IEA GHG – 11th Meeting of the Post-Combustion CO_2 Capture Network

Aqueous Concentrated Piperazine – a Fast, Stable, and Effective Solvent

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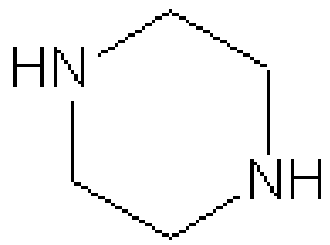
Outline

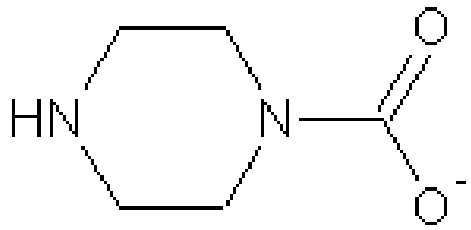
- Introduction to Concentrated Piperazine
  - Previous Work
  - Solid-Liquid Equilibrium
  - Volatility
  - Viscosity
- Energy Performance
  - Vapor-Liquid Equilibrium
  - Kinetics of CO_2 Absorption
- Degradation
  - Oxidative
  - Thermal
- Conclusions

Previous work with Piperazine (PZ)

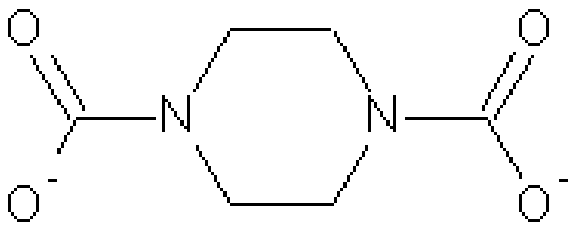
- Piperazine has been used as a promoter at concentrations up to 4 m
  - 7 m MDEA / 2 m PZ
  - 2.5 m K_2CO_3 / 2.5 m PZ



