Pilot Plant Testing of Piperazine (PZ) with High T Regeneration

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Outline

- Project overview
- Energy Features of the PZ process
  - A new flash stripper
- Solvent management with PZ
  - Solution analyses from 3 pilot plants
- Future work on aerosol formation
  - A major challenge for volatile amine
- PZ, a competitive alternative

Project Objectives

- Primary:
  - Quantify robustness of PZ in an integrated system with 150°C regeneration
- Secondary:
  - Optimize equipment design & energy performance of advanced flash regeneration
  - Identify & resolve issues with process control, foaming, solids precipitation
  - Evaluate technical & economic feasibility of full-scale implementation

Project Funding

- DOE funded $3 million
  - Started 10/2010
  - 2-phase project

- $876k cost-shared by UT CO_2 Capture Pilot Plant Project
  - EPRI
  - Luminant, Southern, LG&E-KU
  - B&W, Chevron

Pilot Plant Testing with PZ

- **UT** Separations Research Program (SRP)
  - 0.1 MW air/CO_2
  - 10/2011, 3 week operation (DOE Task)
  - 10/2013, 3 week operation (DOE Task)
- Pilot Plant 2 (PP2)
  - Operated in 2011 on coal flue gas
- **CSIRO**- Tarong (supported by ANLEC)
  - Operated 3 months in 2013 on 0.1 MW coal
- **DOE** National Carbon Capture Center
  - DOE Task
  - To be Operated 3 months on 0.5 MW coal (2014-15)

Piperazine: Superior for Energy

Amine	m	$k_g'_{avg}$*1e7	capacity	$-\Delta H_{abs}$	T_{max}	P_{max}
		mol/s·Pa·m^2	mol/kg	kJ/mol	C	bar
PZ	8	**8.5**	0.75	73	**163**	**20**
AMP/PZ	4_2	8.6	0.80	77	127	5.7
MEA	7	4.3	0.62	77	121	4.0
SarK	6	5	0.27	64	121	2.4

Total Equivalent Work

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

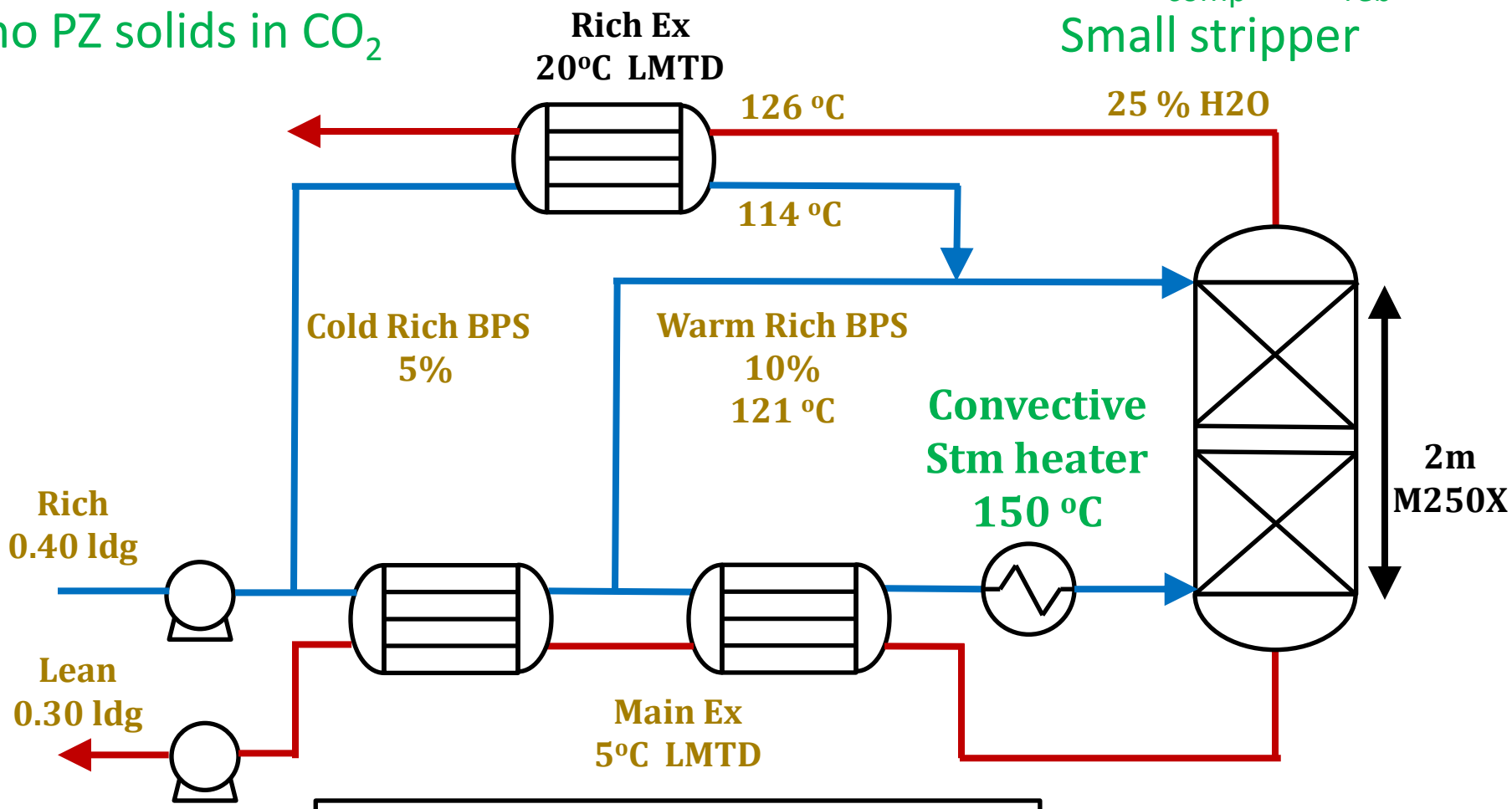
$$W_{total} = W_{reboiler} + W_{comp} + W_{pump}$$

