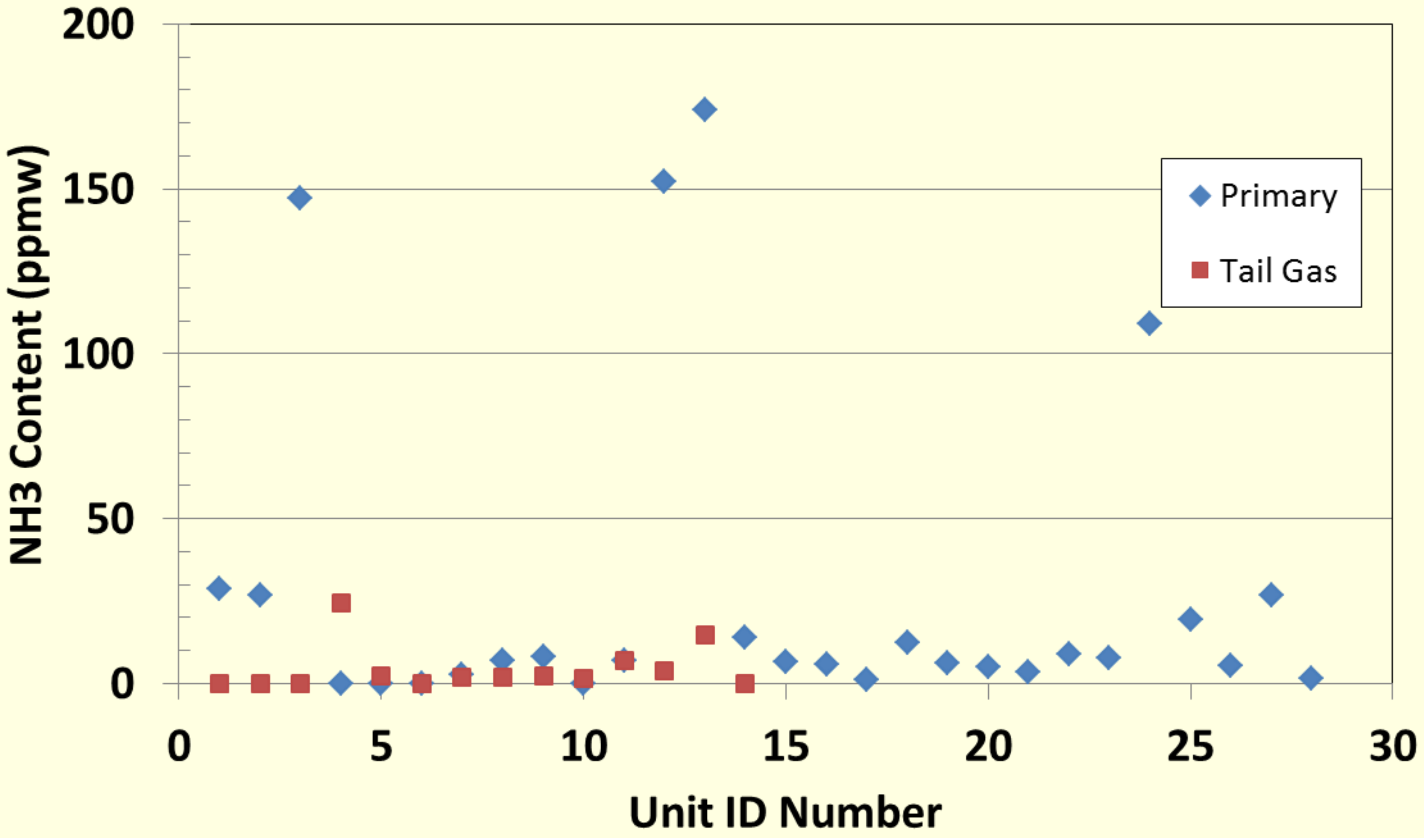
- NH_3 accumulation is not constrained to the reflux wash section.
- Accumulates well below the feed tray
- Incremental heat of reaction → higher reboiler duty or….

