# Aqueous Piperazine as a New Standard for Amine Scrubbing Technology

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Post-Combustion $CO_2$ Capture Workshop
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# Outline

- Amine Scrubbing Technology
- Energy Analysis
  - Irreversibility
  - Maximizing Temperature Swing
- Reagent Robustness
  - Degradation
  - Volatility
  - Reclaiming
- Conclusions

# The "MEA" Standard

- Amine scrubbing with absorption/stripping
  - Post-combustion technology
  - 80 years experience in acid gas treating
  - Amine capture processes (Econamine & KS-1)
- 30 wt% (7 m) MEA benchmark (1st generation)
  - NETL detailed evaluations
  - Most comparisons made to 30 wt% MEA
  - Proprietary solvents make it difficult to compare improvements and new developments





# Concentrated Piperazine (8 m, 40 wt%)

- Second generation amine technology
- Extensive performance data available
- Proprietary 2G solvent technology data unavailable for comparison
- High-temperature 2-stage flash process for piperazine
- Propose concentrated piperazine as new standard for technology comparisons and evaluations

# 8 m Concentrated Piperazine

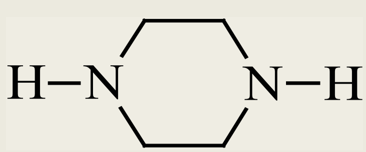
| | 7 m MEA | 8 m PZ |
|---|---|---|
| $CO_2$ Abs Rate (mol/s-Pa-m-$^2$) | 4.3x$10^7$ | 2X |
| Working Capacity (mol/eq) | 0.48 | 1.8X |
| Volatility – Lean (ppm) | 30 | 7 |
| Thermal Stability (°C) | 120 | 150 |
| Oxidative Degradation | 18%/wk | Neglig. |
| Reclaiming – Boil Pt (°C) | 170 | 146 |
| Energy Use (kWh/tonne) | 250 | 10-20% < |



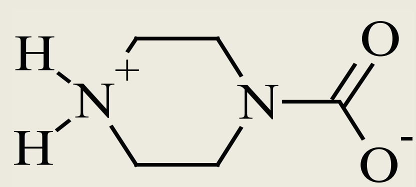


# Piperazine Species

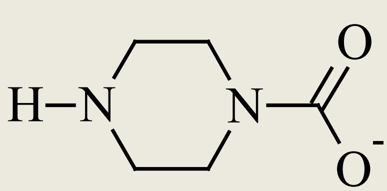
Piperazine (PZ)