$$W_{comp}\left(\frac{kJ}{mol\ CO_2}\right) = \begin{cases} 4.572 \ln\left(\frac{150}{P_{in}}\right) - 4.096 & P_{in} \leq 4.56\ bar \\ 4.023 \ln\left(\frac{150}{P_{in}}\right) - 2.181 & P_{in} > 4.56\ bar \end{cases}$$

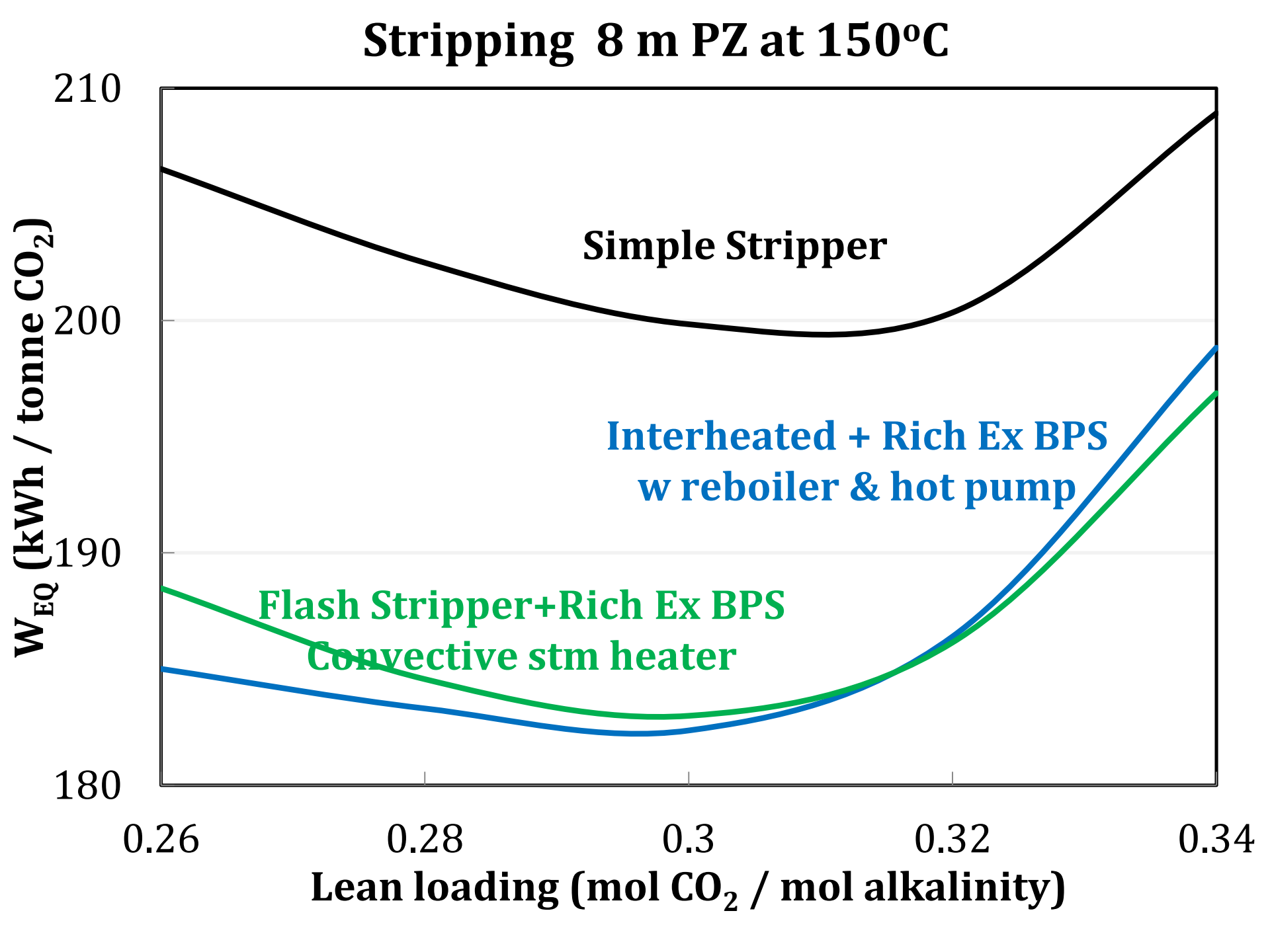
Flash Stripper with Rich Exchanger Bypass

