Amine Scrubbing for CO2 Capture

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Technology Strategy and Planning

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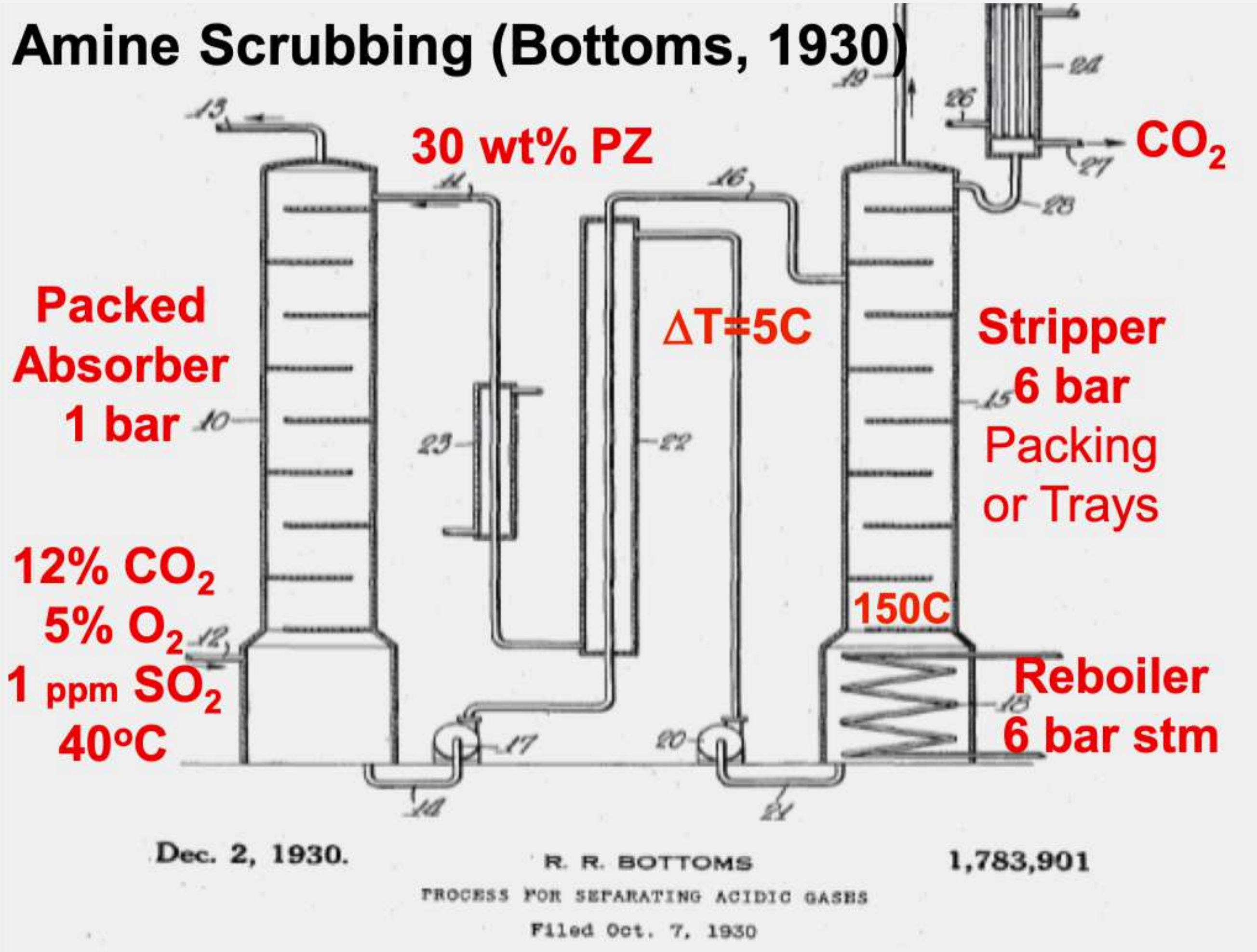
- Amine scrubbing overview
- Advanced absorption
- Advanced regeneration systems
- Advanced solvent systems

Leading CO_2-capture technology is amine absorbent based



Commercial plants of amines for flue gas carbon capture

- More than 30 commercial plants have been constructed to capture CO2 from gas-fired flue gas
  - > 20 employing Fluor technology using 30% MEA
  - > 10 plants employing MHI technology using KS-1

- Only a few plants have been constructed to capture CO2 from coal-fired flue gas.
  - Four operating units employing Lummus technology using 20% MEA
  - Boundary Dam capture project employing Shell Cansolv technology
  - Petra Nova capture project employing MHI technology

Basic chemistry & rates

Class	Typical reaction	$-H_{abs}$(kJ/mol)	Kinetics
Carbonate	$CO_3^{=} + CO_2 + H_2O \leftrightarrow 2\ HCO^-_3$	40	Very slow
Tertiary Amine	$R_3N + CO_2 \leftrightarrow R_3NH^+ + HCO^-_3$	60	Slow
Hindered Amine	$AMP + CO_2 \leftrightarrow AMPH^+ + HCO^-_3$	60-70	Moderate
Secondary or Primary Amines	$2R_2NH + CO_2 \leftrightarrow R_2NHCOO^- + R_2NH_2^+$	70-80	Fast