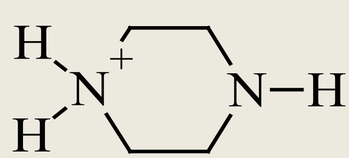
Protonated PZ Carbamate



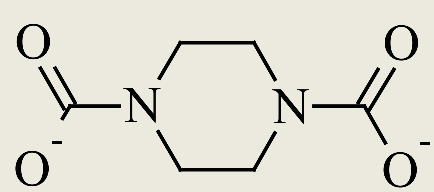
PZ Carbamate



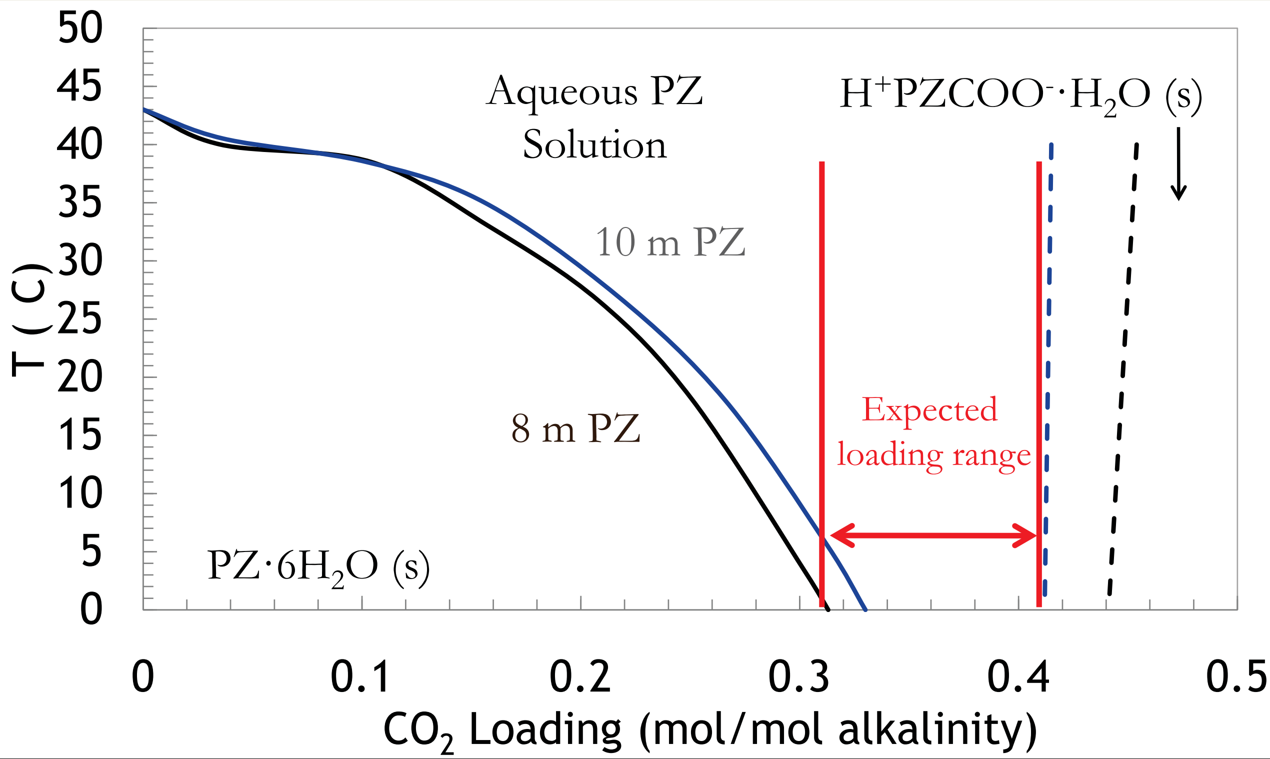
Protonated PZ



PZ Dicarbamate



# Solubility Envelope for Piperazine Permits Concentrated Solvent





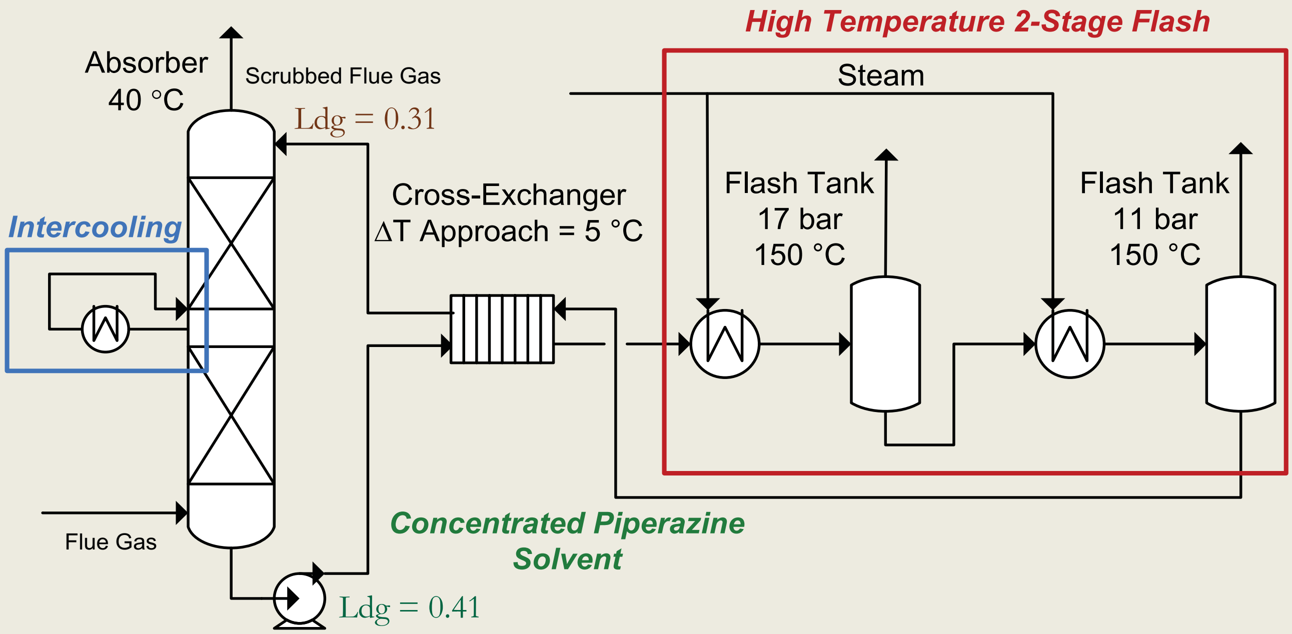



Irreversibility

Maximizing Temperature Swing

# ENERGY ANALYSIS

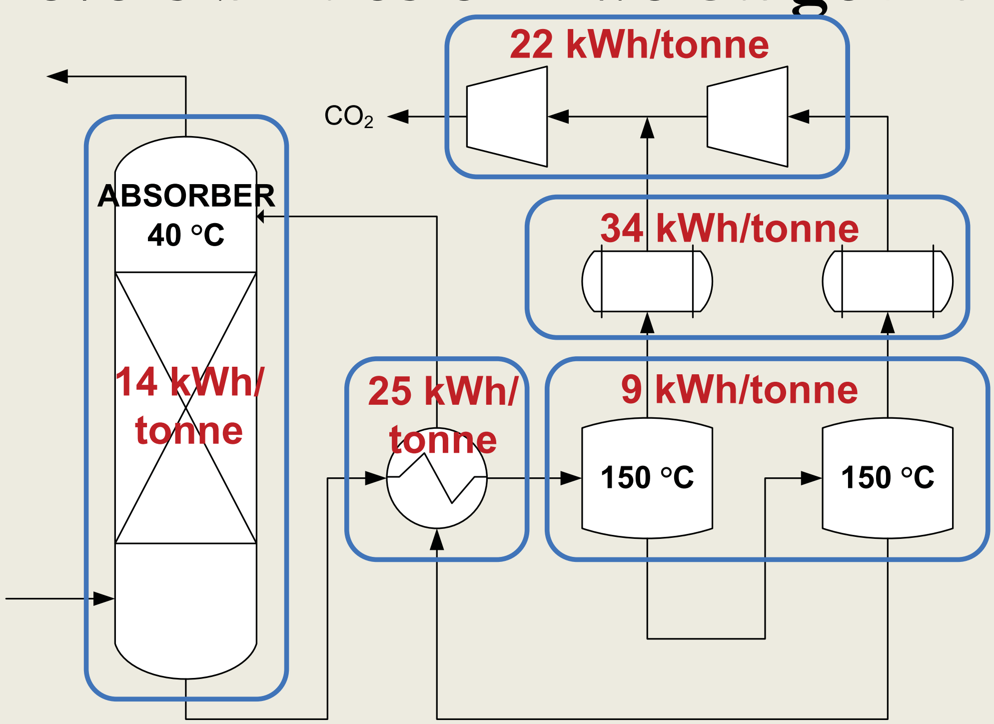
# PZ High Temperature 2-Stage Flash Process Flowsheet








