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Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas

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DOE-NETL Contractor's Meeting
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TRIMERIC CORPORATION

The University of Texas at Austin

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Team Members

- URS
  - Prime Contractor: Detailed Engineering Design, NCCC Task Leader
- UT Austin. CO_2 Capture Pilot Plant Project
  - Technology Provider: Co-funder, task leader for demonstration sites
- Trimeric
  - Major Subcontractor: Process Design, Field Test Support, Feasibility Study

Project Participants

- Team Members
  - **URS** (PjM: Katherine Dombrowski)
  - **University of Texas at Austin** (PI: Gary Rochelle)
  - **Trimeric** (PjM: Kevin Fisher)
- Host Sites
  - **UT**'s Separations Research Program
  - **CSIRO**'s Post Combustion Capture facility at Tarong
  - **DOE**'s National Carbon Capture Center
- Cost-Share Providers
  - CO_2 Capture Pilot Plant Project at UT
    - Funded by EPRI, Luminant, Southern Company, LG&E-KU, Babcock & Wilcox, Chevron

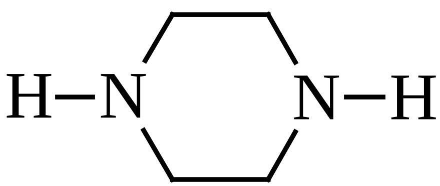
Funding

- Q1 GFY 2011 – Q4 GFY 2014
- DOE: $3,000,000
  - DOE-NETL Project Manager: Bruce Lani
- Cost Share: $866,711
  - University of Texas at Austin: CO_2 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

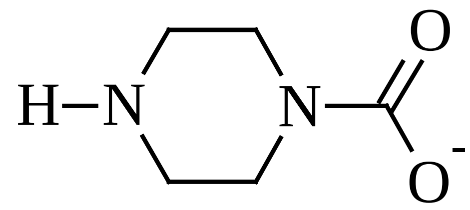
CO_2 Absorption by Piperazine

- **Absorption** of CO_2 with concentrated (8m, 40 wt%) piperazine (PZ)
- **Regeneration** with high-temperature 2-stage flash

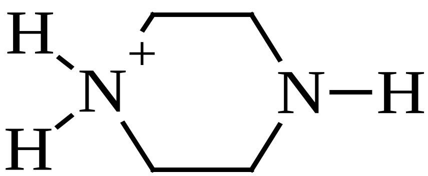
Piperazine (PZ)



