









Evaluation of Concentrated Piperazine for CO₂ Capture from Coal-Fired Flue Gas

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DOE-NETL Contractor's Meeting September 15, 2010



URS Corporation

- Leading Engineering and Construction Services Firms
- Approximately 42,000 employees in 30+ countries
- Annual revenues \$10B
- Process Technologies Office Austin, TX
 - Air pollution controls (SO₂, SO₃, Hg, Se, CO₂)
 - Water/wastewater management
 - Lab scale R&D, pilot plant and demonstration scale projects
 - 32,000 ft² laboratory facility



Project Participants

- Team Members
 - URS (PjM: Katherine Dombrowski)
 - University of Texas at Austin (PI: Gary Rochelle)
 - Trimeric (PjM: Kevin Fisher)
- Host Sites
 - CSIRO's Post Combustion Capture facility at Tarong
 - UT's Separations Research Plant
 - DOE's National Carbon Capture Center
- Cost-Share Providers
 - CO₂ Capture Pilot Plant Project at UT
 - Funded by EPRI, Luminant, E.on, Southern Company



Funding

- Q1 GFY 2011 Q4 GFY 2013
- DOE: \$3,000,000
 - DOE-NETL Project Manager: Bruce Lani
- Cost Share: \$866,711
 - University of Texas at Austin: CO₂ Capture Pilot Plant Project (C2P3)
 - Cash designated by EPRI and utility members to this DOE-NETL project to provide modifications to the 0.1 MW skid

CO₂ Absorption by Piperazine

- Absorption of CO₂ with concentrated (8m, 40 wt%) piperazine
- Regeneration with high-temperature 2-stage flash

Piperazine (PZ)