# Irreversibilities of Two Stage Flash




**$W_{IDEAL}$ = 104 kWh/tonne, $W_{REAL}$ = 219 kWh/tonne**

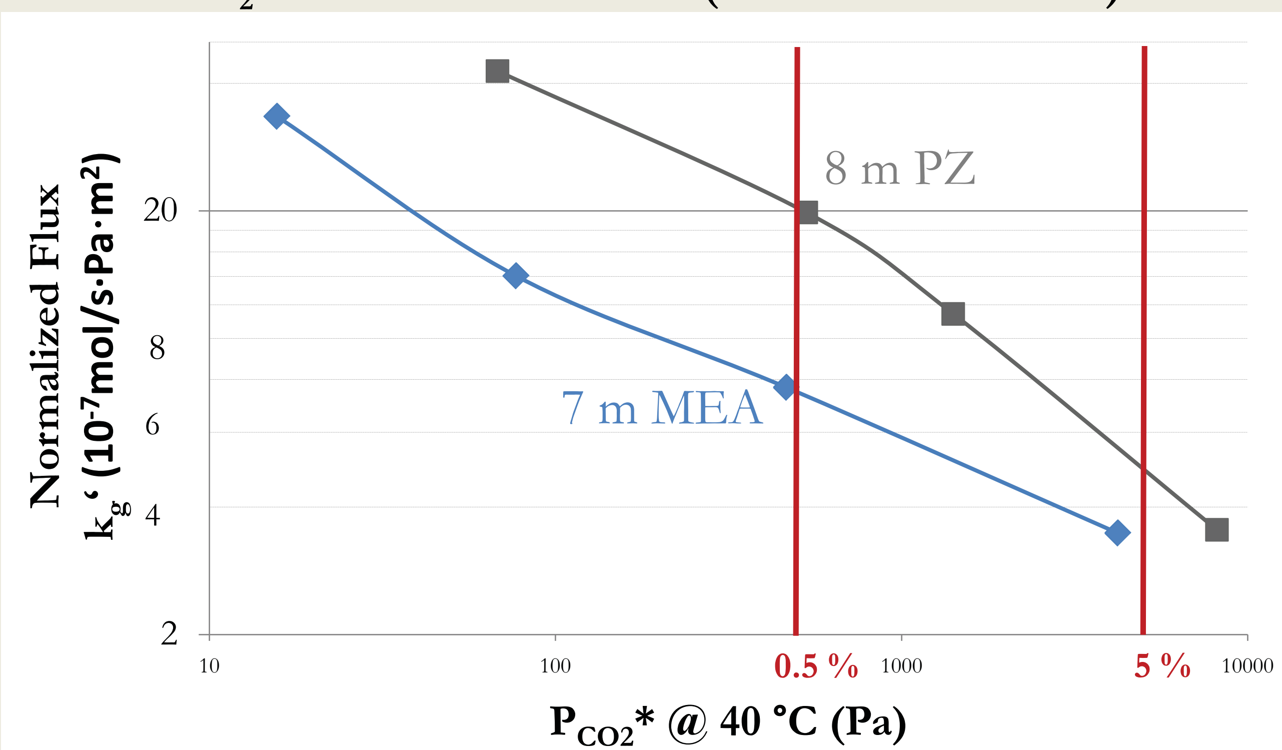
# ABSORBER IRREVERSIBILITY





# Absorber Driving Force

## $CO_2$ Mass Transfer at 40 °C (Wetted Wall Column)



# Absorber Exergy Loss – 14 kWh/tonne

## Estimated Packing Area from $k_g$'

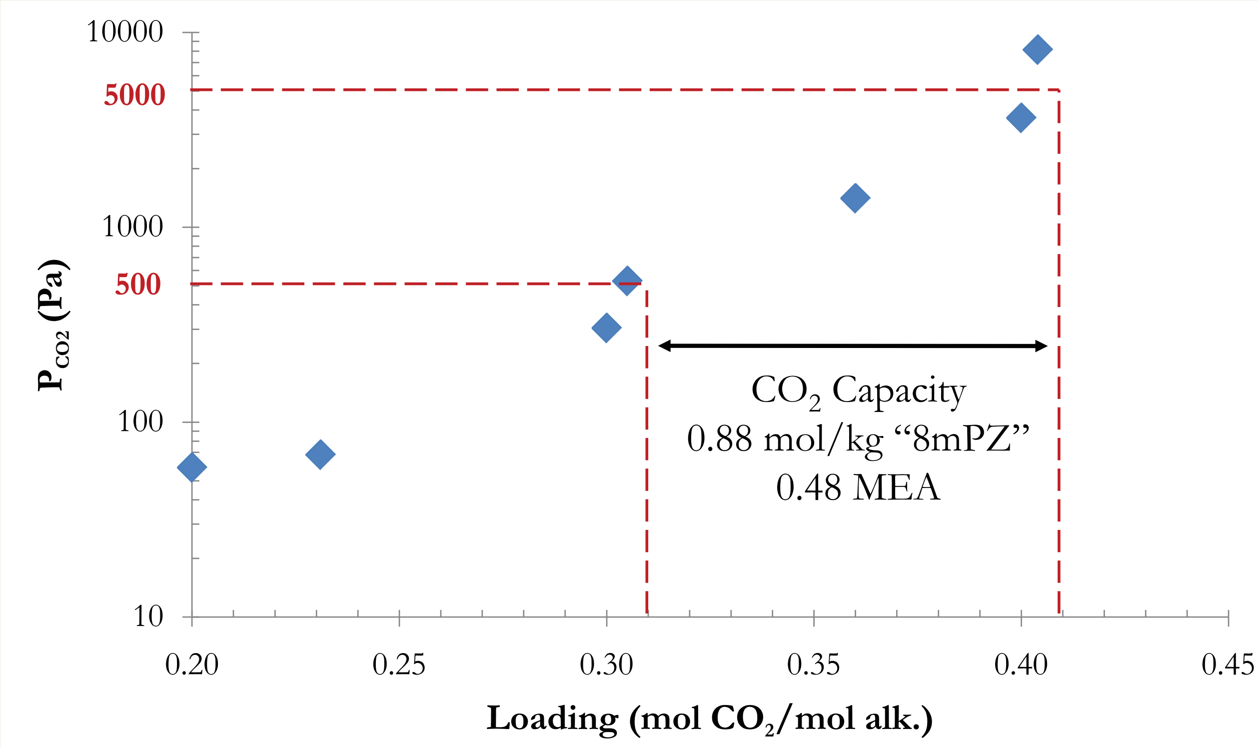
- Ln mean $k_g'\Delta P$ = **2.4e-3 gmol/s-m²**
  - Lean: $k_g'(P_{out}-P_{lean}^*)$= 2.2e-6 *(0.012 – 0.005)*$10^5$
  - Rich: $k_g'(P_{in}-P_{rich}^*)$ = 5e-7*(0.12-0.05)*$10^5$
- Absorber packing volume
  - **1.9e3 $m^3$ for 800 MW**, 250 $m^2/m^3$
    - 0.9 tonne $CO_2$ removed/MW-hr
  - 25 x 25 x 13.5 m
  - 1.5 m/s gas velocity
- Exergy lost/mole $CO_2$
  - $RT\ln(P_g/P^*_{bulk\ liq})$ $=RT\ln(0.12/0.05)$= **14 kwh/tonne $CO_2$**





