Pilot Plant Testing of Piperazine with High T Regeneration

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Outline

- Project Overview
- Features of the piperazine (PZ) process
- 2011 pilot campaign – High T Flash
- Future Work on aerosol formation
- Hot piperazine, a competitive alternative

Project Objectives

- Primary:
  - Quantify robustness of PZ in an integrated system with 150^{o}C regeneration
- Secondary:
  - Optimize equipment design & energy performance of the heated two-stage flash
  - Identify & resolve issues with process control, foaming, solids precipitation
  - Evaluate technical & economic feasibility of full-scale implementation

Project Funding Summary

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

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

Pilot Plant Testing

- **UT** Separations Research Program (SRP)
  - 0.1 MW air
  - 10/2011, 3 week operation
- (**CSIRO**- Tarong, dropped from DOE scope)
  - 0.1 MW coal
  - 2012, 6 months
- **DOE** National Carbon Capture Center
  - 0.5 MW coal
  - 2014, 3 months

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**	**20.2**
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

PZ: Superior for Solvent Management

- PZ is resistant to oxidation.
  - At absorber conditions (mM/hr)

    PZ<0.15 MEA – 2
  - Reacts with dissolved/entrained O_2 at >130ºC
- PZ volatility is just right.
  - At lean abs conditions (ppm)

    PZ – 8 MEA - 30
  - Nonvolatile impurities removed by thermal reclaiming
  - Condenses on aerosols in the absorber
- Nitrosamines should be manageable.
  - PZ + NO_2/NO_2^- → mononitrosopiperazine (MNPZ)
  - Decomposes at 150ºC to leave 1 mM MNPZ