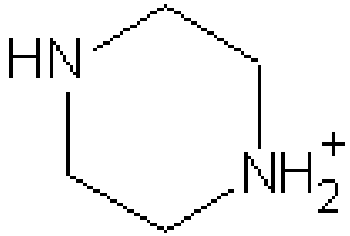
PZ



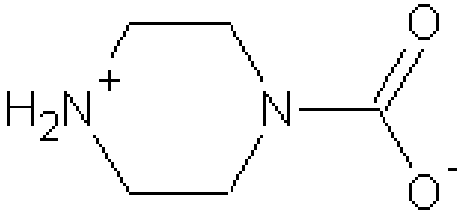
PZ COO^-



PZ $(COO^-)_2$



H^+PZ

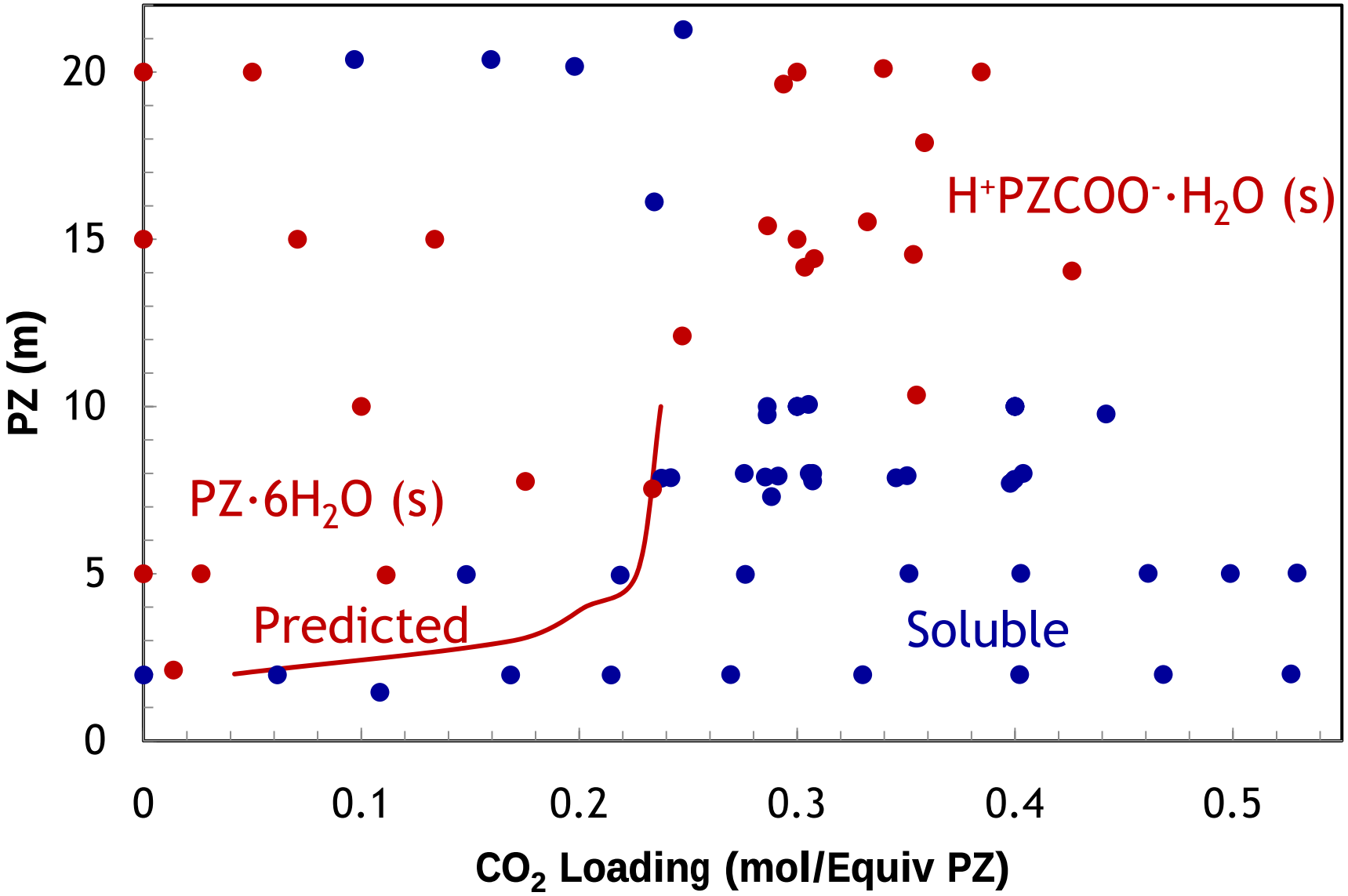


$H^+PZ\ COO^-$

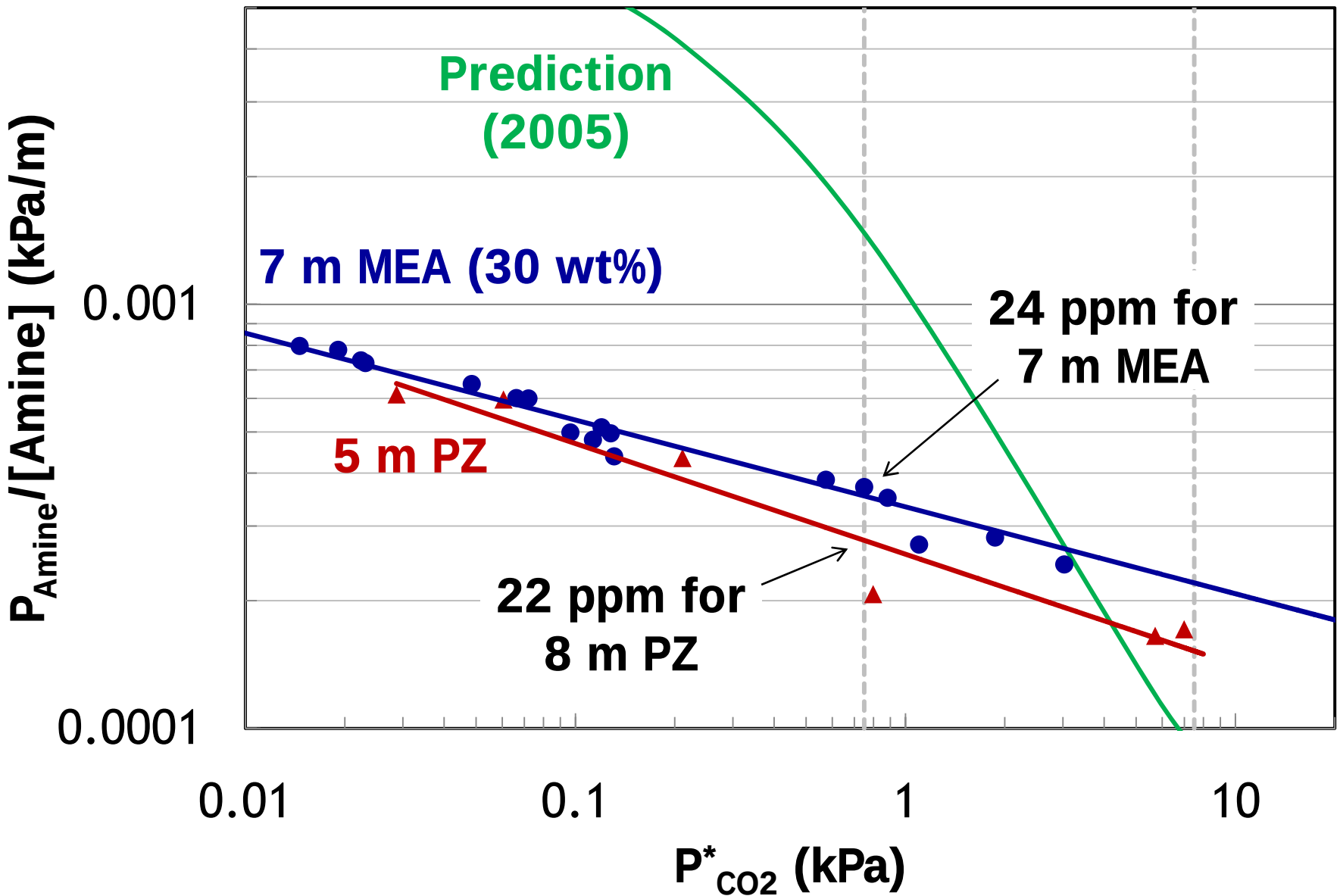
Introduction

- Why didn't we consider PZ before?
  - Solubility = 1.75 m PZ
    - PZ has low capacity at 1.75 m PZ
  - Boiling point is lower than MEA
    - Expected volatility is greater than MEA
- What's New?
  - We can prepare 8 m solutions at useful loadings
  - Non-ideality results in volatility equivalent to MEA