# CROSS-EXCHANGER IRREVERSIBILITY

# $CO_2$ Solubility in 8 m PZ (40 °C)








# Cross-Exchanger Exergy Loss – 25 kWh/tonne

## Steam Makeup for Unrecovered Sensible Heat Loss

$$Q = C_p \Delta T / \text{capacity}$$
$$= (3.5 \text{ J/mole} - \text{K}) * 5\text{K} / (0.88 \text{ mole/kg})$$
$$= 20 \text{ kJ/mole } CO_2 \text{ Steam at } 155\ °\text{C}$$

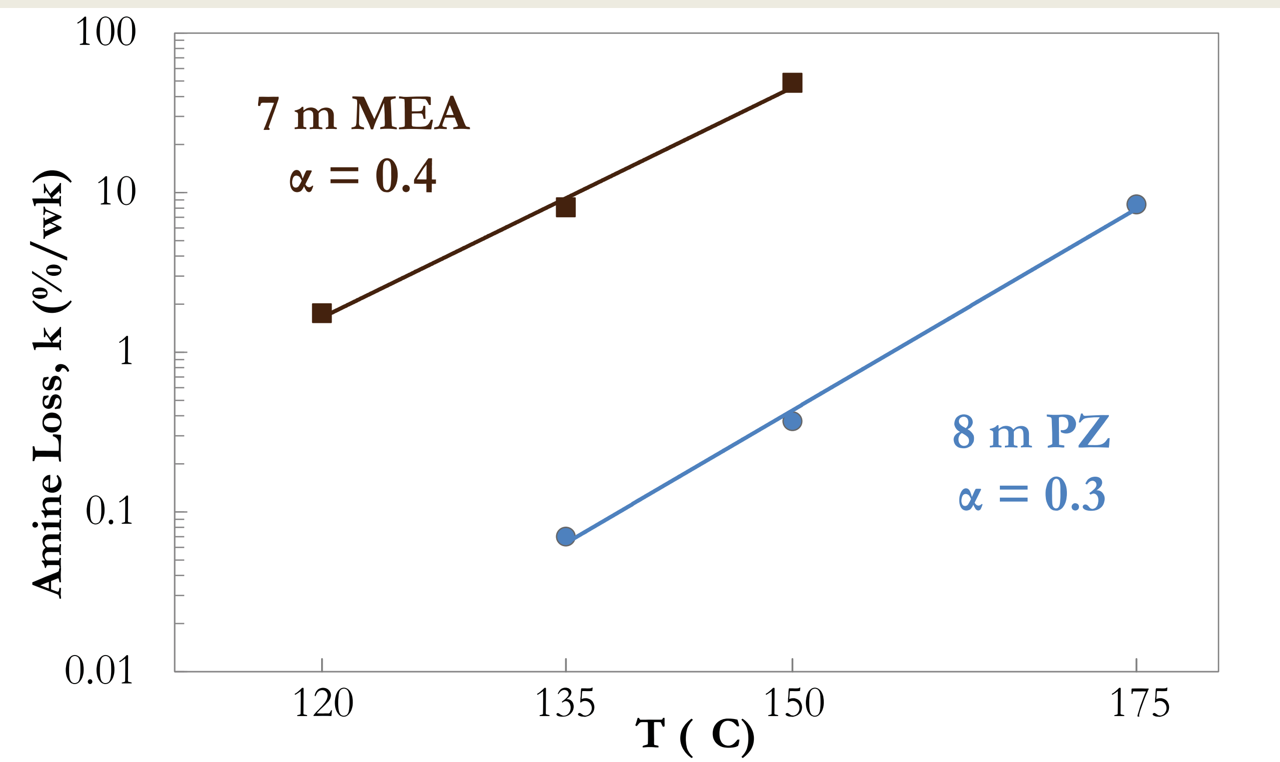
$$W_{loss} = 0.75 Q \frac{T_{stm} - T_{sink}}{T_{stm}}$$
$$= 0.75 * 20 * \frac{155 - 40}{155 + 273} \frac{1e6}{44 * 3600}$$
$$= 25 \text{ kWh/tonne } CO_2$$