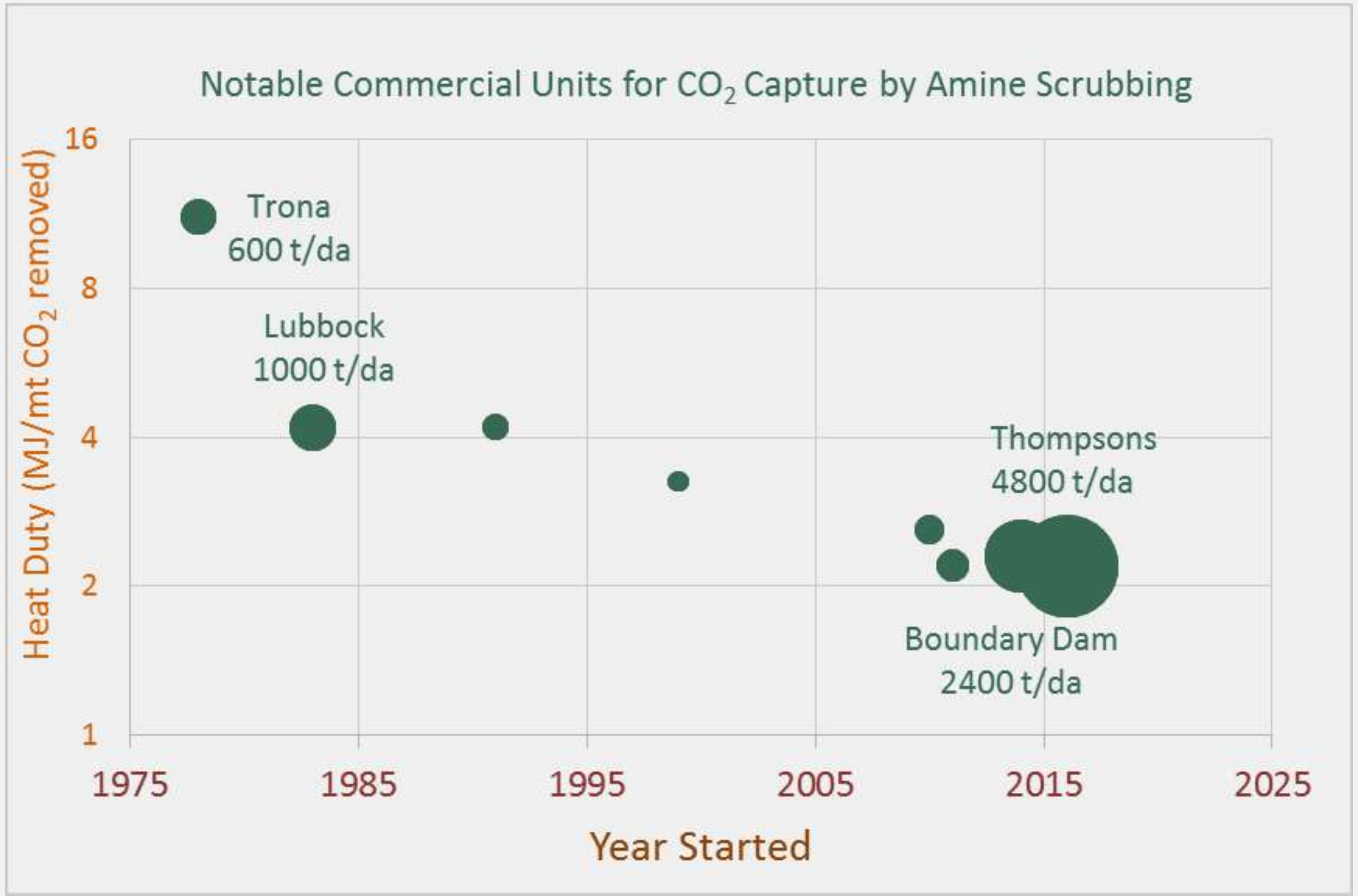
These four classes of aqueous solvents differ in heat of CO_2 absorption, kinetics of CO_2 absorption, and intrinsic CO_2 stoichiometry

Applications for amine scrubbing

Application	Total P (bar)	$P_{CO2\ in}$ (bar)	$P_{CO2\ out}$ (bar)	Gas Volume (m^3/hr)
Natural Gas	20-100	1-20	0.001 - 0.005	$2\ 10^4 - 5\ .10^5$
Hydrogen	20-100	4-20	0.002 - 0.01	
LNG	30-100	0.5-4	0.002	$1.5.10^5$
Coal flue gas	1	0.12	0.01	$5.e10^6$
Simple cycle gas turbine	1	0.035	0.0035	$5.e10^6$