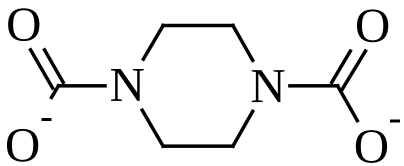
PZ Carbamate



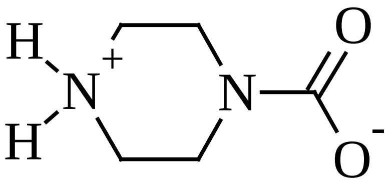
Protonated PZ



PZ Dicarbamate



Protonated PZ Carbamate



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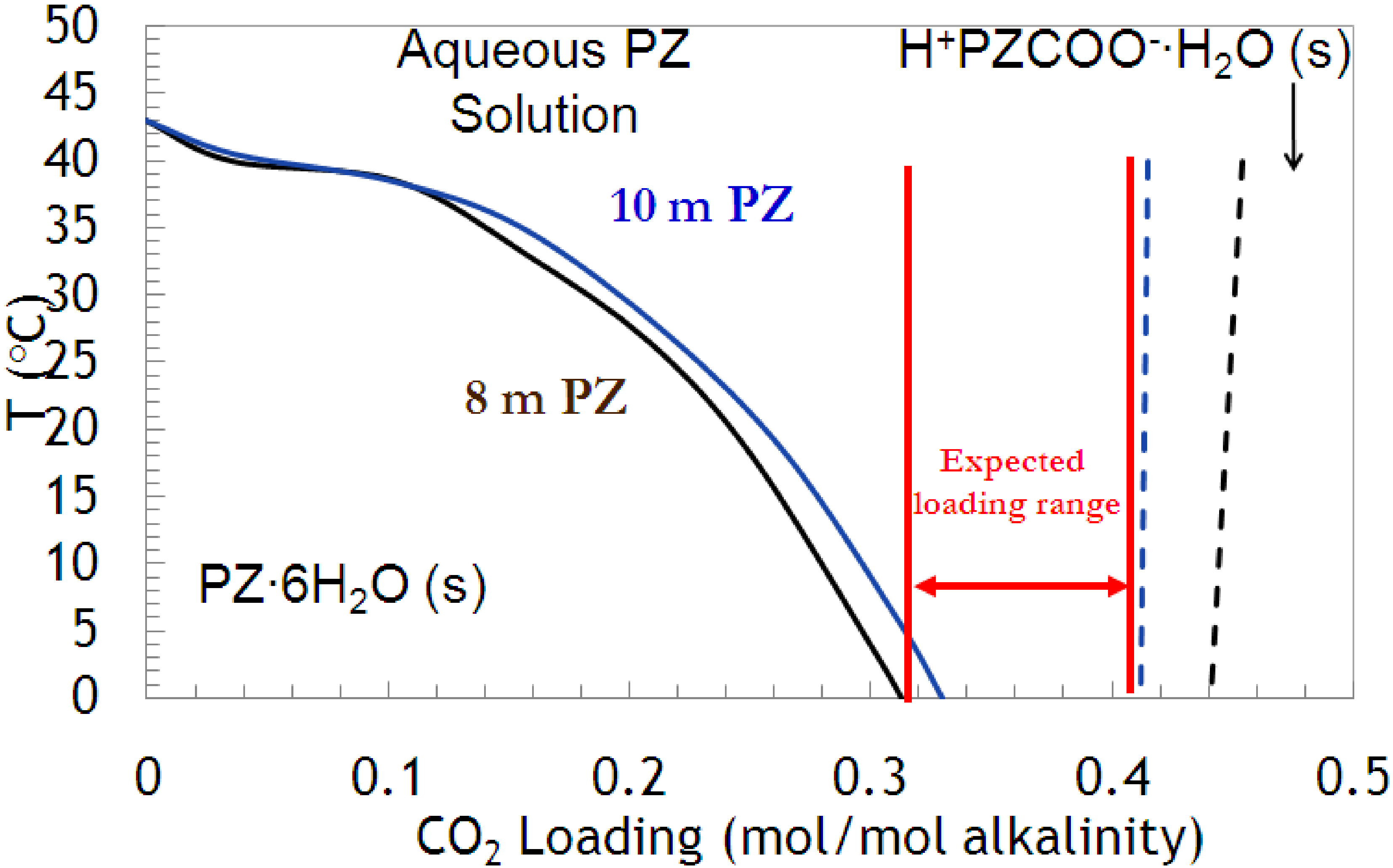
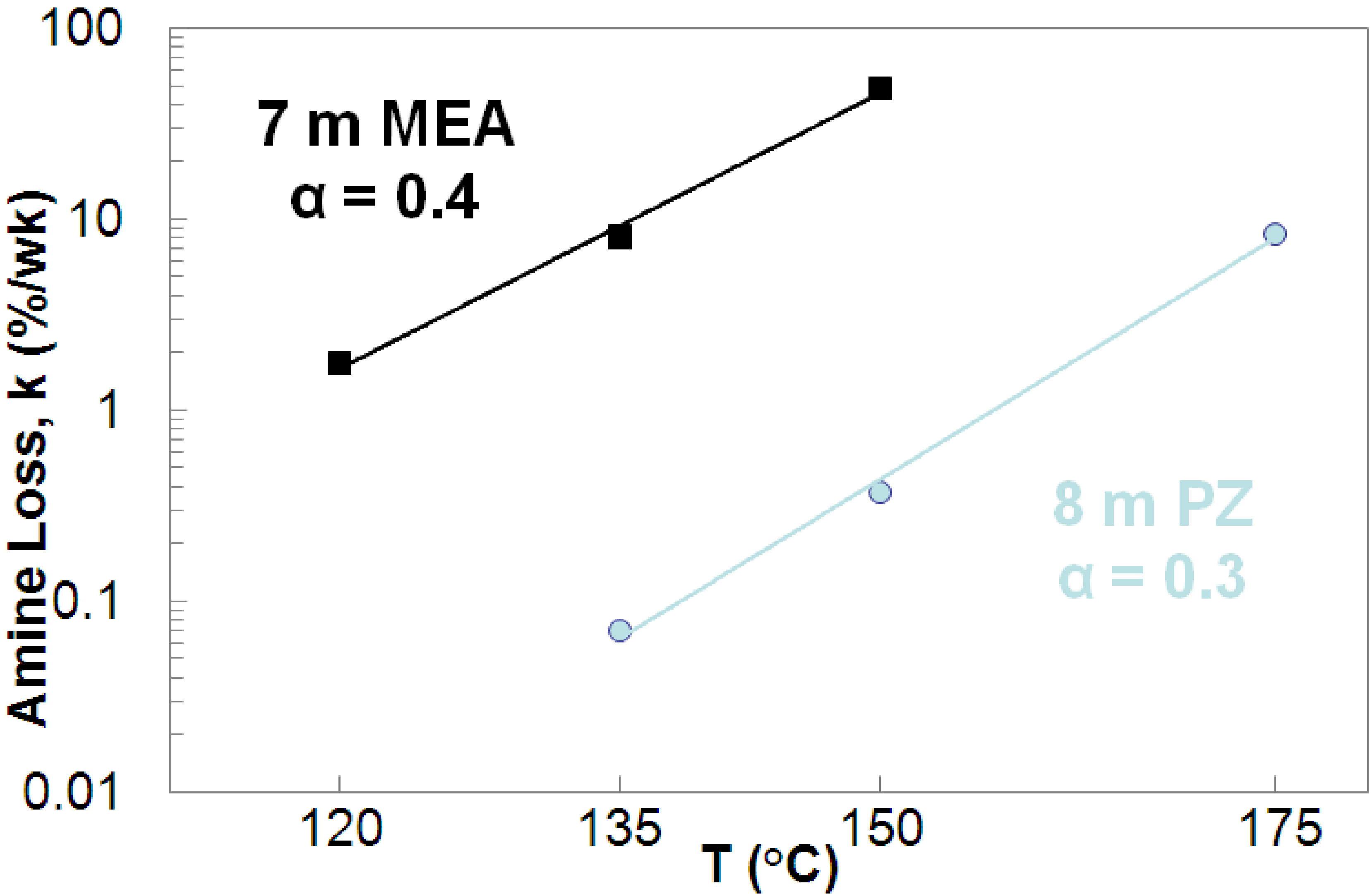
Advantages of Piperazine