# TWO-STAGE FLASH IRREVERSIBILITY

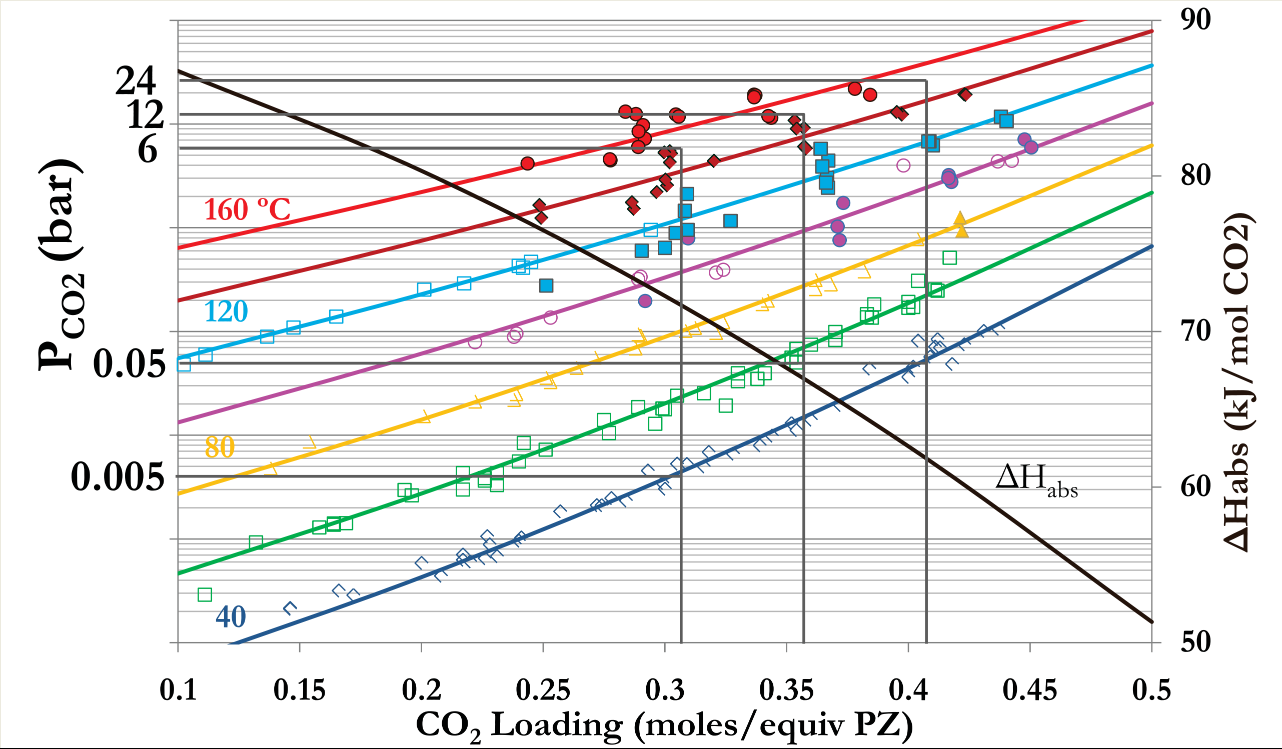




# Thermal Stability Permits 150 °C Stripping



# 8 m PZ Provides High P at 150 °C








# Two-Stage Flash Regeneration Exergy Losses - 43 kWh/tonne

- Flash losses – 9 kWh/tonne
  - Pressure loss of finite flash stages - 4 kWh/tonne
    - $W_{loss} = 0.25RTln(29/17) + 0.25RTln(17/11)$
  - Temperature driving force – 5 kWh/tonne
    - $W_{loss} = 0.75Q_{flash}\Delta T/T = 0.75*95*5/423$
- Condenser loss – 34 kWh/tonne
  - 0.625 moles $H_2O$/mole $CO_2$
  - Condense at 125 °C
  - $W_{loss} = 0.625*40*(125-40)/(125+273)$

# Total Equivalent Work

## Single Stage Flash

- Calculate total equivalent work for generic single stage flash
- $\Delta H_{CO2}$ for 60, 70, 80 kJ/mol
- T = 90 to 150 °C
- Correlate to $(\Delta H_{CO2} - \Delta H_{H2O})\Delta\left(\frac{1}{T}\right)[=]\left(\frac{kJ}{gmol-K}\right)$

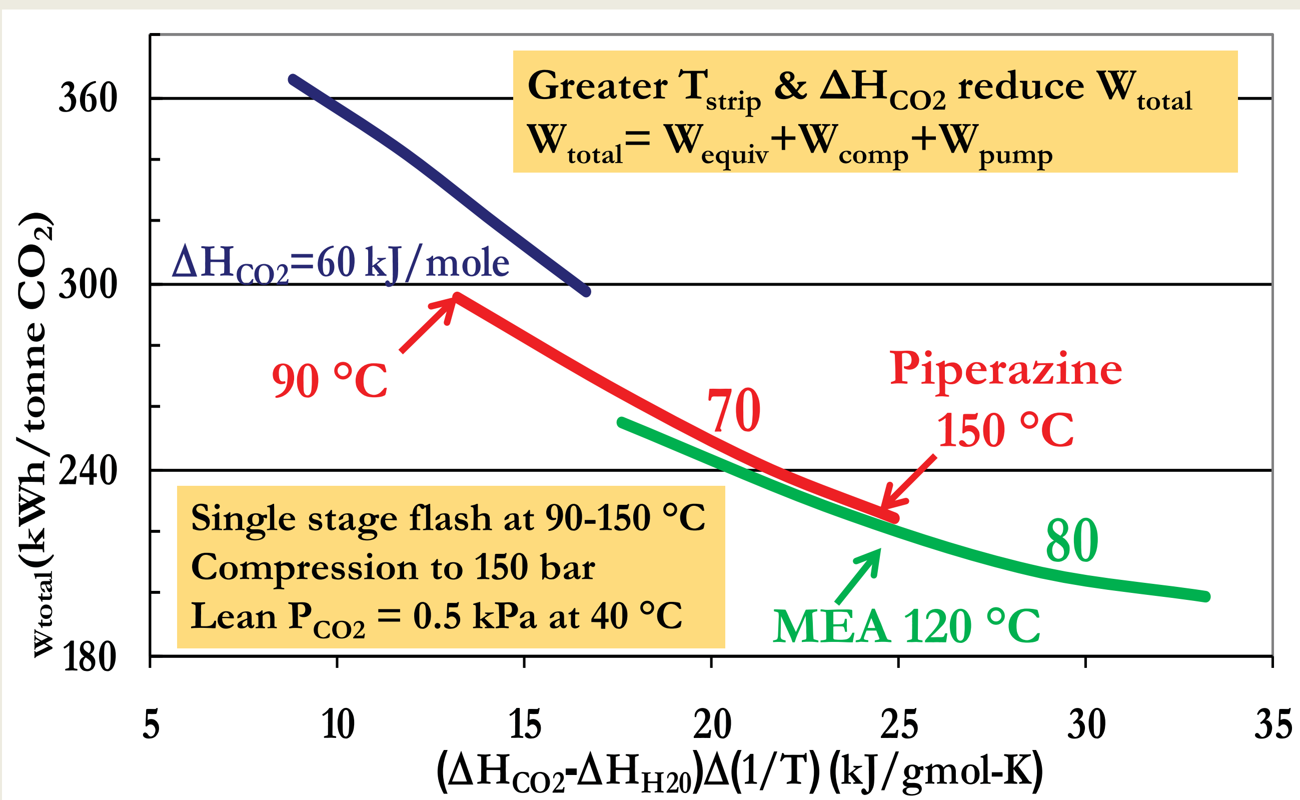
$$W_{total} = W_{equiv} + W_{comp} + W_{pump}$$