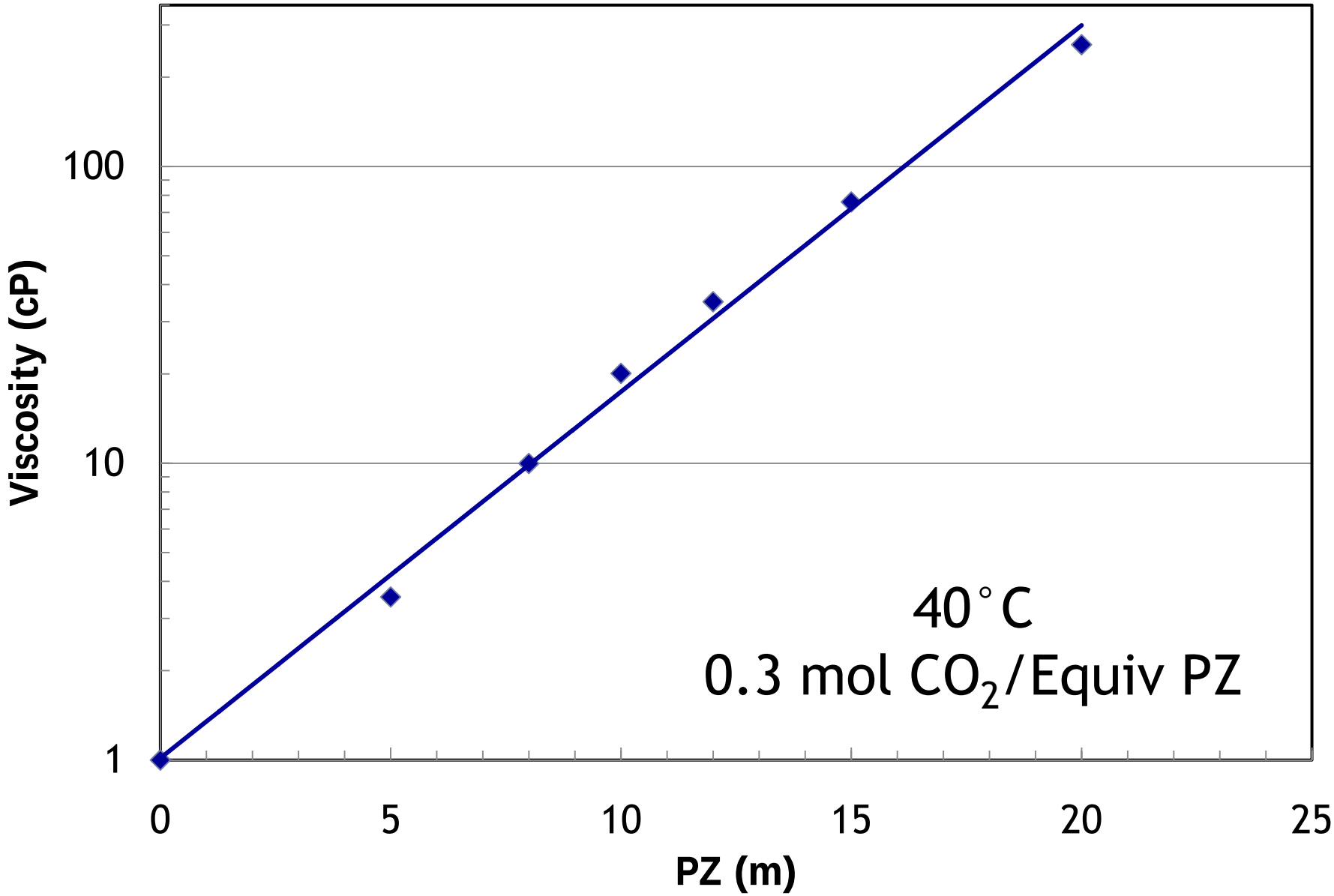
Solid Solubility at 21°C



Normalized Amine Volatility at 40°C

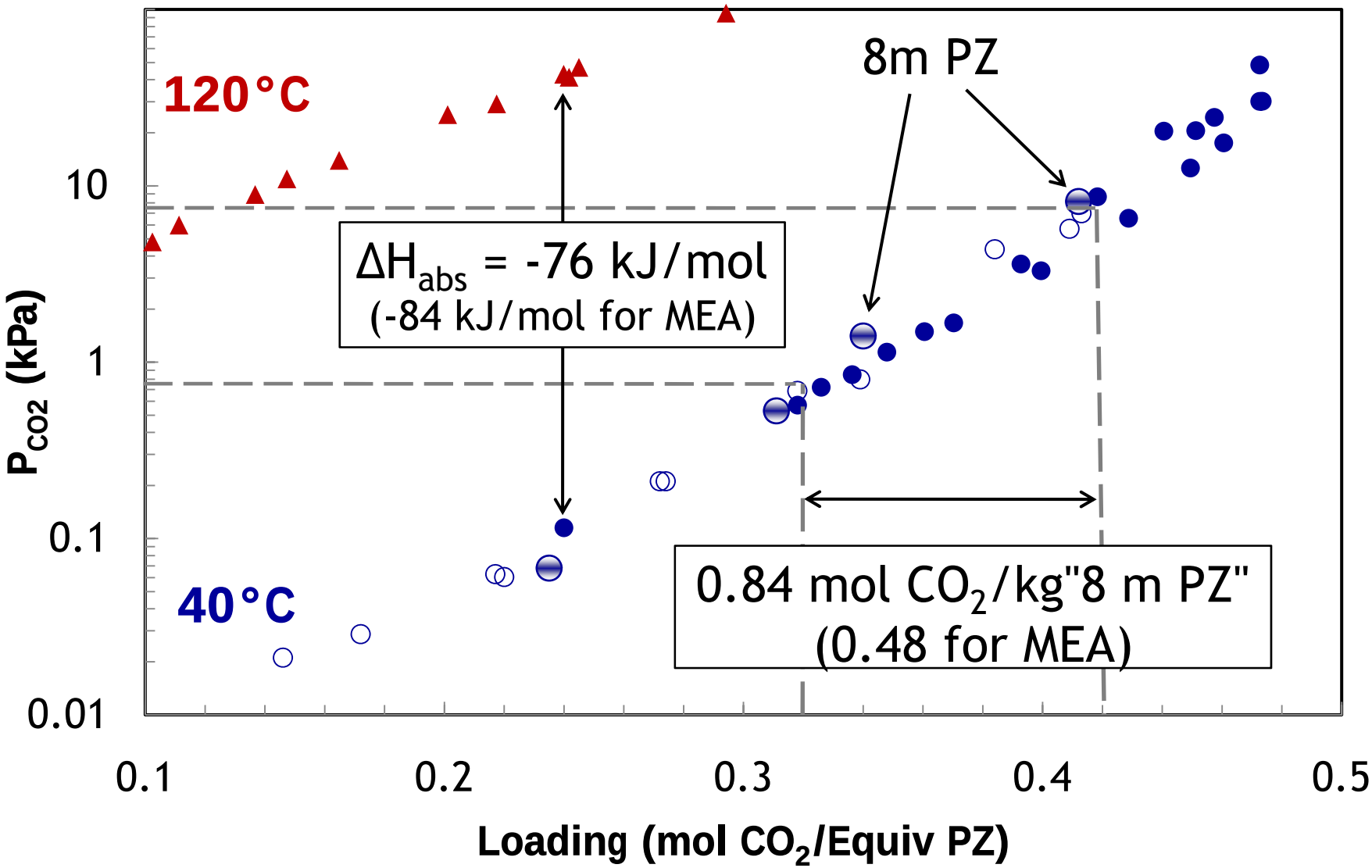


PZ is highly viscous above 8 m

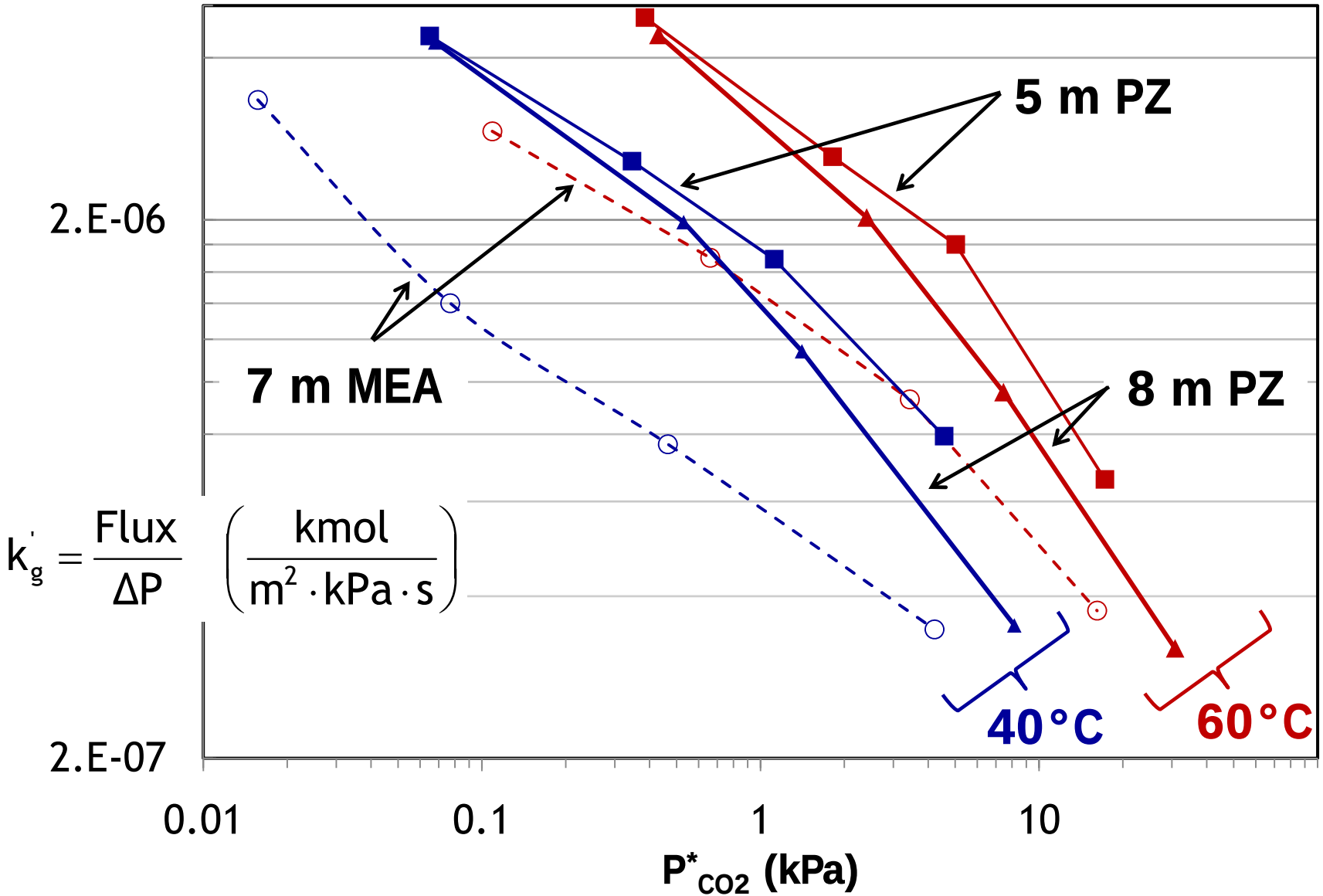


Thermodynamics of PZ-H_2O-CO_2

4.0 m (Ermatchkov 2006), 3.6 to 8.0 m (This Work)



5 to 8 m PZ Doubles Rate of CO_2 Absorption



Simple Stripper Energy Requirement

- Interpolated from Oyenekan (2007)
- CO_2 product delivered at 10 MPa

	7 m MEA	8 m PZ	Ideal
ΔH_{abs} (kJ/mol)	84	76	
CO_2 Capacity (mole/kg soln)	0.46	0.84	
Rich P_{CO2} at 40°C (kPa)	5	7.5	12
Equiv Work (kJ/mole)	30.9	28.2	18

Degradation Products

- Anion and cation chromotgraphy (Dionex)
- HPLC for molecular products
- Primary degradation products:
  - Amines: Ethylenediamine (EDA)
  - Amides: formamide, oxamide
  - Carboxylic acids: formate, oxalate
  - Nitrite and nitrate
  - (Ammonia)
- Total acid = acid + amide