Innovative Stripper Features

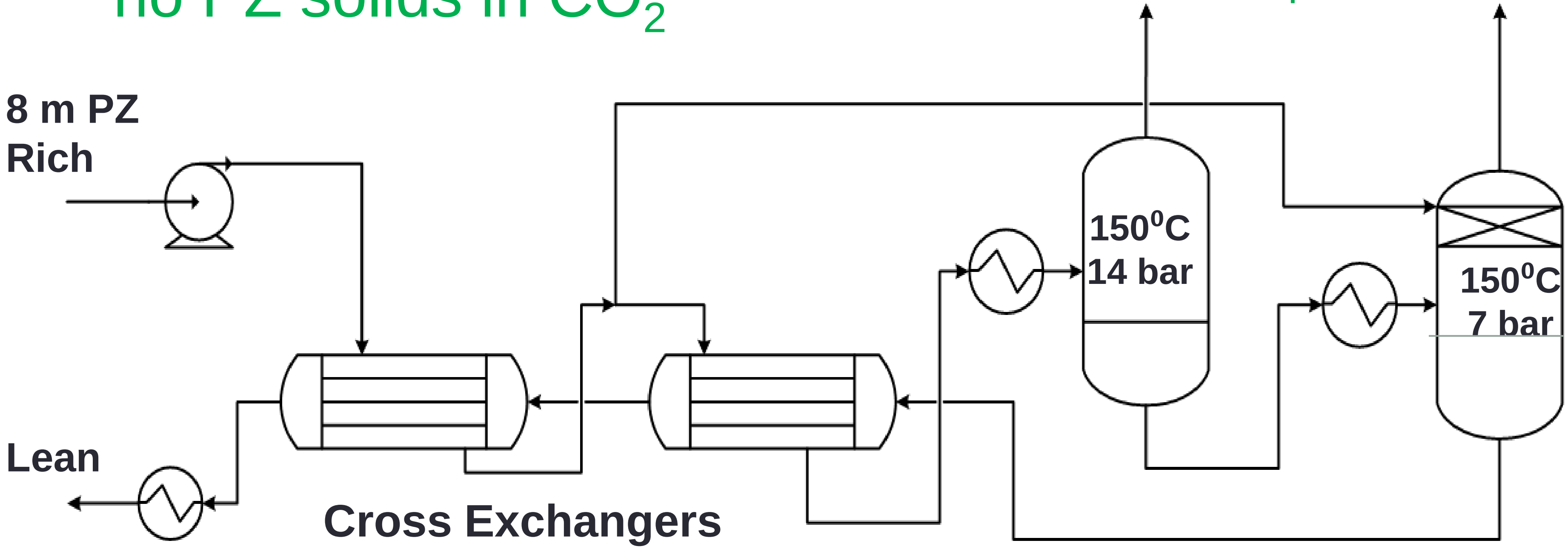
Cold/Warm Rich Bypass

lower Q_{loss} in vapor

no PZ solids in CO_2

150ºC regen at 7-14 bar

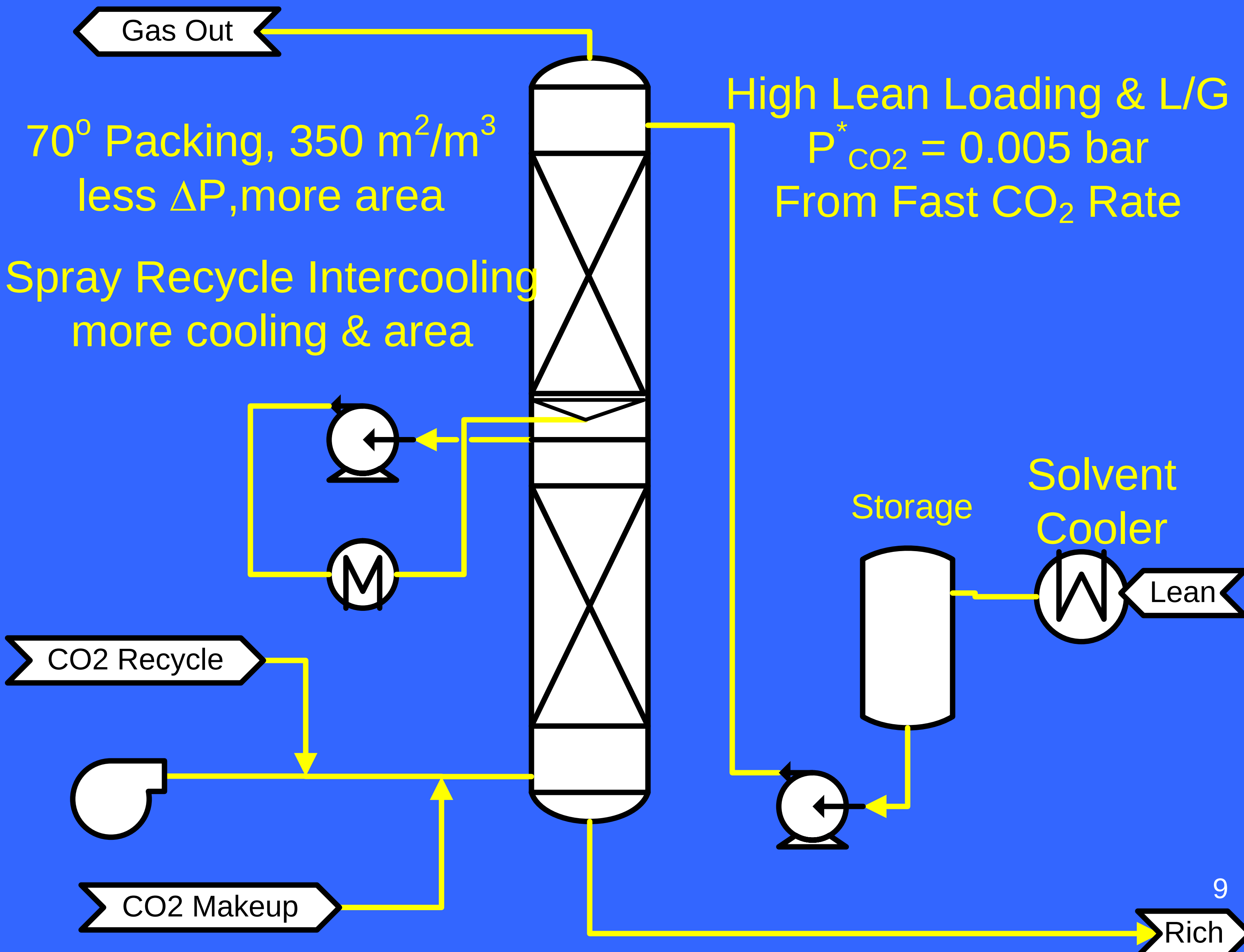