$$W_{equiv} = 0.75Q_{flash}\frac{T_{flash}+5-T_{sink}}{T_{flash}+5}$$

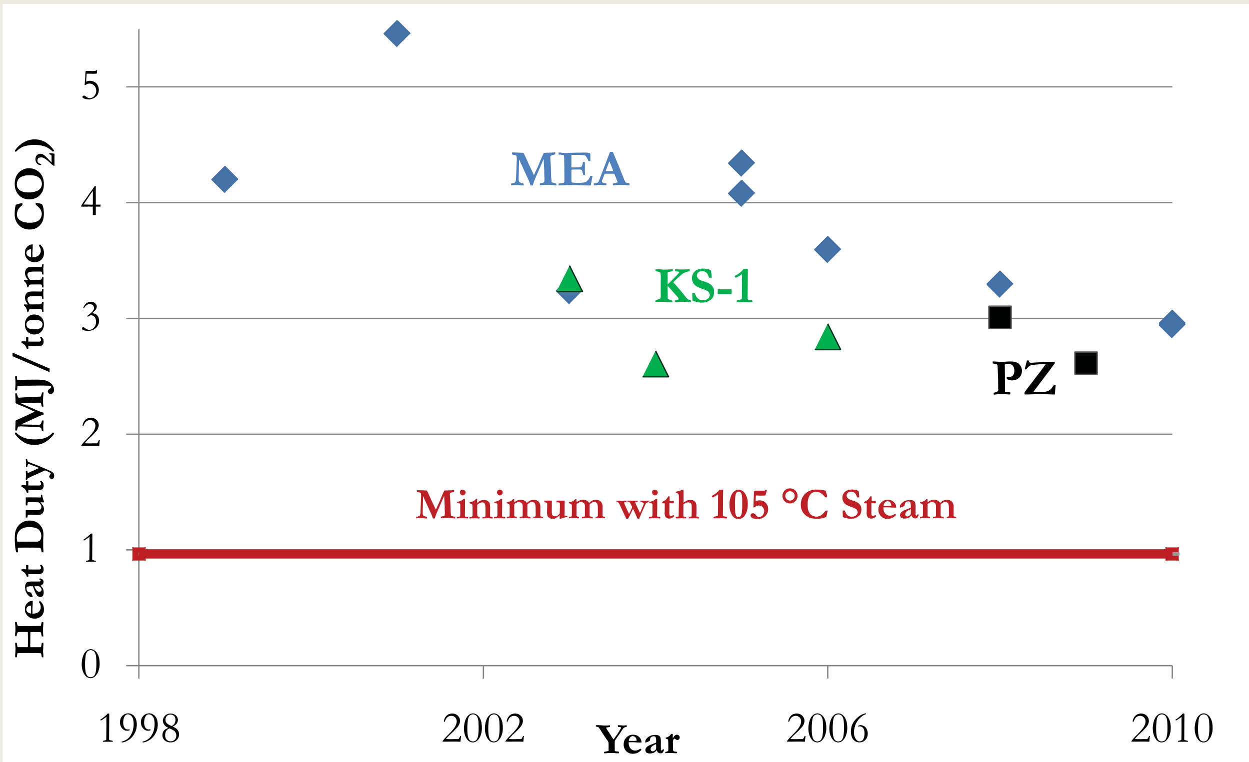




# Maximizing Temp Swing Reduces Total Equiv Work



# Reboiler Duty of Amine Scrubbing

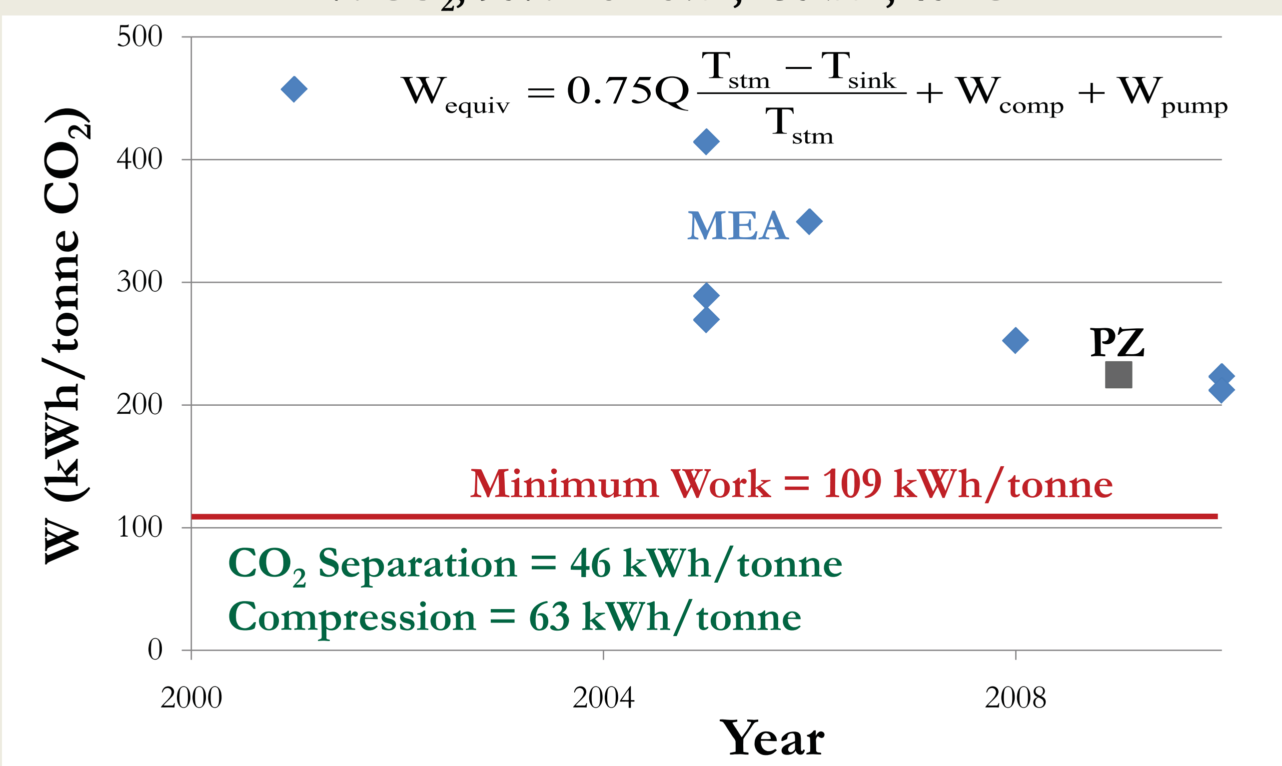







# Estimated Total Equivalent Work

**12% $CO_2$, 90% Removal, 150 bar, 40° C**



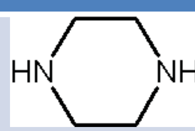
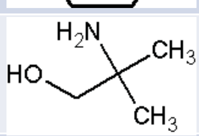
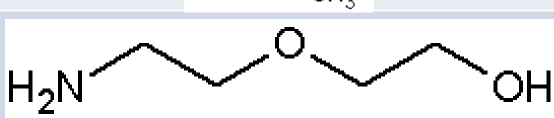
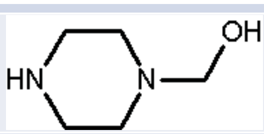