2 Rich Bypasses
less Q_{loss} in vapor
no PZ solids in CO_2

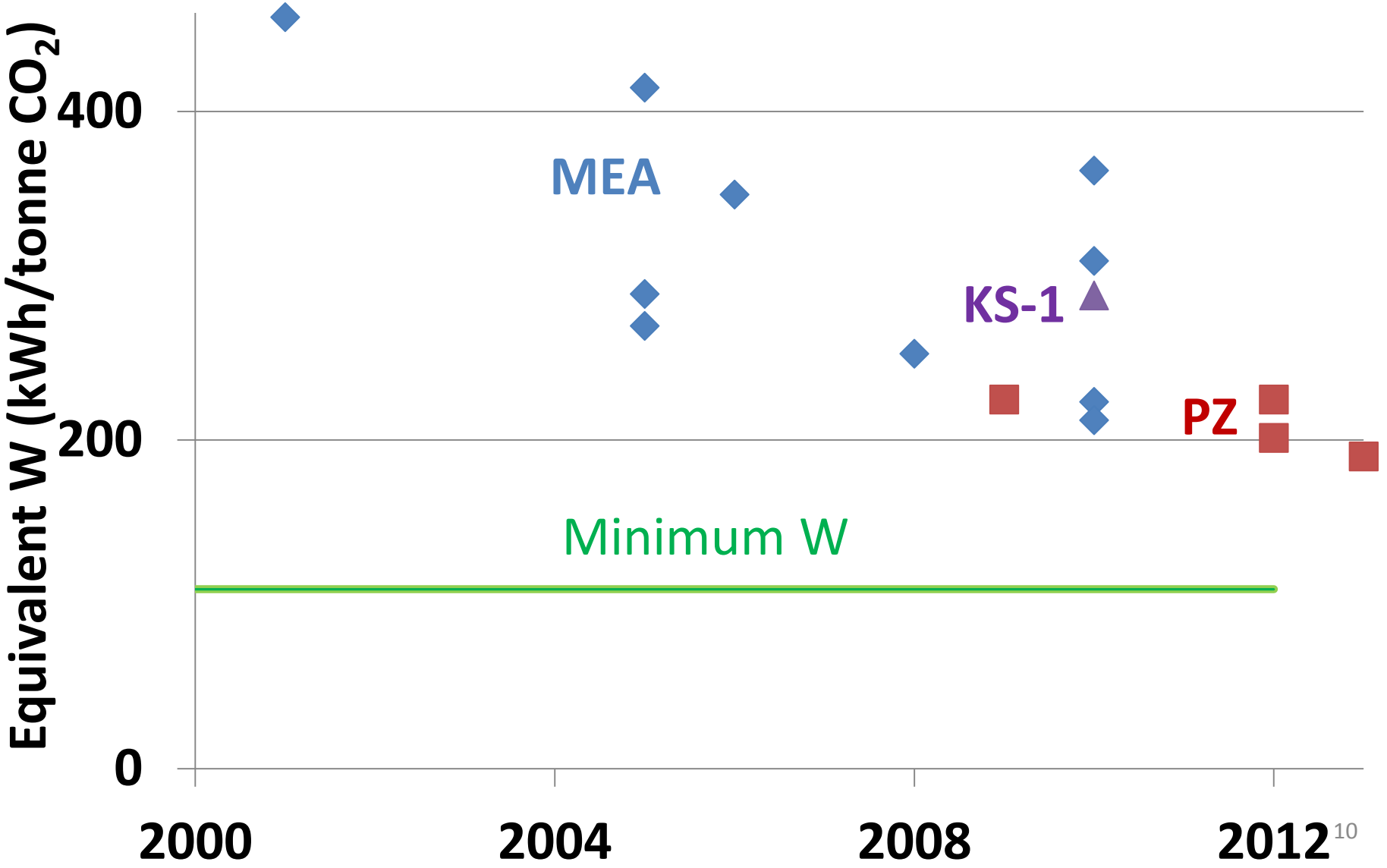
regen at 7-10 bar
less W_{comp} & Q_{reb}
Small stripper