lower W_{comp} & Q_{reb}



2-St Flash w conv stm heat

lower comp & reboiler Cost

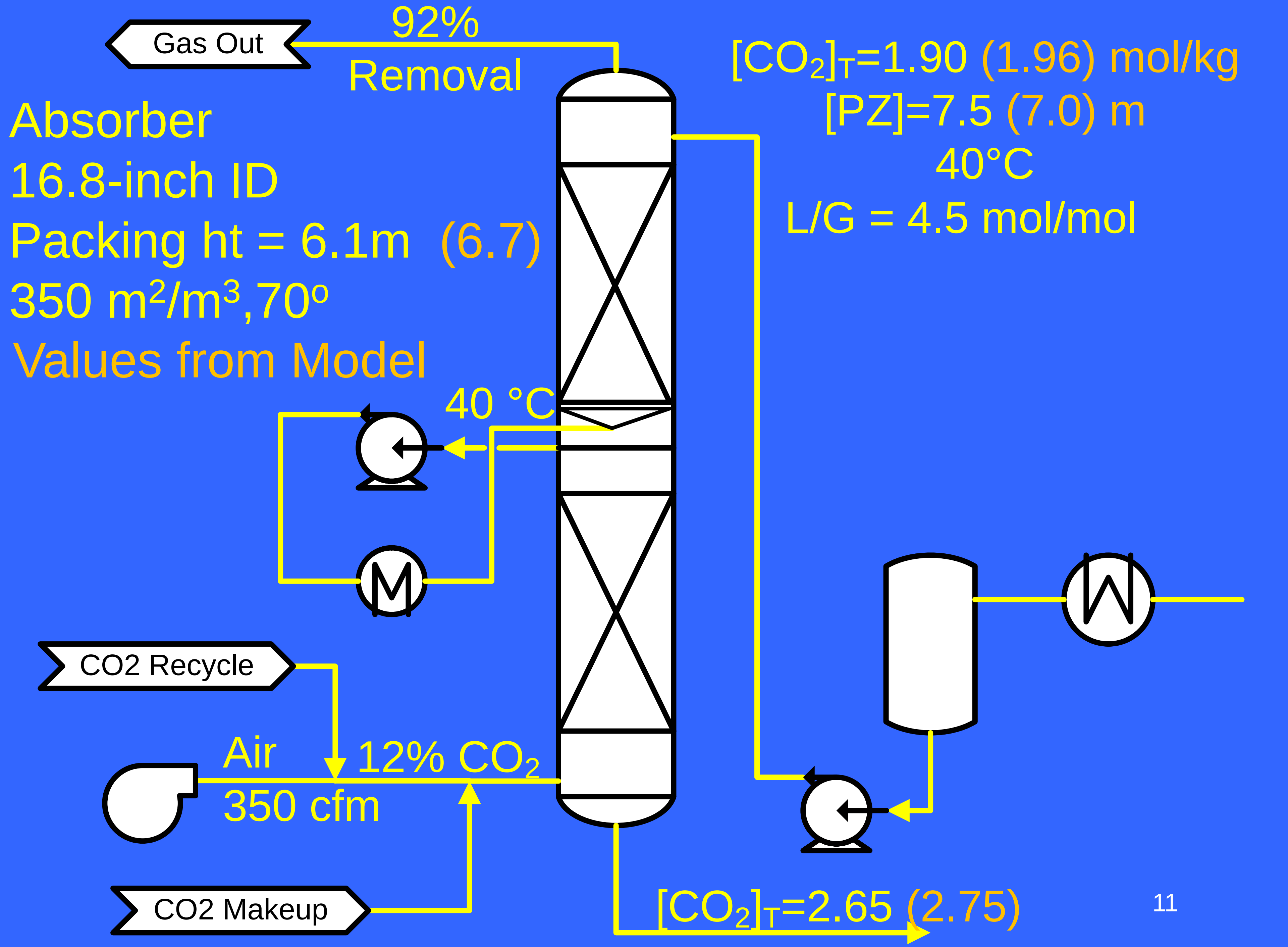
Innovative Absorber Features



Results of SRP Campaign
October 2011