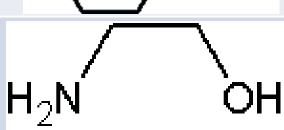
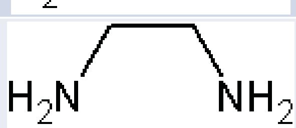
Thermal Degradation
Oxidative Degradation
Amine Volatility
Corrosion Result
Solvent Reclaiming

# ROBUST SOLVENT MANAGEMENT



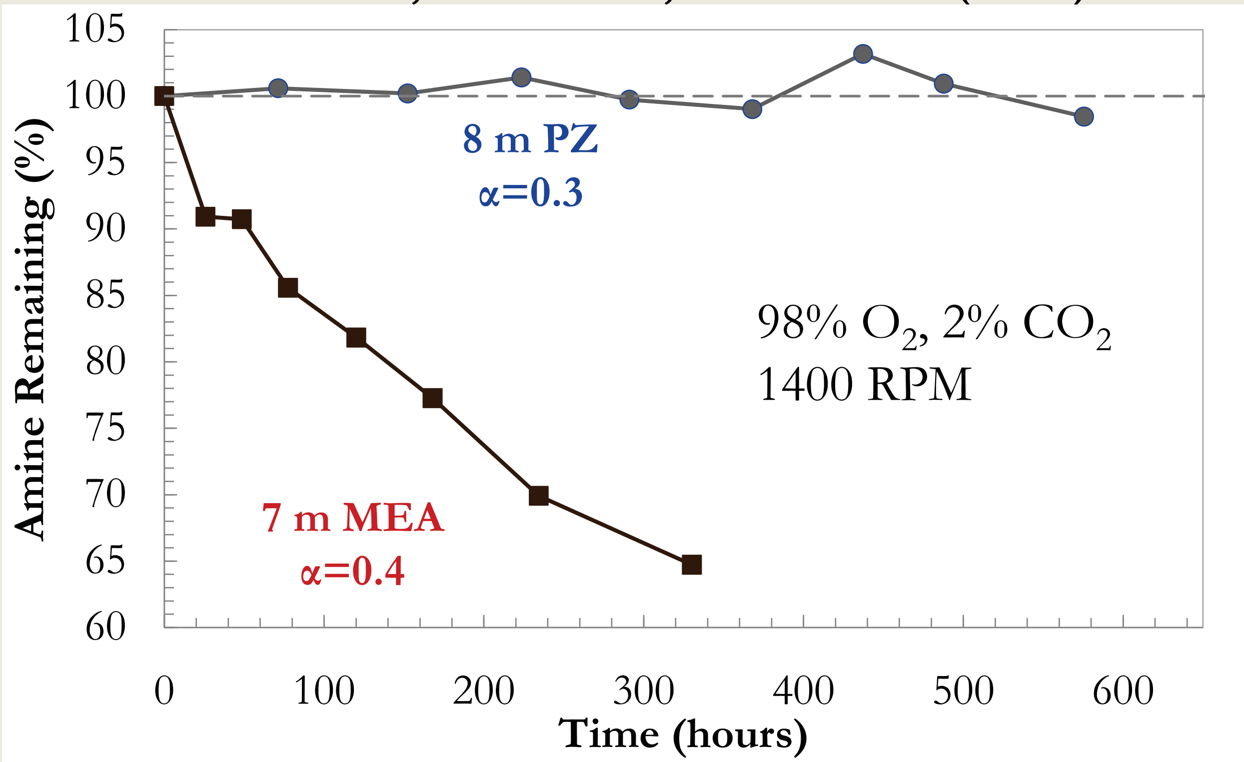
THE UNIVERSITY OF TEXAS AT AUSTIN
Luminant Carbon Management Program


# Thermal Degradation at 135 °C

| Amine | Structure | k (%/wk) |
|---|---|---|
| PZ |  | 0.07 |
| AMP |  | 1.2 |
| DGA |  | 2.1 |
| HEP |  | 2.8 |
| MEA |  | 8.1 |
| EDA |  | 10.1 |