	7 m MEA	8 m PZ
CO_2 Abs Rate (mol/s-Pa-m-^{2})	$4.3x10^7$	2X
Volatility – Lean (ppm)	30	7
Thermal Stability (°C)	120	150
Oxidative Degradation	18%/wk	Neglig.
Energy Use (kWh/tonne)	250	10-20% <
Working Capacity (mol/eq)	0.48	1.8X
Reclaiming – Boil Pt (°C)	170	146

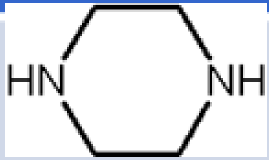
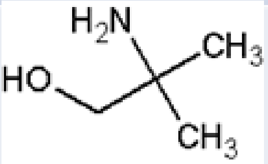
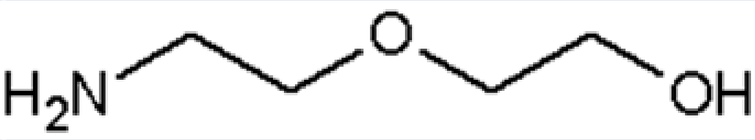
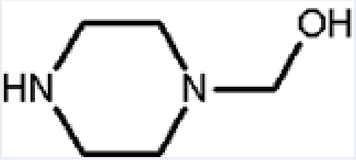
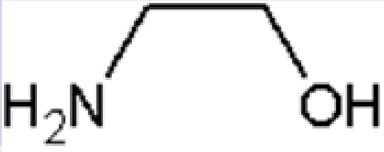
Solubility Envelope for PZ Permits Concentrated Solvent