12 steady-state conditions

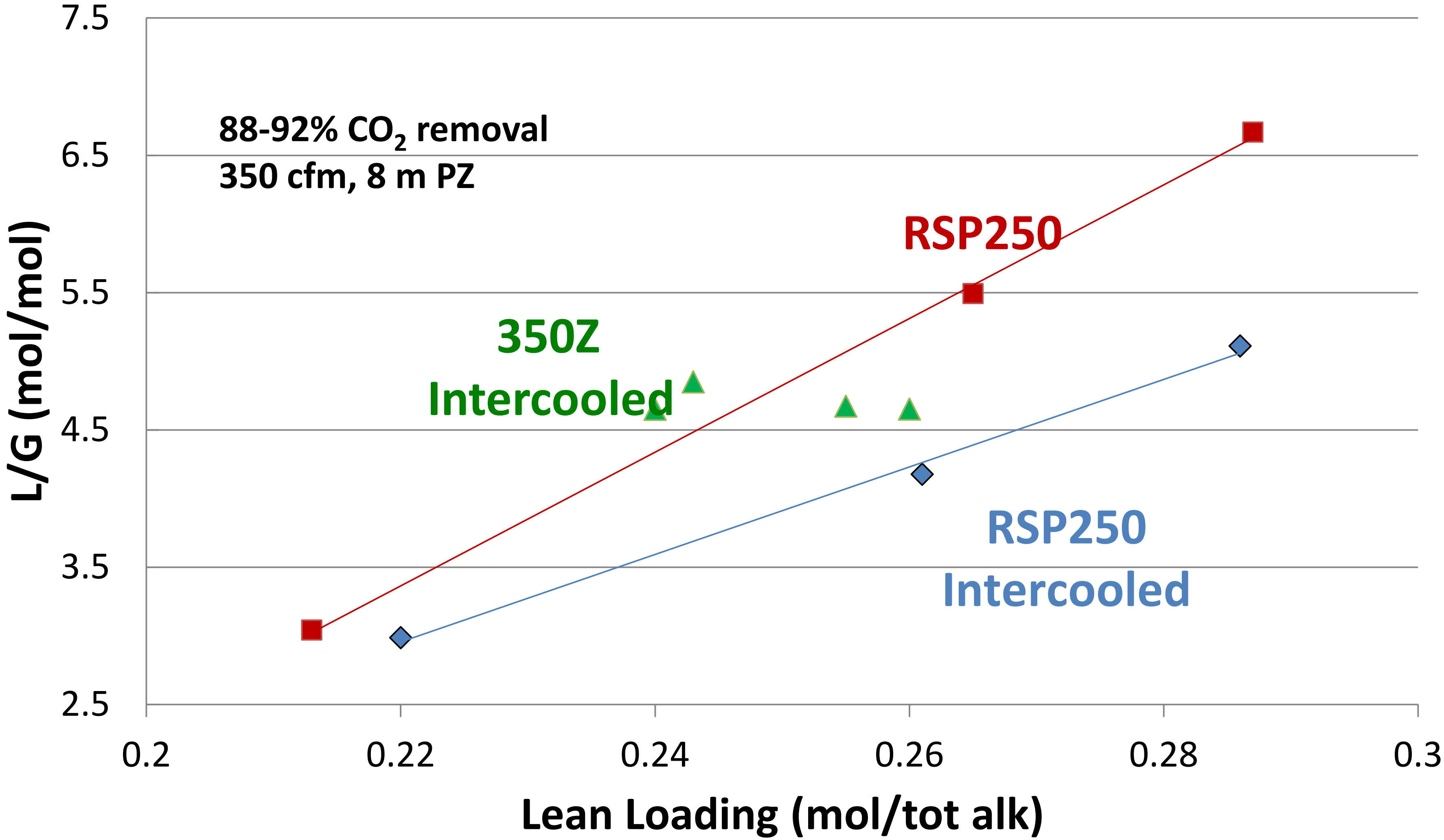
3 weeks of operation


Gas Out
92%
Removal
[CO2]T=1.90 (1.96) mol/kg
[PZ]=7.5 (7.0) m
40°C
L/G = 4.5 mol/mol
Absorber
16.8-inch ID