# Oxidative Degradation

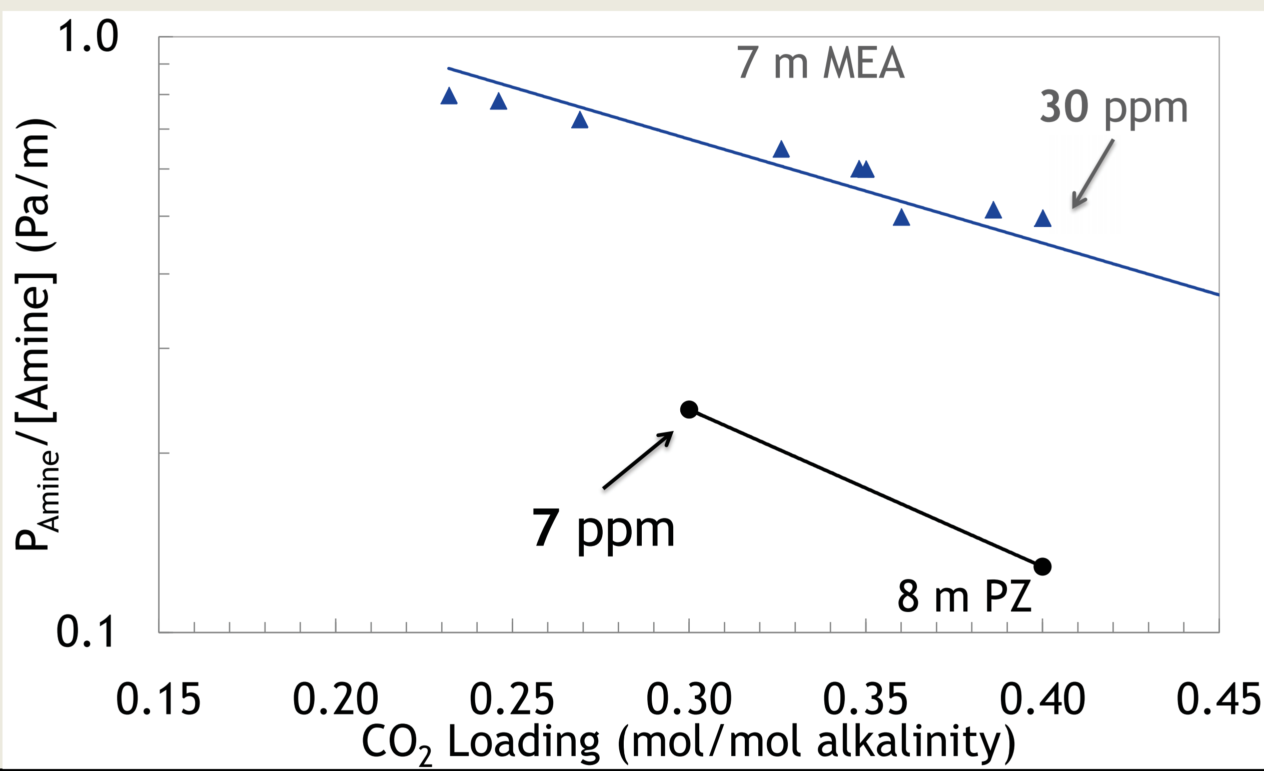
**0.4 mM $Fe^{2+}$, 0.1 mM $Cr^{3+}$, 0.05 mM $Ni^{2+}$ (55 °C)**





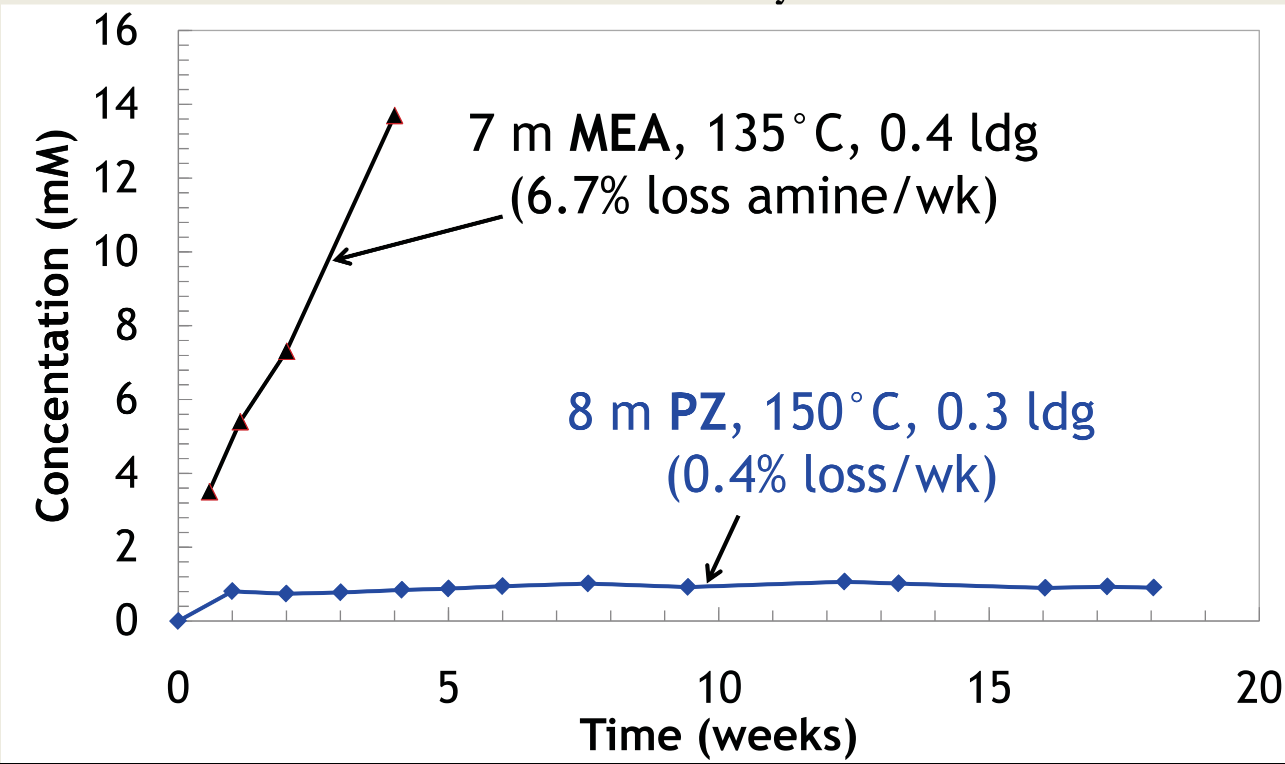



# Amine Volatility at 40 °C



# Thermal Degradation Experiment

## Trace $Fe^{2+}$ in SS316 Cylinders








# Reclaiming Concepts

- Traditional Thermal or distillation Reclaiming
  - Atm or vacuum
  - Boiling Point (°C): PZ=146, MEA=170
  - PZ thermally stable
- Ion Exchange or electrodialysis as with MEA
- $K_2SO_4$ crystallization with addition of KOH
  - 0.17 m sulfate solubility

# Conclusions for Concentrated PZ

- A published amine system that requires only 2.6 $MJ_t$ or 220 $kWh_e$ per tonne $CO_2$ ($\eta$ = 50%)
- 10-20% less energy than 30 wt% MEA
  - Double the $CO_2$ mass transfer rate
  - 1.8 x capacity
  - High P (17 – 11 bar) stripping at 150 °C
- Easier solvent management than MEA
  - Thermally stable
  - Oxidatively stable
  - Less volatile than 7 m MEA
  - Good opportunities for reclaiming





# Questions?