PZ is resistant to Oxidation

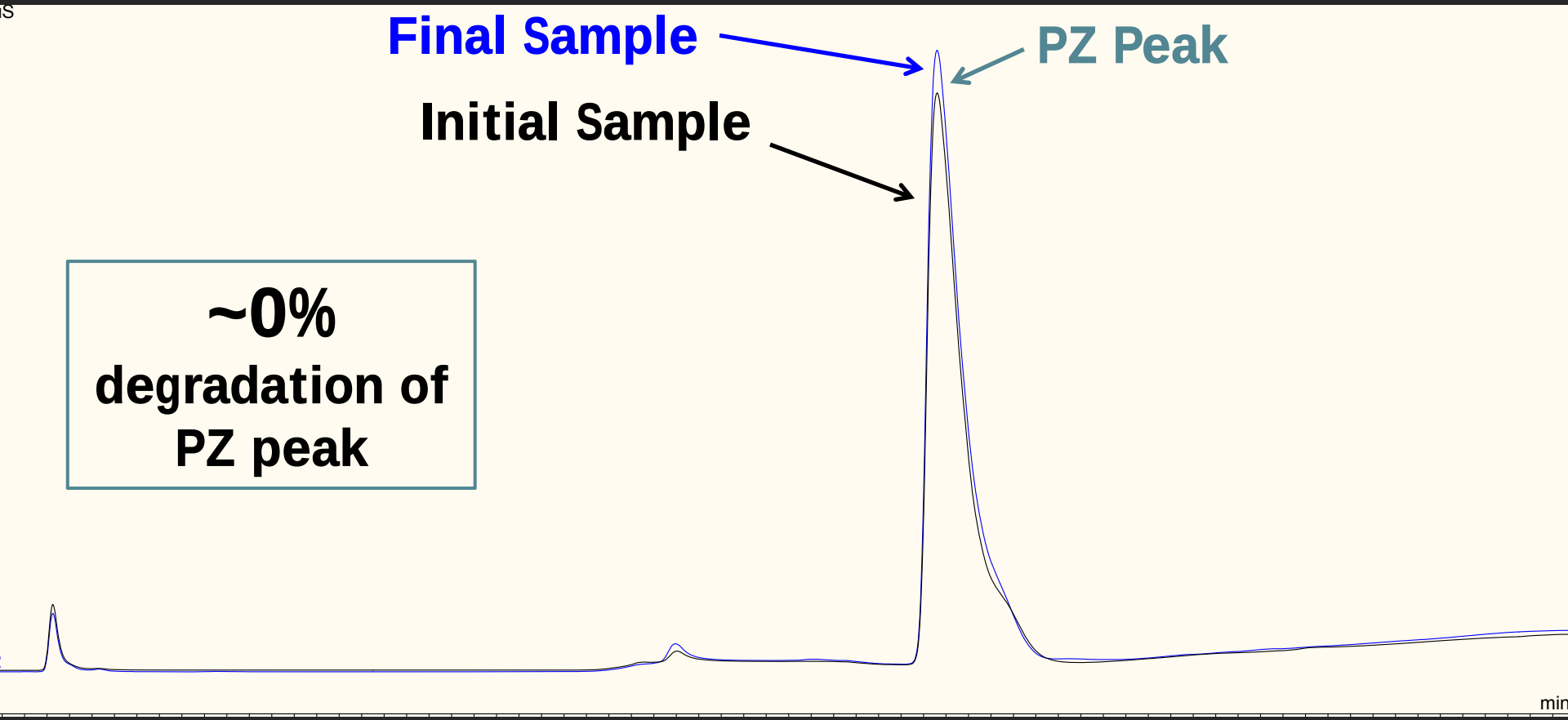
- 55°C, 100 mL/min O_2 w/ 2% CO_2 in 350 mL

AMINE	7 m MEA	10 m PZ	8 m PZ	10 m PZ
Additives **(mM)**	0.6 Fe	4.0 Cu	5.0 Cu 0.1 Fe 100 "A"	0.1 Fe 0.1 Ni 0.6 Cr
		Production Rates (mM/hr)		
Ethylenediamine	-	0.43	-	-
Total Formate	0.40	0.36	0.03	0.01
Total Oxalate	0.04	0.02	0.001	-
Nitrate/Nitrite	0.46	0.01	0.001	0.0003