Slumped Regeneration Temperatures With NH_3

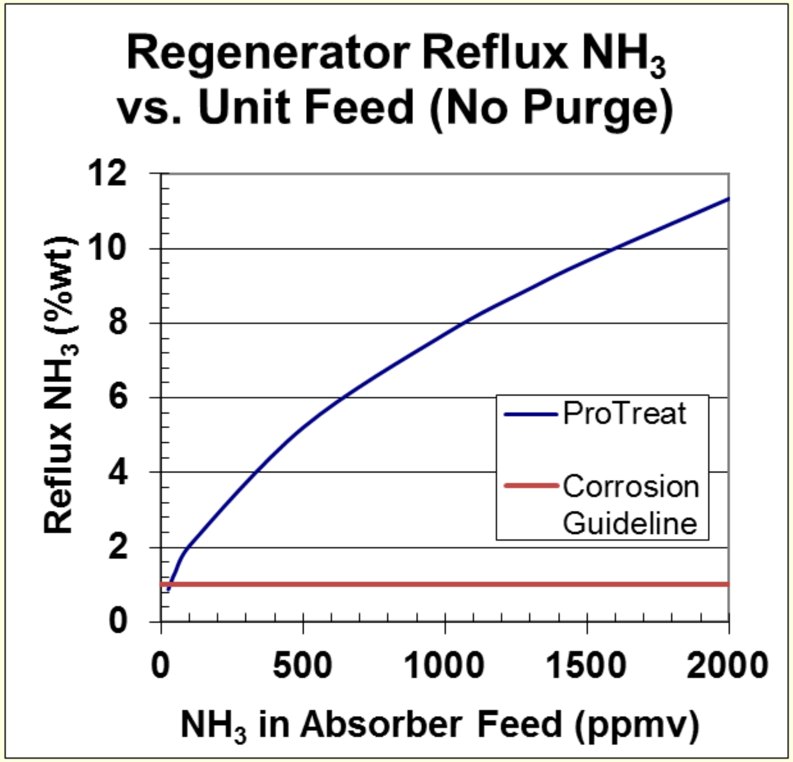


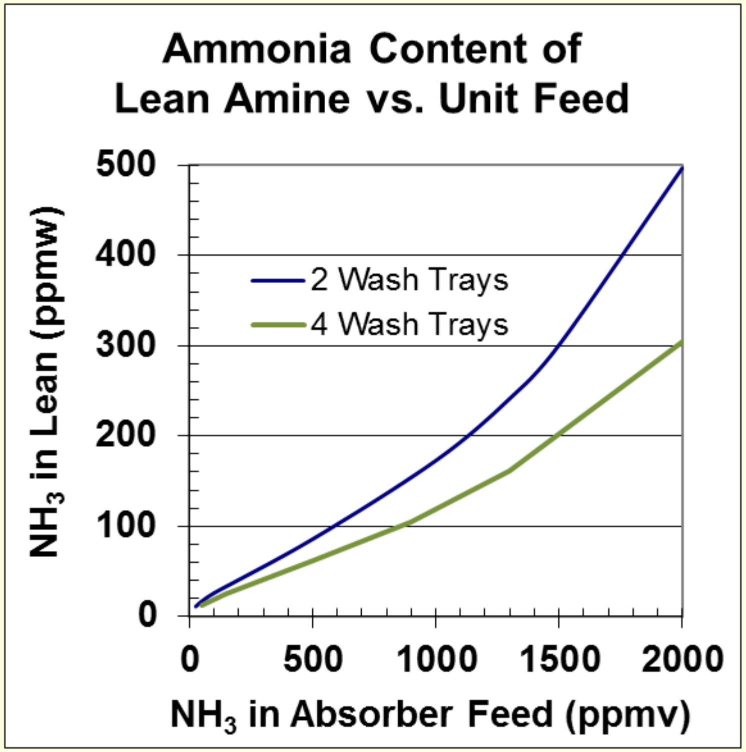
- At constant reboiler duty, more energy goes into boiling and condensing NH_3 and trapped H_2S
- “Foaming” is an urban legend as vapor traffic is reduced.

Measured NH_3 in Lean Amines

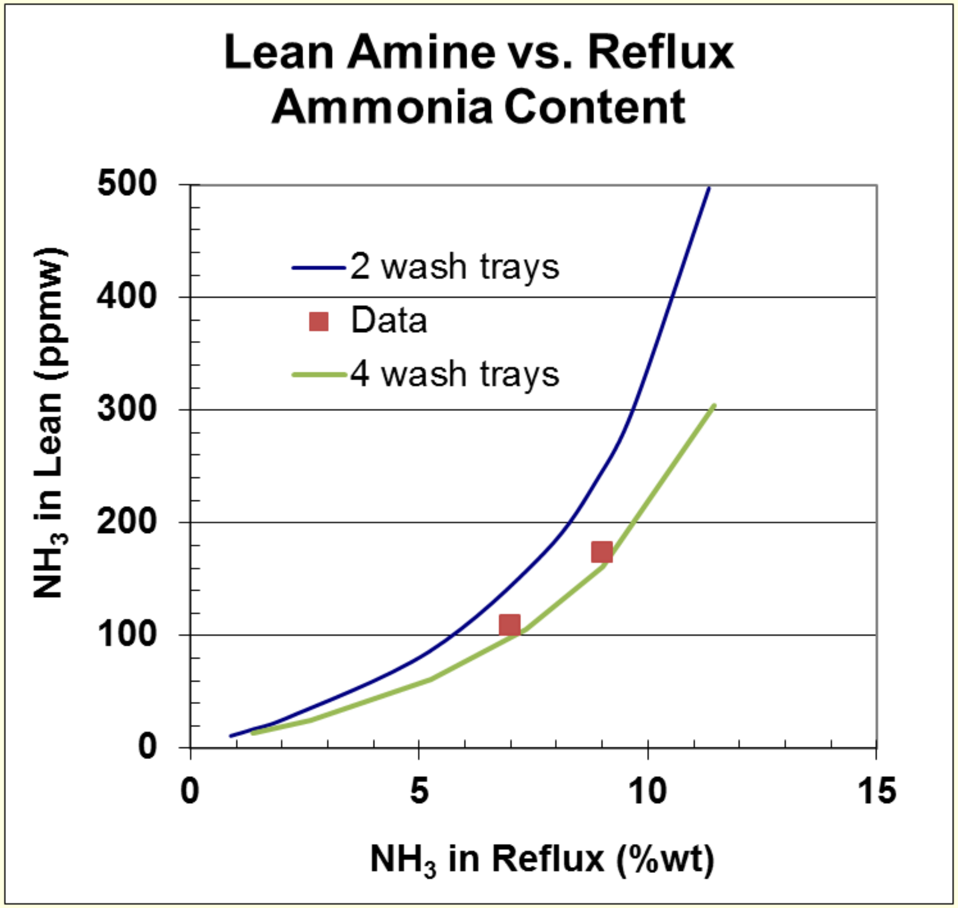


NH_3 Levels in Unpurged Amine Units





Plant Data Validation



Conclusions

- Very little NH_3 contamination can lead to Regenerator reflux corrosion concerns and purging needs
- Ammonia slip to product streams can be expected and minimized by purging reflux
- Model provides some guidance on relationships between NH_3 levels in unit feed, reflux, and acid gas
- Results depend upon unit configuration and should be viewed on a case-by-case basis

Acknowledgments

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