W_{EQ} = 184 kWh/tonne CO_2


Stripping 8 m PZ at 150°C
210
200
190
180
W_{EQ} (kWh / tonne CO_2)
Simple Stripper
Interheated + Rich Ex BPS
w reboiler & hot pump
Flash Stripper+Rich Ex BPS
Convective stm heater
0.26
0.28
0.3
0.32
0.34
Lean loading (mol CO_2 / mol alkalinity)

Energy is approaching a practical limit



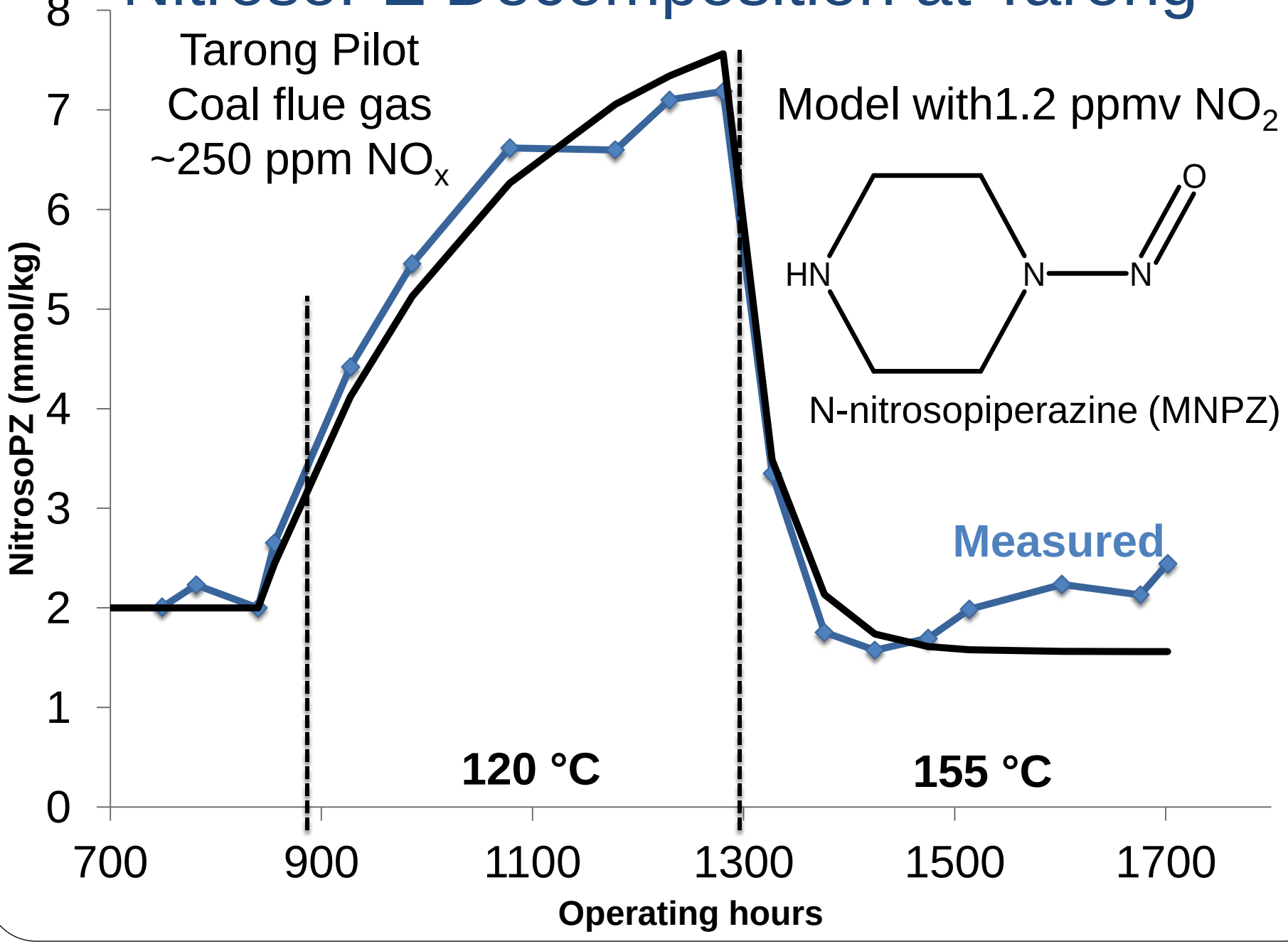
PZ: Superior for Solvent Management

- PZ is resistant to oxidation.
  - At absorber conditions (mM/hr)
    PZ<0.15 MEA – 2
  - With dissolved metals & O_2 PZ oxidizes at >130°C
- PZ volatility is just right.
  - At lean abs conditions (ppm)
    PZ – 8 MEA - 30
  - Thermal reclaiming removes nonvolatile impurities
  - PZ condenses out aerosols in the absorber
- Nitrosamine is manageable.
  - PZ + NO_2/NO_2^- → mononitrosopiperazine (MNPZ)
  - Decomposes at 150°C with stoich oxidation of PZ to leave only 1 mM MNPZ at steady state

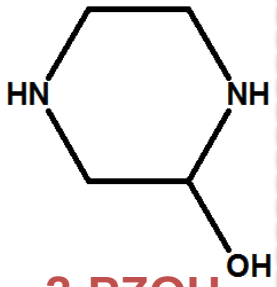
Degradation Products (mmol/kg) in PZ pilot plants at 1300 to 1700 hrs

Component	SRP	PP2	Tarong
Total Formate	2.4	76.6	110.2
2-PZOH	25.8	71.6	56.0
NitrosoPZ	0.09	1.2	2.4
Fe^{2+}	0.02	1.15	0.54
Other metals	0.04	4.22	0.07
Nitrate	0.1	4.8	21.8
Sulfate	0	7.1	26.9

NitrosoPZ Decomposition at Tarong



Corrosion Effects: Tarong



2-PZOH

Total formate

Fe^{2+}

120 °C

155 °C

Total formate & 2-PZOH (mmol/kg)

Fe (mmol/kg)