PZ Carbamate

$$H-N$$
 N
 O

Protonated PZ

$$H$$
 N H N H

PZ Dicarbamate

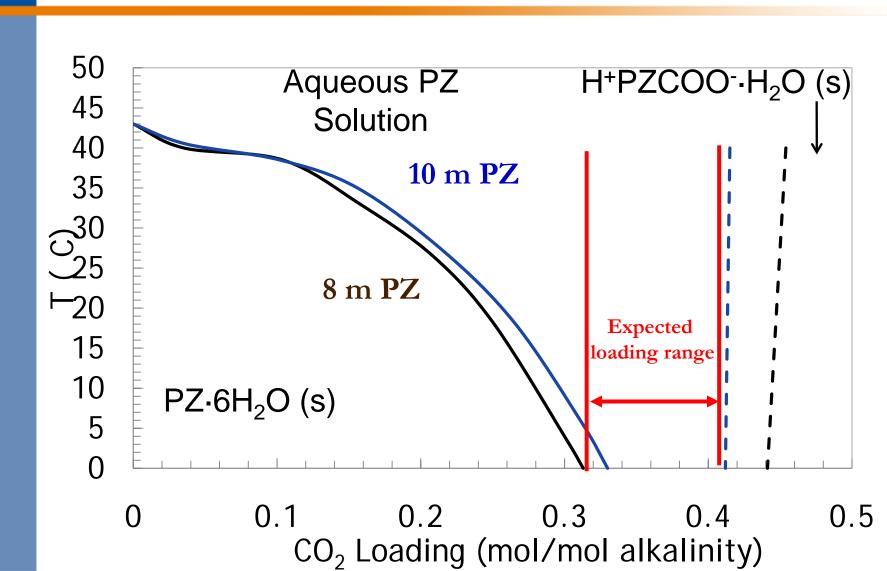
$$\begin{array}{c}
O \\
N
\end{array}$$

Protonated PZ Carbamate

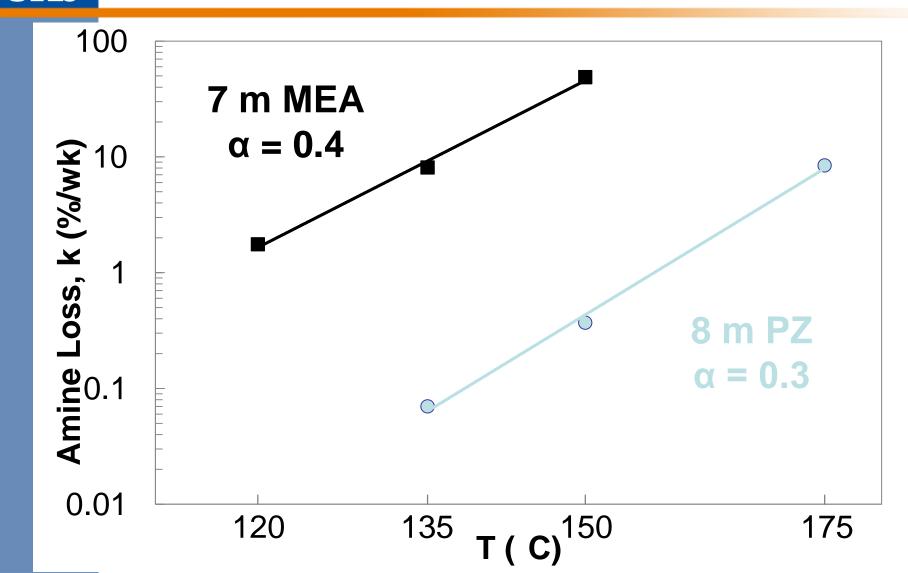
$$H$$
 N N O



Solubility Envelope for PZ Permits Concentrated Solvent



Thermal Stability Permits 150 C Stripping

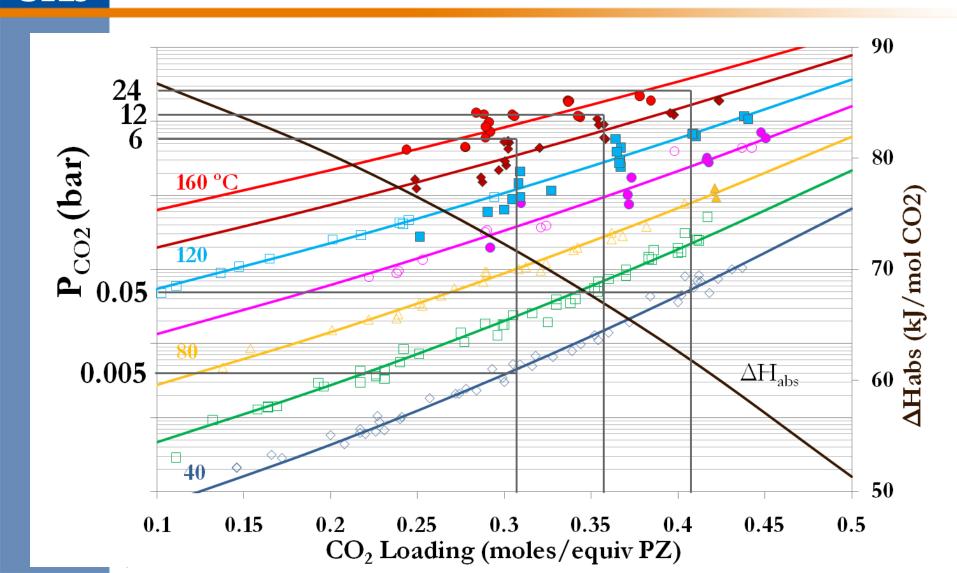


Thermal Degradation at 135 C

Amine	Structure	k (%/wk)
PZ	ни	0.07
AMP	HO CH ₃	1.2
DGA	H ₂ N OH	2.1
HEP	HN OH	2.8
MEA	H_2N OH	8.1
EDA	H_2N NH_2	10.1

8m PZ Provides High P at 150 C

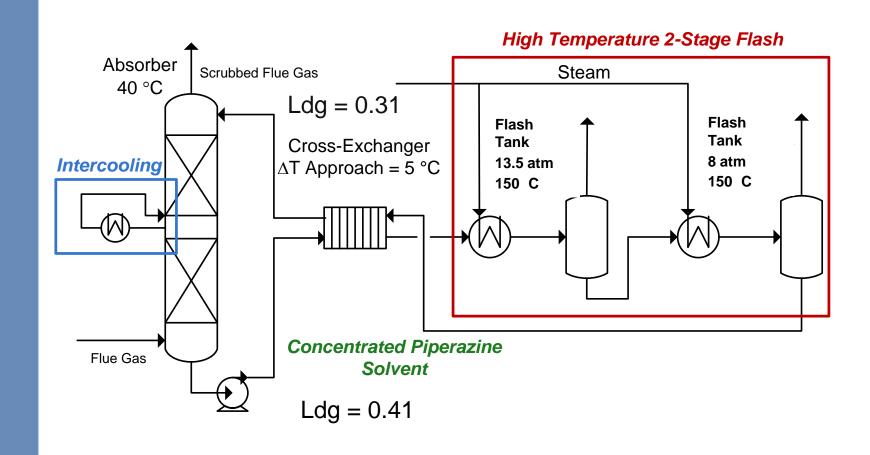
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Advantages of Piperazine