Amine system energy performance continues to improve with time

- At Lubbock in 1983 the reboiler duty decreased with the substitution of 30% MEA for 20% MEA.
- At the MHI plant in 1999, 30% MEA was replaced with KS-1
- At a newer MHI plant in 2009, additional energy savings from stripper process modifications
- Cansolv plant at Boundary Dam achieved energy savings with a new aqueous amine and the use of lean vapor compression at the stripper

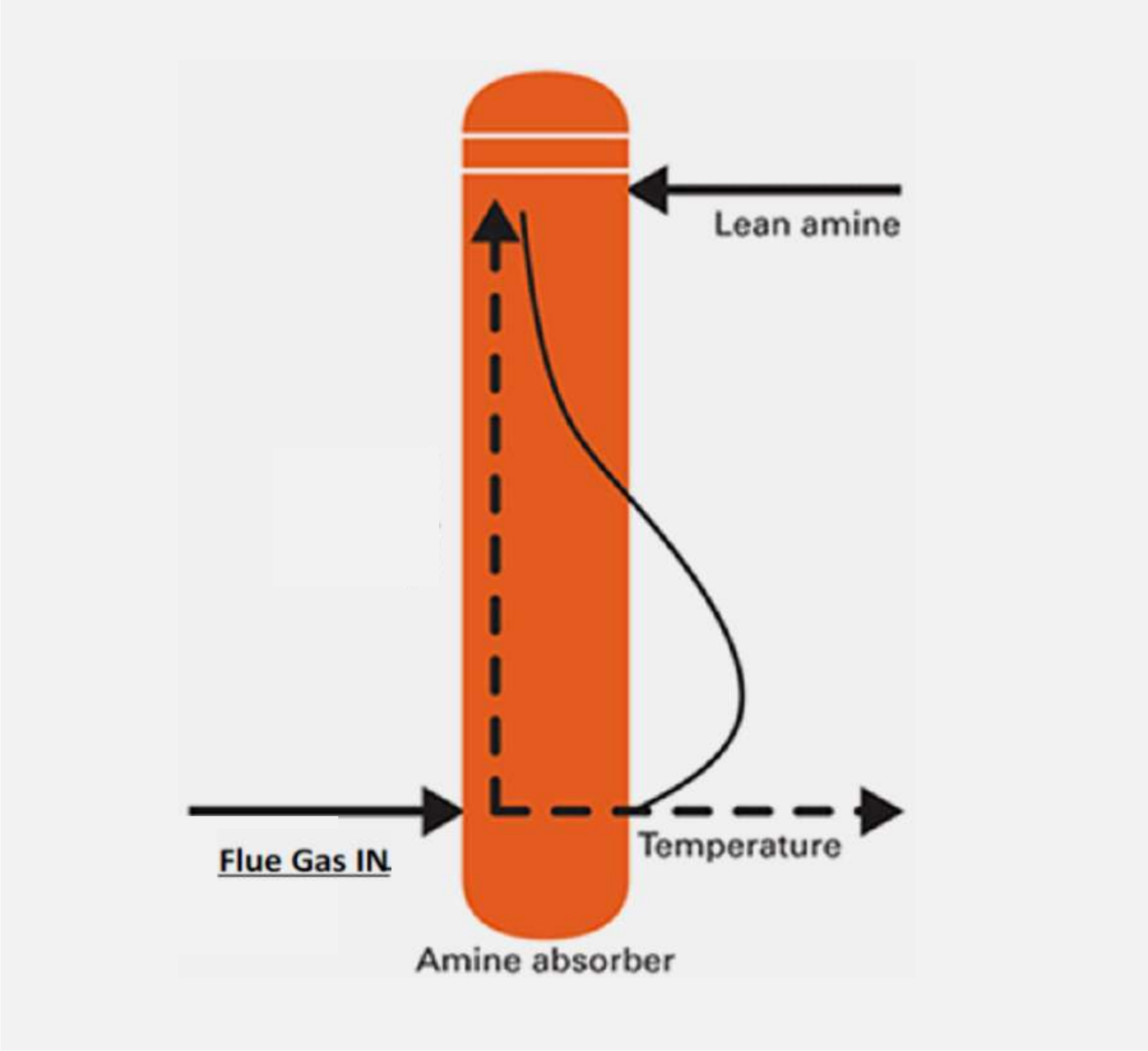


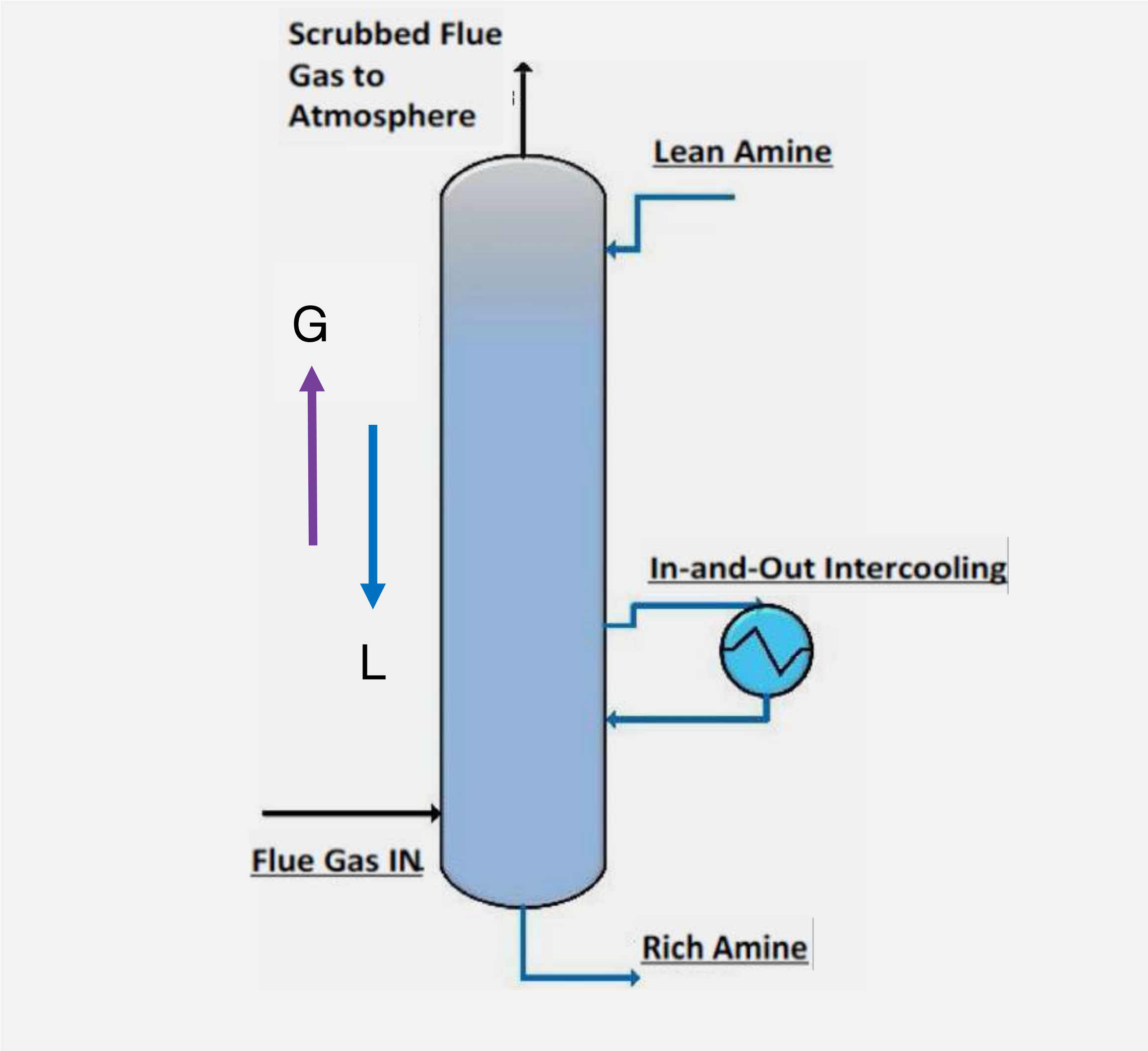
Source: G.T. Rochelle, 2016

Analogy to limestone slurry scrubbing

$CaCO_3$	Event	Amine
1936	1st commercial plant	1980
1958	“Almost Insurmountable difficulties” (Bienstock et al. 1958) ”Although … technically feasible, it is an expensive method” (Booras and Smelzer, 1991)	1991
1960-75	Government funds research on advanced alternatives	1995-
1970-85	Government & EPRI fund test facilities	2010-
1968	60–250 MW prototypes	2014-
1977	500+ MW deployed per regulations	2025
2015	First choice dominates	???