Packing ht = 6.1m (6.7)
350 m2/m3,70o
Values from Model
40 °C
CO2 Recycle
Air
12% CO2
350 cfm
CO2 Makeup
[CO2]T=2.65 (2.75)

Spray Intercooling increases CO_2 removal
Lean Ldg = 0.24-0.25, L/G = 4

IC Spray	Gas (acfm)	CO_2 Removal	ΔCO_2 Removal
OFF	350	85	-
ON		91	6
OFF	475	80	-
ON		88	8

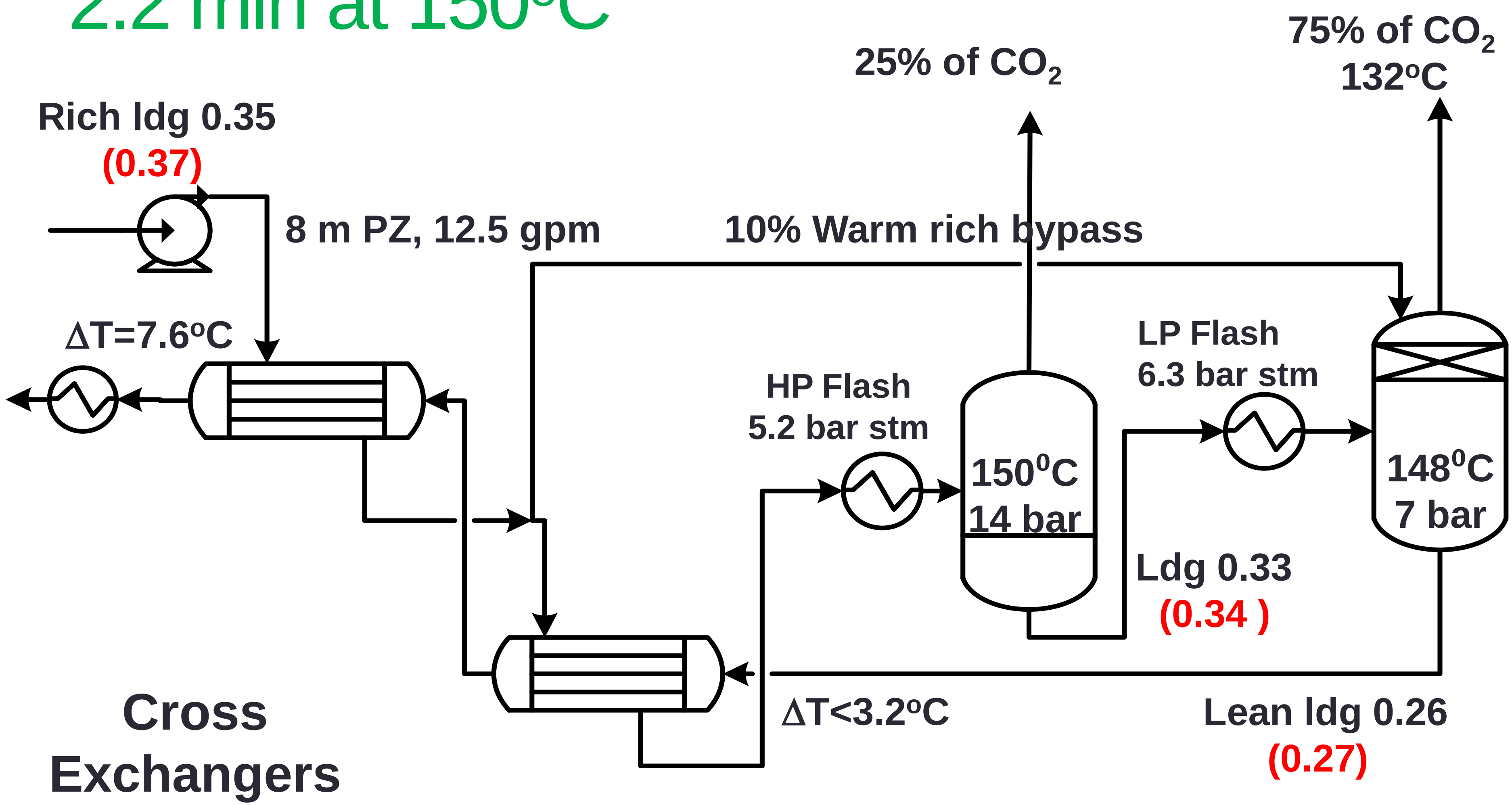
Energy use in 10/2011 was high because the absorber was ineffective.