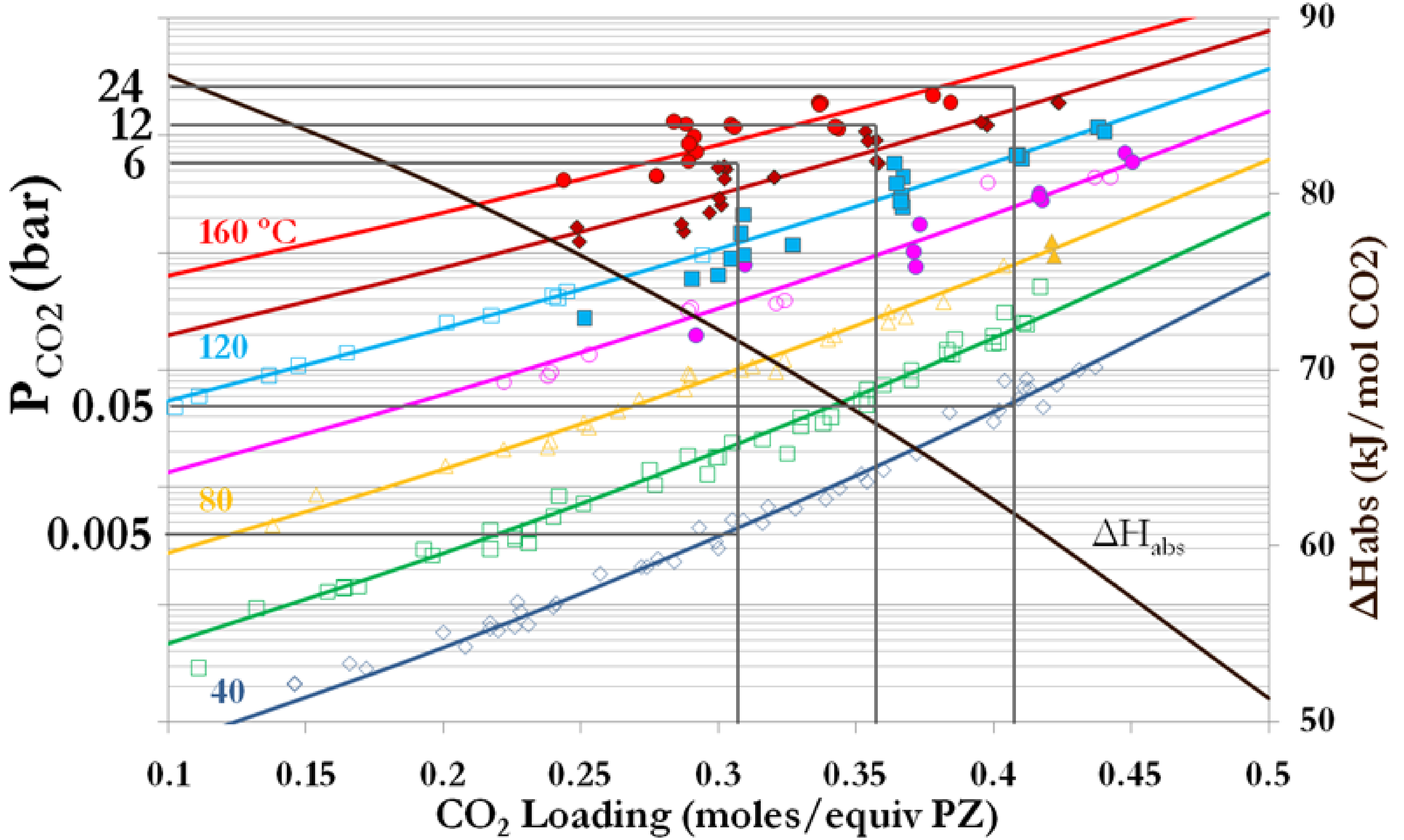
Thermal Stability Permits 150 °C Stripping