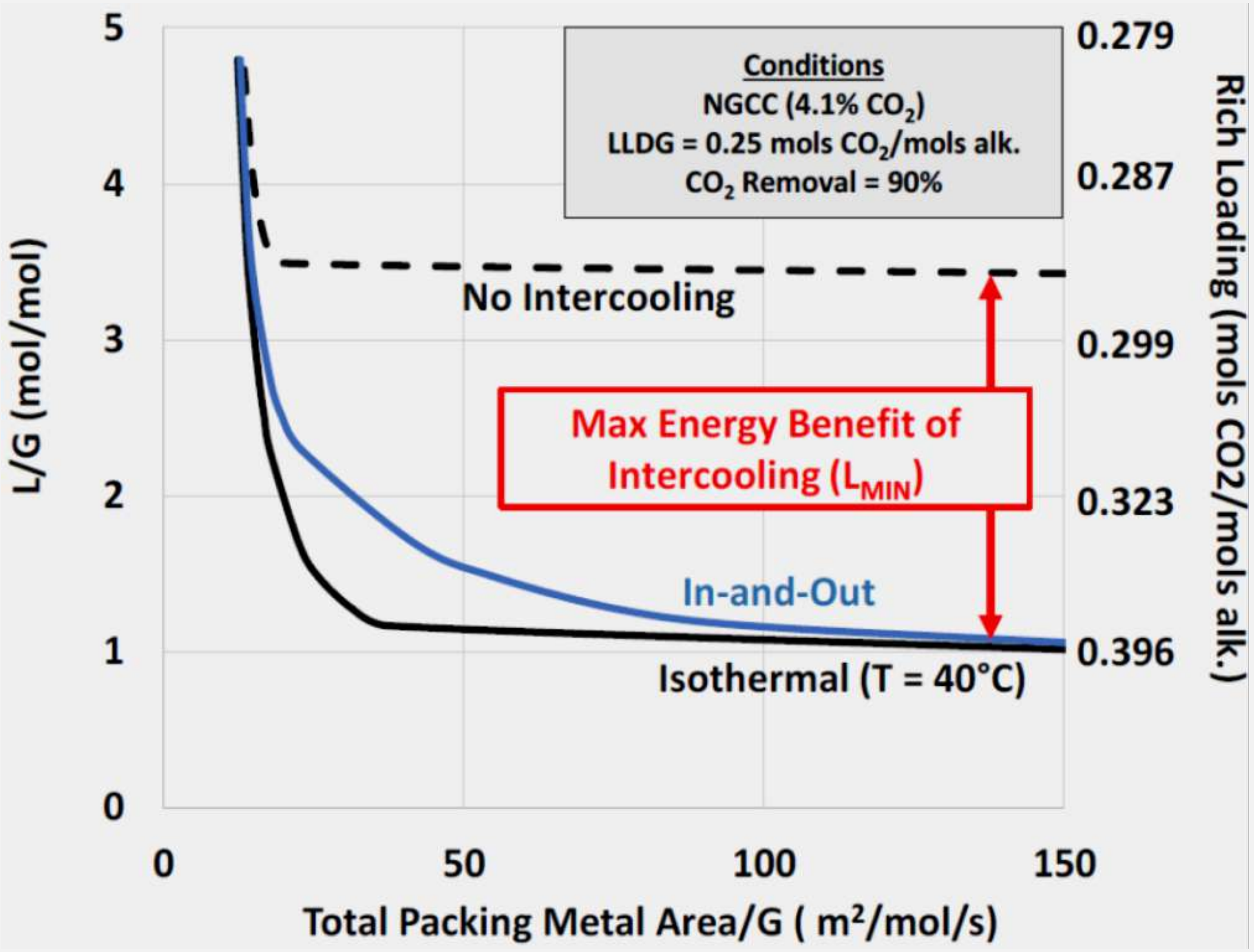
Absorber intercooling in CO2 absorption





Effect of intercooling on packing area, 8 m PZ

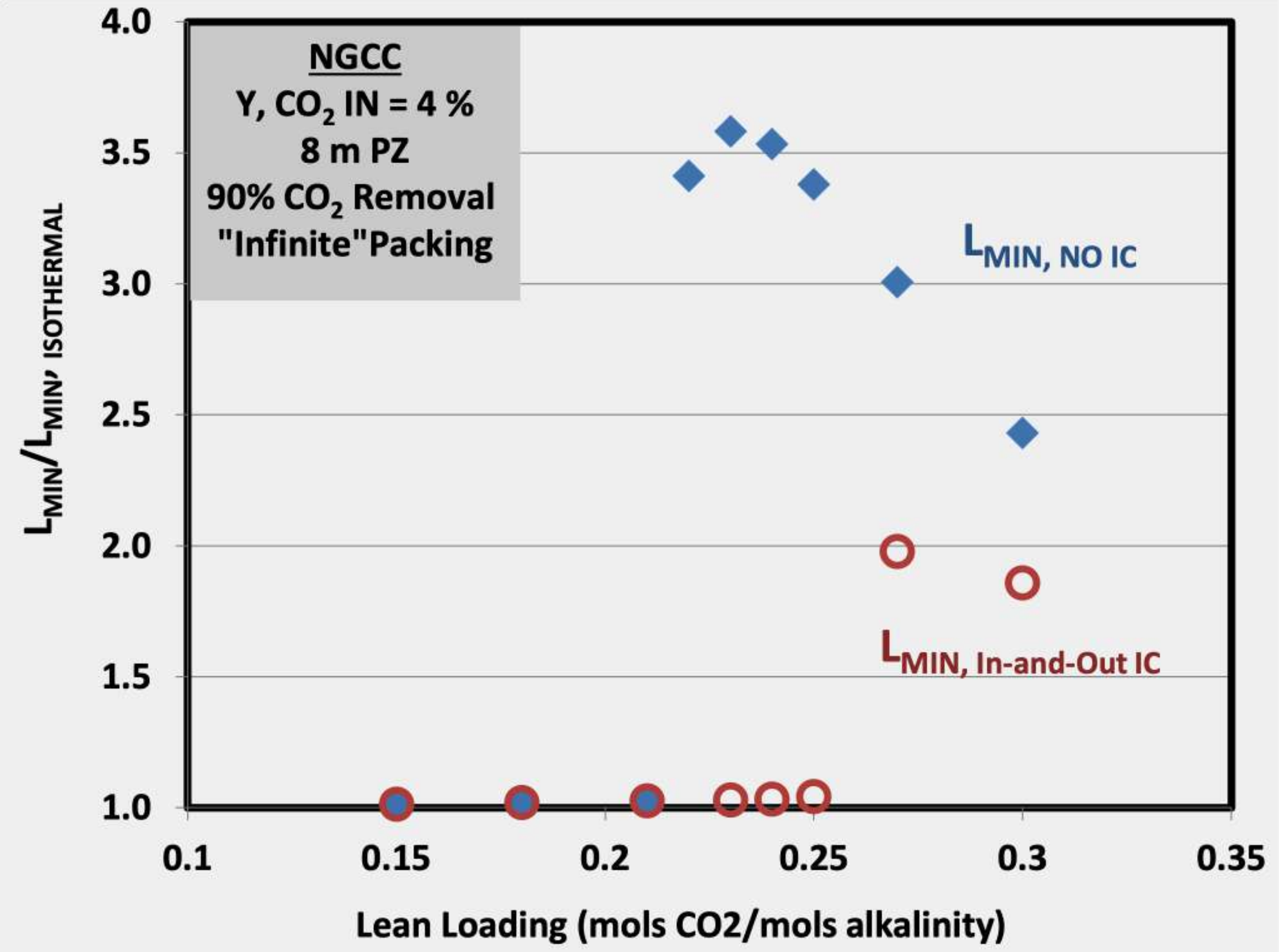
- An isothermal absorber would require less packing and a lower liquid rate to achieve the same performance
- In many cases intercooling may be used to reduce the absorber packing cost and increase the rich loading