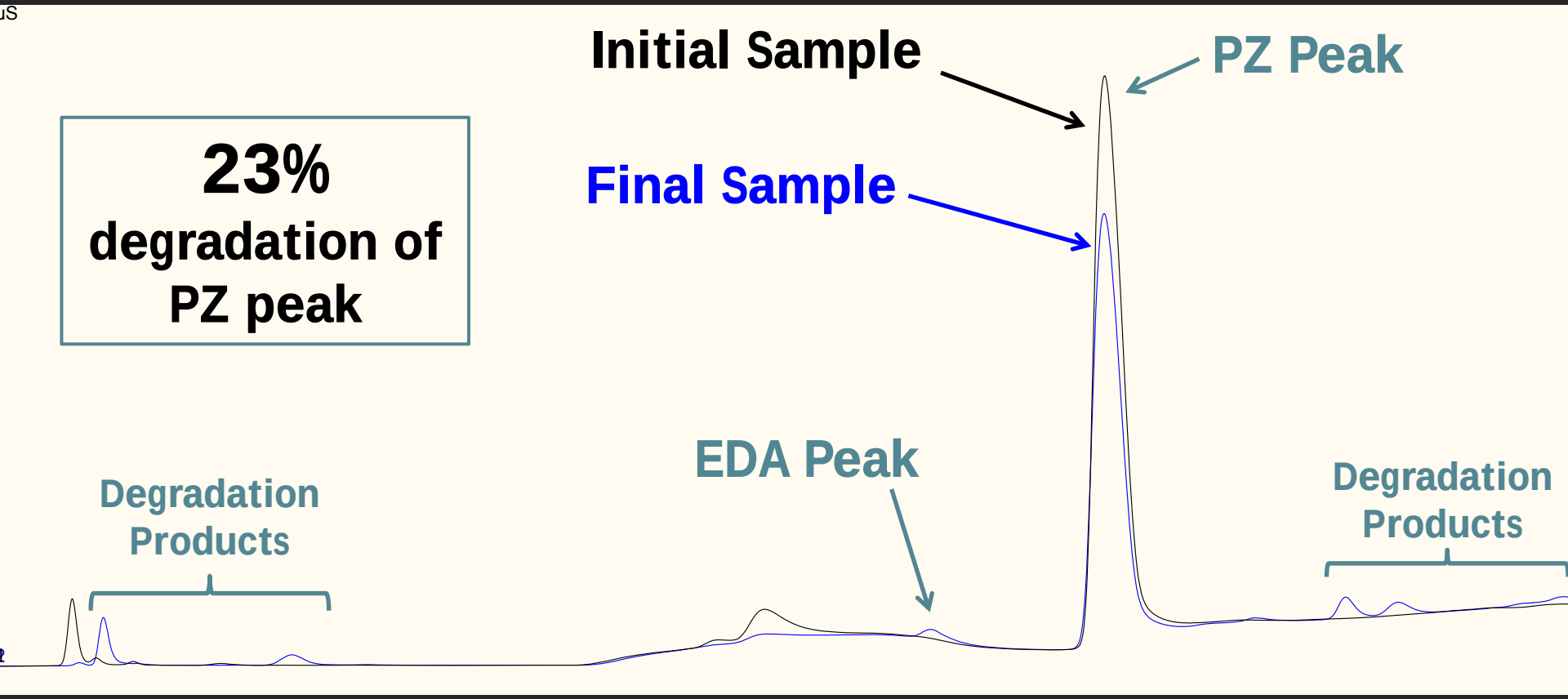
Thermal Degradation of Piperazine

- SS bombs in forced convection ovens
- Degradation negligible up to 150°C
- Degradation not catalyzed by metals
  - Cu + Fe
  - Fe + Ni + Cr
  - Cu + Fe + Inhibitor "A"

5 m PZ at 135°C, 8 wks, α=0.5



8 m PZ at 175°C, 5 wks, α=0.3



Conclusions

- 8 m PZ is soluble at 0.25-0.4 mol CO_2/Equiv PZ
- Viscosity becomes prohibitive above 8 m PZ
- PZ volatility less than predicted & equiv to MEA
- CO_2 capacity is double that of 7 m MEA
- CO_2 absorption rate is double that of 7 m MEA
- Thermal degradation of PZ is negligible
- Oxidative degradation
  - Negligible with Fe, Cr, Ni, V, and Cu/"A"
  - Significant with Cu alone