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

8m PZ Provides High P_{CO_2} at 150 °C



High Temperature Two-Stage Flash Regeneration Skid

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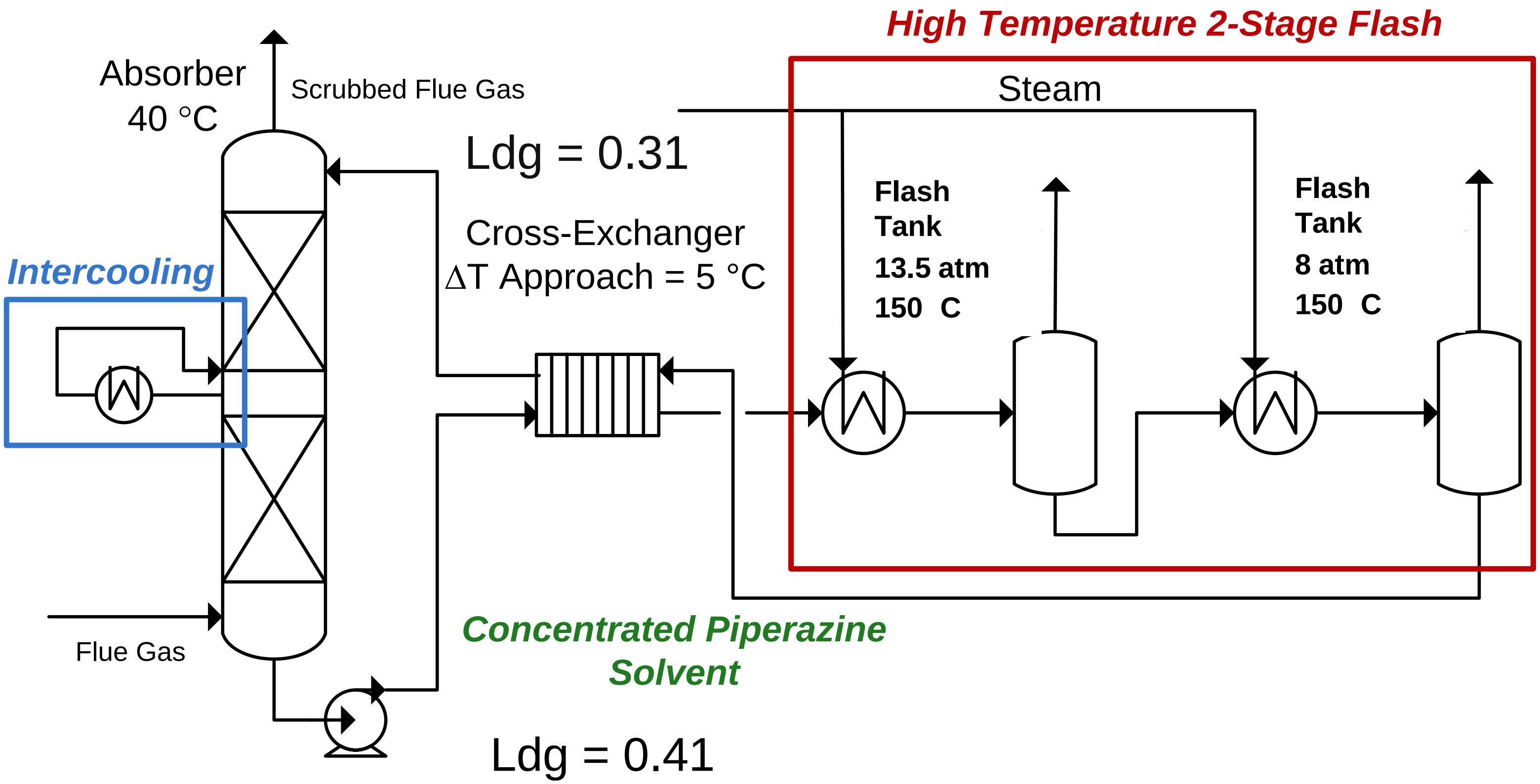
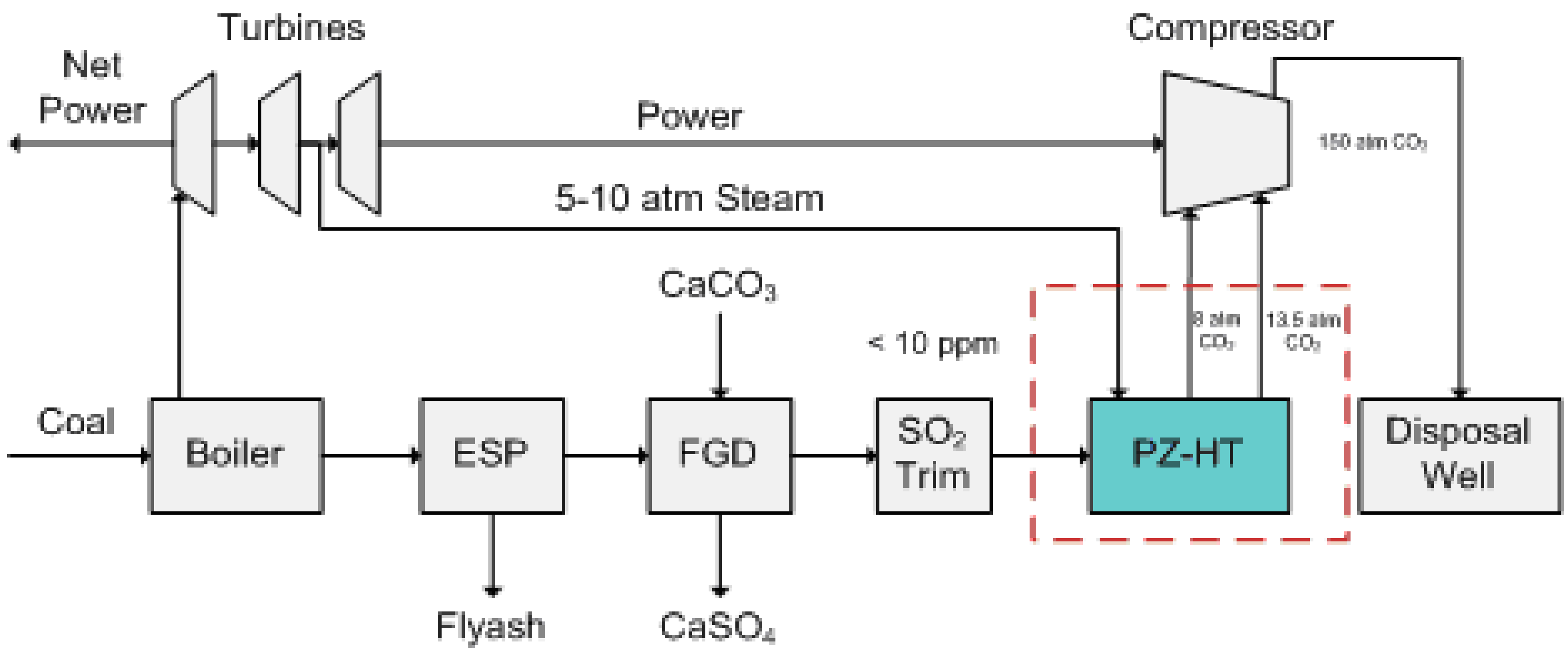
Process Flow Diagram



Integration of Piperazine-High Temperature (PZ-HT) Process into Power Plant



Production of CO_2 at elevated pressure, lowering compression costs

Economic Advantages

	% 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

**Note: Analysis from DOE/NETL-2007/1281*

- **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 CO_2 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
  - Includes process control, foaming, solids precipitation
- Evaluate technical and economic feasibility of full-scale implementation of the process