Source: Sachde and Rochelle, 2014

Effect of intercooling on liquid rate

- At a lean loading of 0.21 the minimum flow is more than 3.5 times that of an isothermal absorber.
- A single stage of in-and-out intercooling reduces this effect to a factor of two at a greater lean loading of 0.26



Source: Sachde and Rochelle, 2014

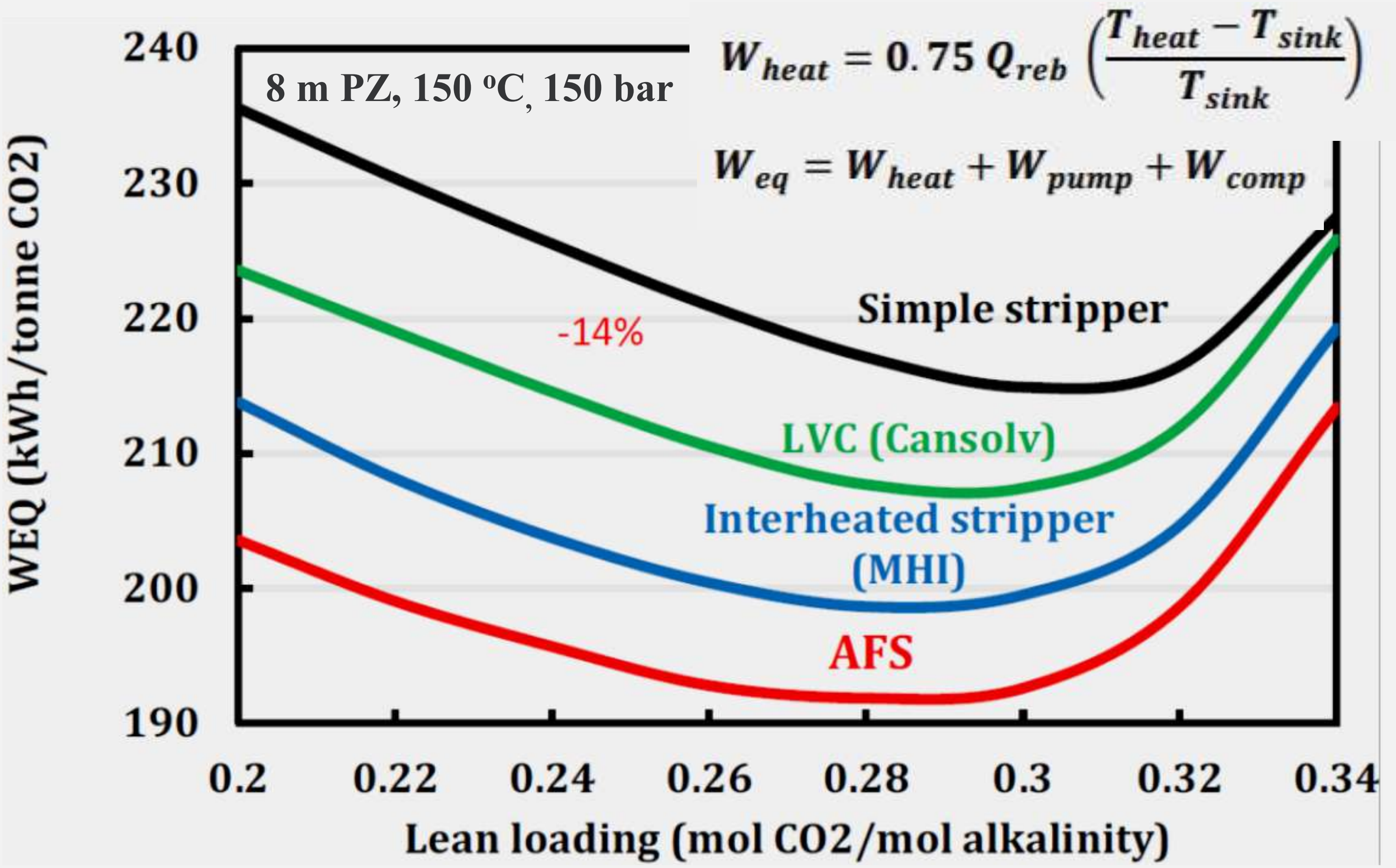
Absorber design

- The larger demonstrations use modern structured packing with larger corrugation angle
- The earliest absorbers in capture systems were round vessels