Operating hours

120
100
80
60
40
20
0

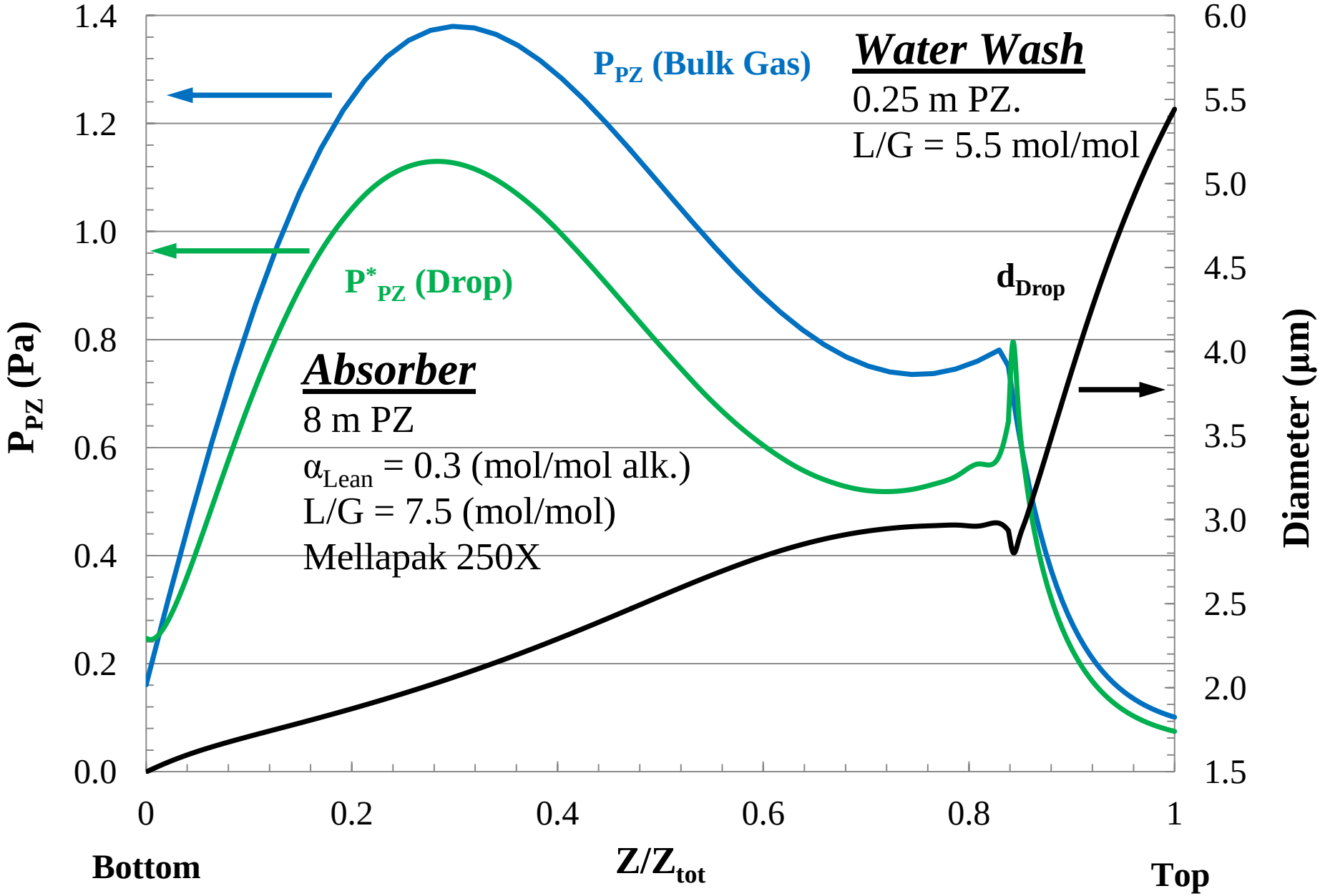
0.6
0.5
0.4
0.3
0.2
0.1
0

700
900
1100
1300
1500
1700

Amine Aerosol - a Major Challenge

- Nucleation sites in flue gas
  - SO_3/H_2SO_4
  - Submicron fly ash
- + Droplet growth
  - Amine/CO_2 moves from solvent to aerosol
  - Water condensation
- + Poor droplet collection in water wash
- = Unacceptable amine emissions

Aerosol Grows by PZ Diffusion



Planned Aerosol Testing
SRP Pilot plant, Air/CO_2, Fall 2013

- Inject vaporized H_2SO_4 to vary aerosol
- Measure
  - Amine with FTIR using heated sample point
  - Drop Size with Phase Doppler Interferometry
- Grow aerosol in absorber packing
- Collect aerosol in impingement tray

Future Work with 150°C PZ

- Fall 2013 – SRP campaign
  - Flash Stripper with 2 bypasses
  - Aerosol characterization & collection
  - Oxidation management
  - Absorber intercooling
  - Reclaiming
- Fall 2014 – NCCC

Conclusions

- 8 m PZ with 150°C advanced flash stripper is a promising new baseline capture technology
  - 190 kWh/ton CO_2, (7%<simple stripper)
  - 61% Increase in COE ($58/tonne CO_2)
  - No significant thermal degradation
- PZ oxidation and nitrosation are manageable
  - Oxidation appears to degrade < 2%/wk
  - Nitrosamine reaches steady-state at 1-2 mM
- PZ aerosol emissions will be addressed in SRP pilot plant, Fall 2013

- **ANLEC:** Pilot plant samples from Tarong were provided by CSIRO. CSIRO acknowledges financial assistance from Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

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