New solvent/process development areas for project

- 40 wt% PZ solvent with fast CO_2 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 contaminants, thermal and oxidative degradation of concentrated PZ with coal-fired flue gas
  - Particular focus on quantification of nitrosamine formation and fate
- Scale-up from 0.1 to 0.5 MW of the optimized high temperature two-stage flash process

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Work Plan

- Field Campaign #1: UT SRP 0.1 MW
  - 3-week test in CO_2/air
  - Test modifications of 2-stage flash prior to CSIRO testing
- Field Campaign #2: CSIRO 0.1 MW
  - 3-month test
  - Low-sulfur bituminous coal with caustic scrubber
  - First test in coal-fired flue gas
- Field Campaign #3: NCCC 0.5 MW
  - 3-month test
  - Medium-sulfur bituminous coal with limestone scrubber

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Schedule

- 48 month project
- Tests with 0.1 MW Regeneration Skid
  - SRP Test: September – October 2011
  - CSIRO Test: 2012
- Design/Build 0.5 MW Regeneration Skid: 2013
- Test with 0.5 MW Regeneration Skid
  - NCCC Test: 2014

Current Project Activities

- SRP test plan formulation
- Modifications to 0.1 MW regeneration skid
- Contracting with CSIRO
- Tarong integration process design review

Planned SRP Test Parameters

PARAMETER	
Concentration of PZ (wt%)	40
Lean Loading (mol CO_2/mol total alk)	0.26 - 0.30
Gas Rate (acfm)	350 – 600
L/G Ratio (mol/mol)	3.0 – 4.5
Intercooling (40°C)	On
CO_2 Removal (%)	64 – 99%
High Pressure Flash P	150, 200 psia
Low Pressure Flash P	100, 130 psia
Flash T	150°C
Direct Contact Cooling	On, Off

Skid Modifications

- Two-stage flash regeneration skid built by UT prior to DOE award
- First operational test of skid in January 2011 identified problems that need to be addressed:
  - Improve Heat Duty/Energy Performance
  - Reduce PZ Volatility and Entrainment
  - Improve Process Control

Improve Heat Duty

Problem:

- Underrated flash vessels and undersized cross exchanger reduced operating T&P range
- Resulted in inappropriate flashing and increased heat duty

Actions Taken:

- Re-rated flash vessels, steam heaters, relief valves
- Installed multi-pass HP cross exchanger
- Installed control valve downstream of HP cross exchanger to prevent flashing
- Added P and dP measurements to monitor flashing

Benefits:

- Improved heat duty
- Reduced occurrence of undesired flashing

Reduce PZ Volatility

Problem:

- 3 wt% PZ in overhead condenser accumulator and precipitation of solids in flow straightener downstream of flash vessels

Solution:

- Developed scheme for direct contact cooling of gas exiting low pressure flash vessel

Benefits:

- Predicted to reduce PZ in LP overhead gas by 70%

Reduce PZ Entrainment

Problem:

- PZ entrainment and solids precipitation observed at various points in process
- Confirmed potential for fogging with bench-scale simulations of process conditions

Actions Taken:

- Installed sight glasses to observe if fogging is occurring on pilot unit
- Implemented routine cleaning procedures as part of weekly shutdowns

Flash Skid Process Control

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Problem:

- Evaluate various advanced process control schemes to address following issues
  - Low volume holdup
  - Integration of multiple heat exchangers

Actions Taken:

- Emerson Process Management donated ~$100,000 process instrumentation for 0.1 MW skid to improve controls
- Implemented feed-forward control on steam heater temperature
- Implemented multi-variable control algorithm (DeltaV Model Predictive Control)

Plans for Future Development

- Pending successful testing of PZ-HT process at 0.1 MW and 0.5 MW
  - Test Objective: Confirm Expected Benefits
    - Increased reaction rate, reduced volatility, resistant to degradation, reduced energy consumption
  - 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