- Boundary Dam uses a rectangular absorber
- The MHI design at Thompsons uses a rectangular absorber
- Full-scale commercial designs will probably use a single rectangular absorber

Source: G.T. Rochelle, 2016

Three stripper enhancements to that of simple stripping

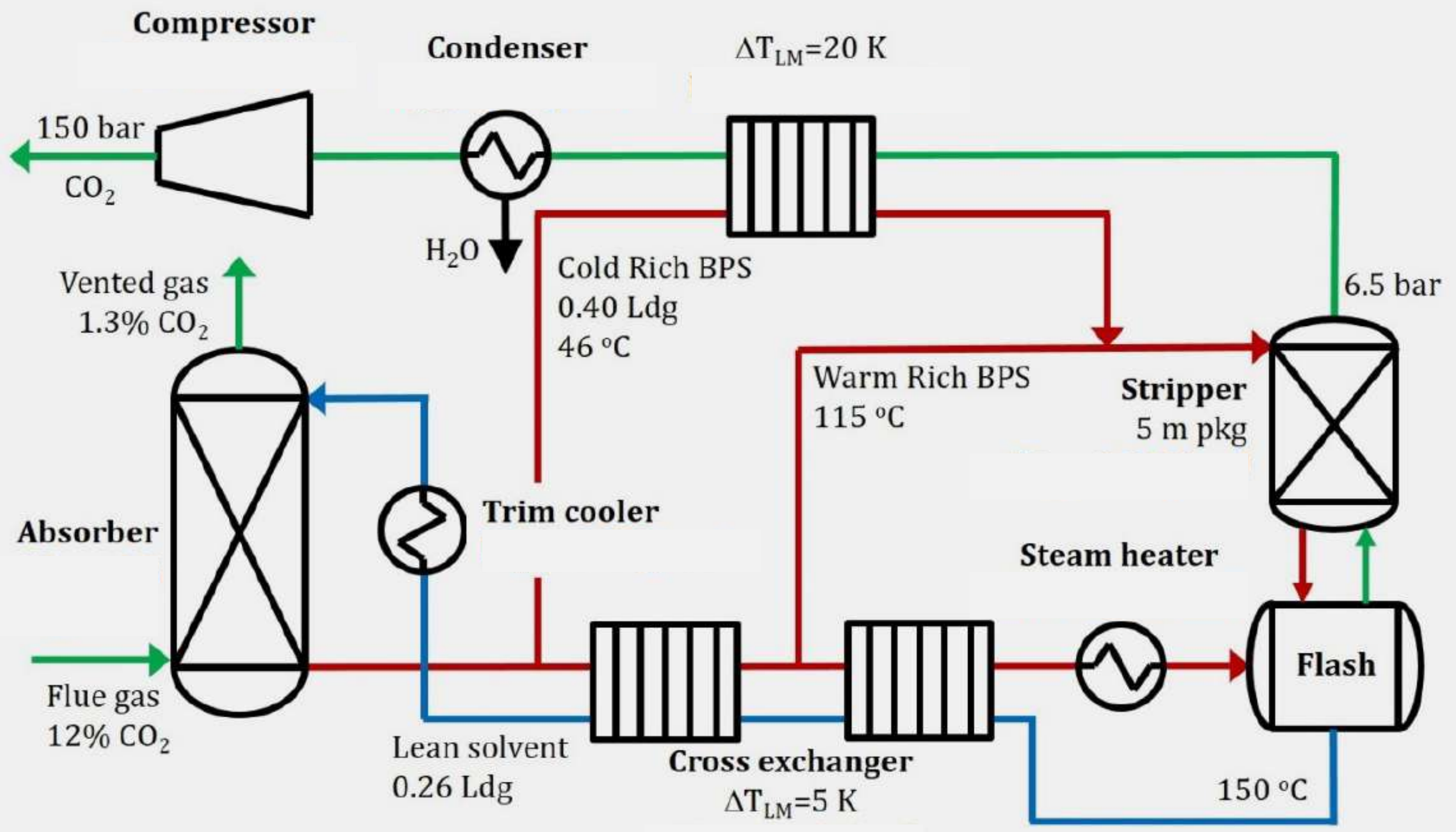
- Simple stripper loses efficiency because of water vapor that passes overhead and is condensed without heat recovery
- Large scale commercial applications will probably utilize these or similar configurations to enhance energy performance