solvent degradation or poor packing.

SRP Pilot Plant
16.8-inch ID flash tanks
2.2 min at 150°C

High fidelity model.



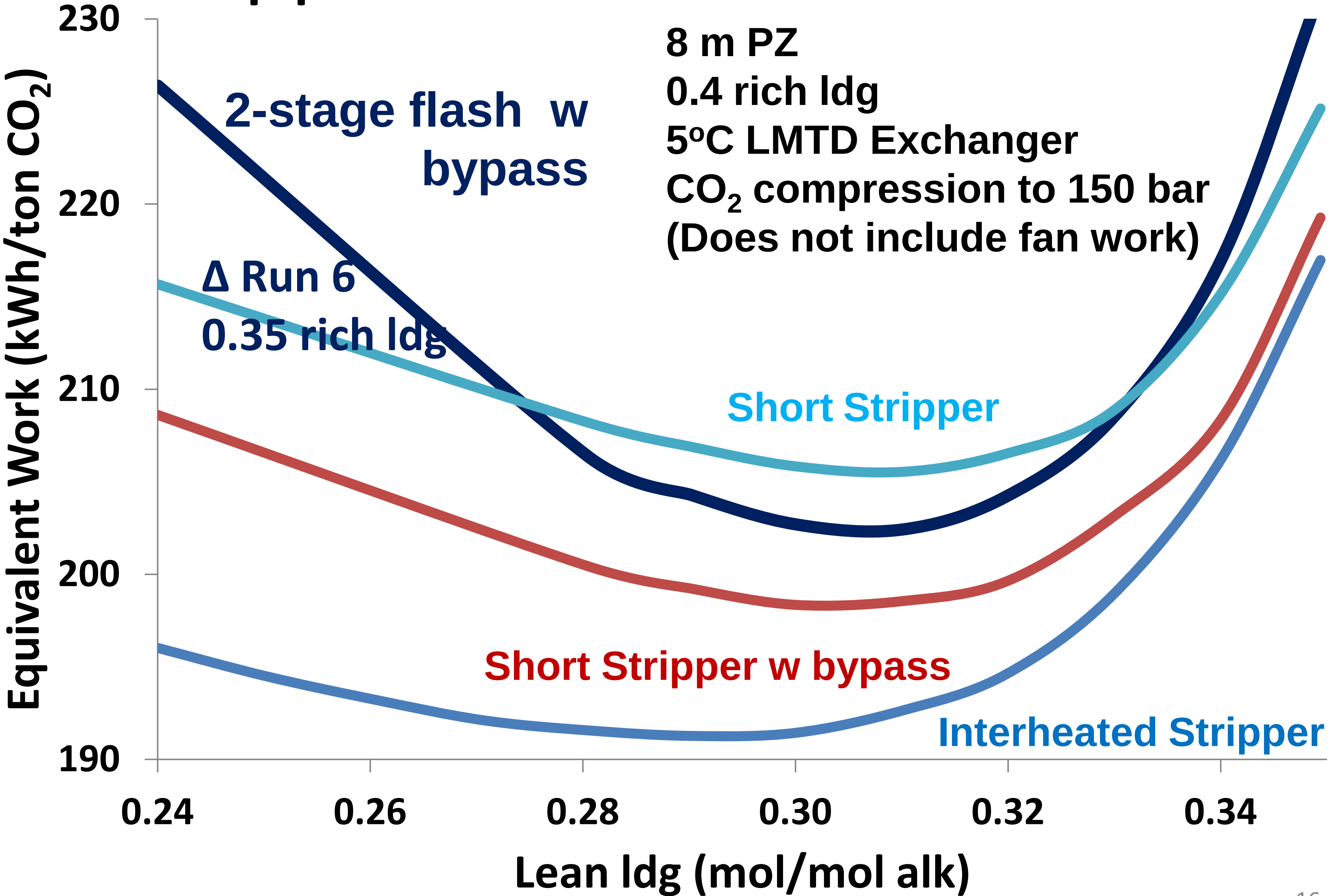
Total Equivalent Work

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

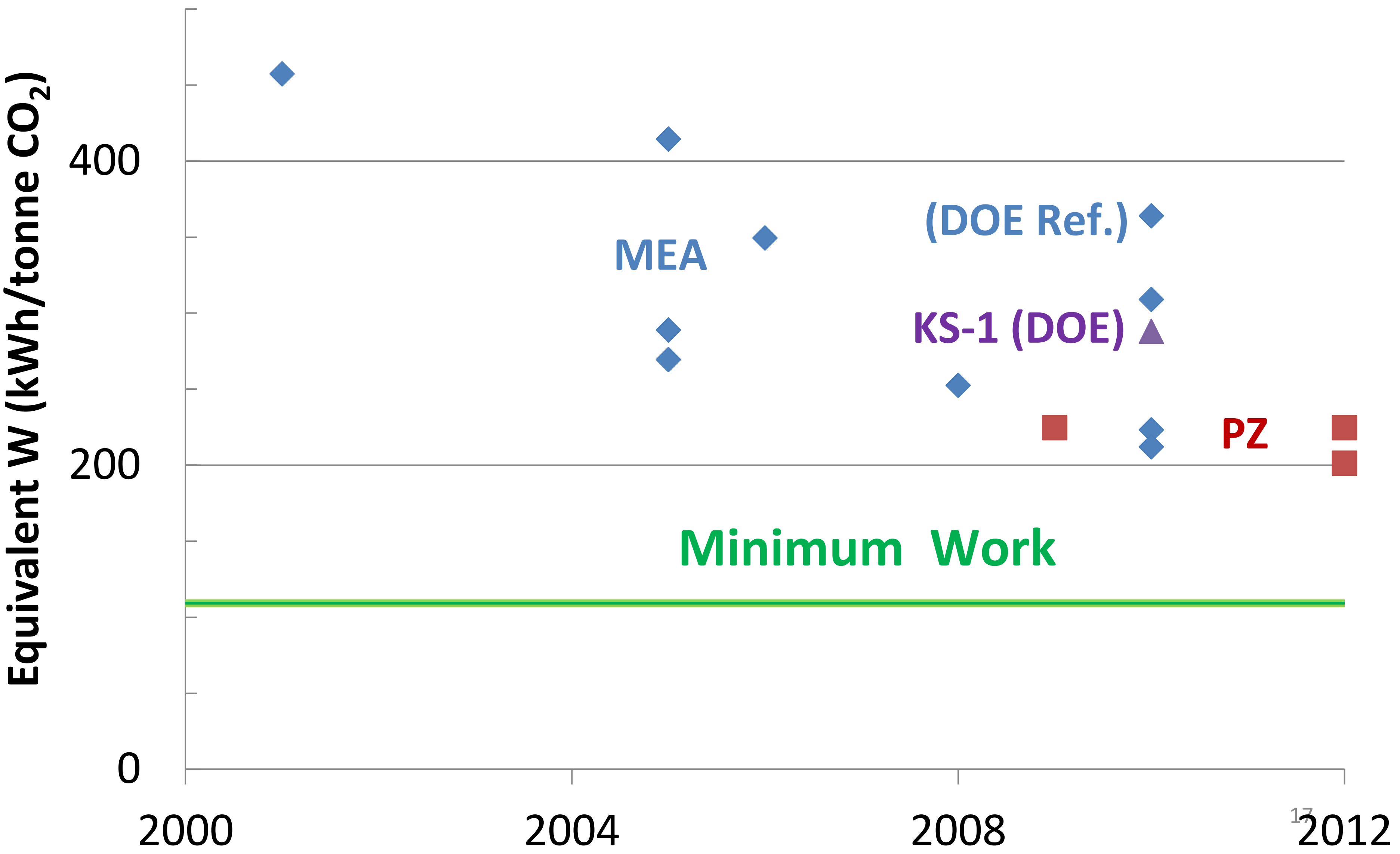
$$W_{reboiler} = 0.75 Q_{flash} \frac{T_{flash} + 5 - T_{sink}}{T_{flash} + 5}$$

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

Stripper Performance at 150^0C



Energy is approaching a practical limit



Economic Analysis
New Plant, 90% Avoided

	Energy (kWh/MT CO_2 removed)	CapEx ($/net kwh)	COE (¢/kWh)	Increase in COE (%)
DOE No Capture		1650	5.9	0
DOE MEA Case 12	350	2910	10.7	82
PZ short stripper	230	2570	9.6	63
PZ-2 stage flash	230	2520	9.5	61

Future Work with 150°C PZ

- 2012 – Tarong (CSIRO)
  - High NOx, Nitrosamine decomposition
- Spring 2013 – SRP campaign
  - Aerosol characterization & collection
  - Oxidation management
  - Absorber intercooling
  - Reclaiming
- Spring 2014 – NCCC

Amine Aerosol is 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 Water Wash
- = Unacceptable amine emissions

Conclusions

- 8 m PZ with 150^{o}C Regen is attractive as a new baseline technology for CO_2 capture
  - 230 kWh/ton CO_2
  - 61% Increase in COE
  - No significant thermal degradation
- Rich bypass reduces work & eliminates PZ solids in CO_2 product.
- Interheated stripper uses 6% less energy than 2-stage flash
- Spray recycle increased removal by 6-8% compared to simple intercooling.

Remaining Challenges

- Aerosols increase amine emissions
  - test tray in next SRP campaign
- Oxidation in regeneration by dissolved O_2
  - Sparge with N_2 or flash at $T<100^{o}C$
- Nitrosamine management with NO_x in gas
- Thermal reclaiming of degraded solvent

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