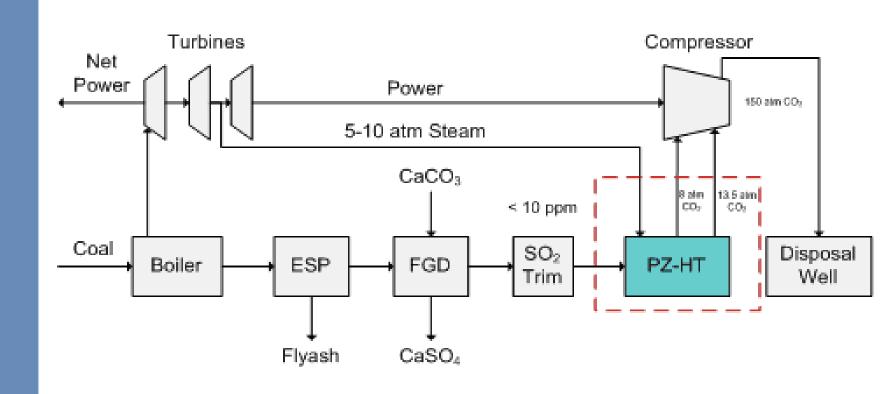
	7 m MEA	8 m PZ
CO ₂ Abs Rate (mol/s-Pa-m- ²)	$4.3x10^7$	2X
Working Capacity (mol/eq)	0.48	1.8X
Volatility – Lean (ppm)	30	7
Thermal Stability (C)	120	150
Oxidative Degradation	18%/wk	Neglig.
Reclaiming – Boil Pt (C)	170	146
Energy Use (kWh/tonne)	250	10-20% <

Process Flow Diagram



Integration of PZ-HT into Power Plant

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Production of CO₂ at elevated pressure, lowering compression costs



Economic Advantages

From DOE/NETL-2007/1281

	% CO ₂ Capture	Energy (MWh/ton CO ₂ removed)	CapEx (\$/net kwh)	COE (¢/kwh)
No capture	0%	0	1549	6.4
30% MEA	87%	0.38	2895	11.9
PZ-HT	90%	0.23	2330	9.4

- Additional savings in COE may be achieved by
 - Optimization of absorber packing
 - Flue gas pre-treating
 - Compressors
 - Heat exchangers
 - Design improvements realized as part of this project



Challenges

- Robustness of concentrated PZ in flue gas must be demonstrated
 - PZ more expensive to replace than MEA
- Robustness of process to excursions in CO₂ loading, temperature and water balance must be demonstrated
 - Quantify effect on solids precipitation
 - Quantify effect on plant operation

Project Objectives

- Demonstrate robustness of PZ in integrated absorption/HT-stripping system
- Optimize equipment design and energy performance of PZ-HT
- Identify and resolve operational and design issues, including process control, foaming, solids precipitation
- Evaluate technical and economic feasibility of full-scale implementation of the process

Work Plan

- Field Campaign #1: CSIRO 0.1 MW
 - 3-month test
 - Low-sulfur bituminous coal with caustic scrubber
 - First test in coal-fired flue gas
- Field Campaign #2: UT SRP 0.1 MW
 - 3-week test in CO₂/air
 - Test modifications of 2-stage flash prior to 0.5 MW design
- Field Campaign #3: NCCC 0.5 MW
 - 3-month test
 - Medium-sulfur bituminous coal with limestone scrubber



Schedule

- 36 month project
- Tests with 0.1 MW Regeneration Skid
 - CSIRO Test: March May 2011
 - SRP Test: November December 2011
- Design/Build 0.5 MW Regeneration Skid: 2012
- Test with 0.5 MW Regeneration Skid
 - NCCC Test: February April 2013

New solvent/process development areas for project

- 40 wt% PZ solvent with fast CO₂ absorption rates, high capacity, and thermal stability
- Integrated process with absorber intercooling and solvent regeneration by a high temperature two-stage flash with concentrated PZ
- Quantification of thermal and oxidative degradation of concentrated PZ with coal-fired flue gas with a cyclic absorber/high temperature flash
- Scale-up from 0.1 to 0.5 MW of the optimized high temperature two-stage flash process and PZ solvent with coal-fired flue gas.

Plans for Future Development

- Pending successful testing of PZ-HT process at 0.1 MW and 0.5 MW, future steps include
 - Deployment of lessons learned in this project to future tests
 - Larger scale demonstrations, eventually leading to integration with power plant steam cycle
 - Longer-term demonstrations on a variety of coal types