Source: G.T. Rochelle, 2016

Advanced flash stripper (UT Austin)

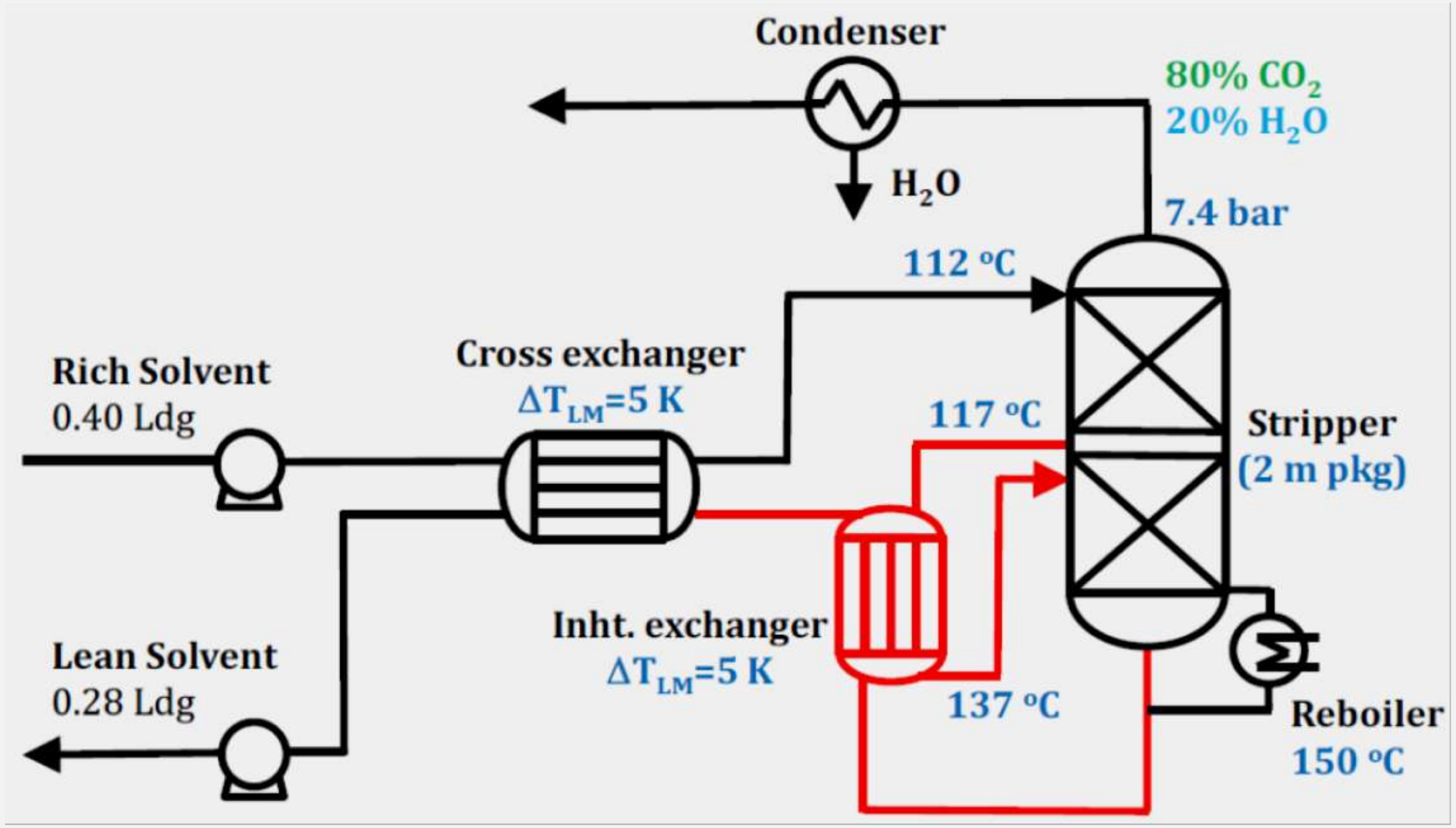
This configuration has been successfully tested in the pilot plant at the University of Texas



Source: Rochelle, 2014

Inter-heated stripper (MHI)

- An important part of the Energy Saving Process used by MHI in several commercial units
- The design has no optimization variables, so it is usually less efficient than the advanced flash stripper

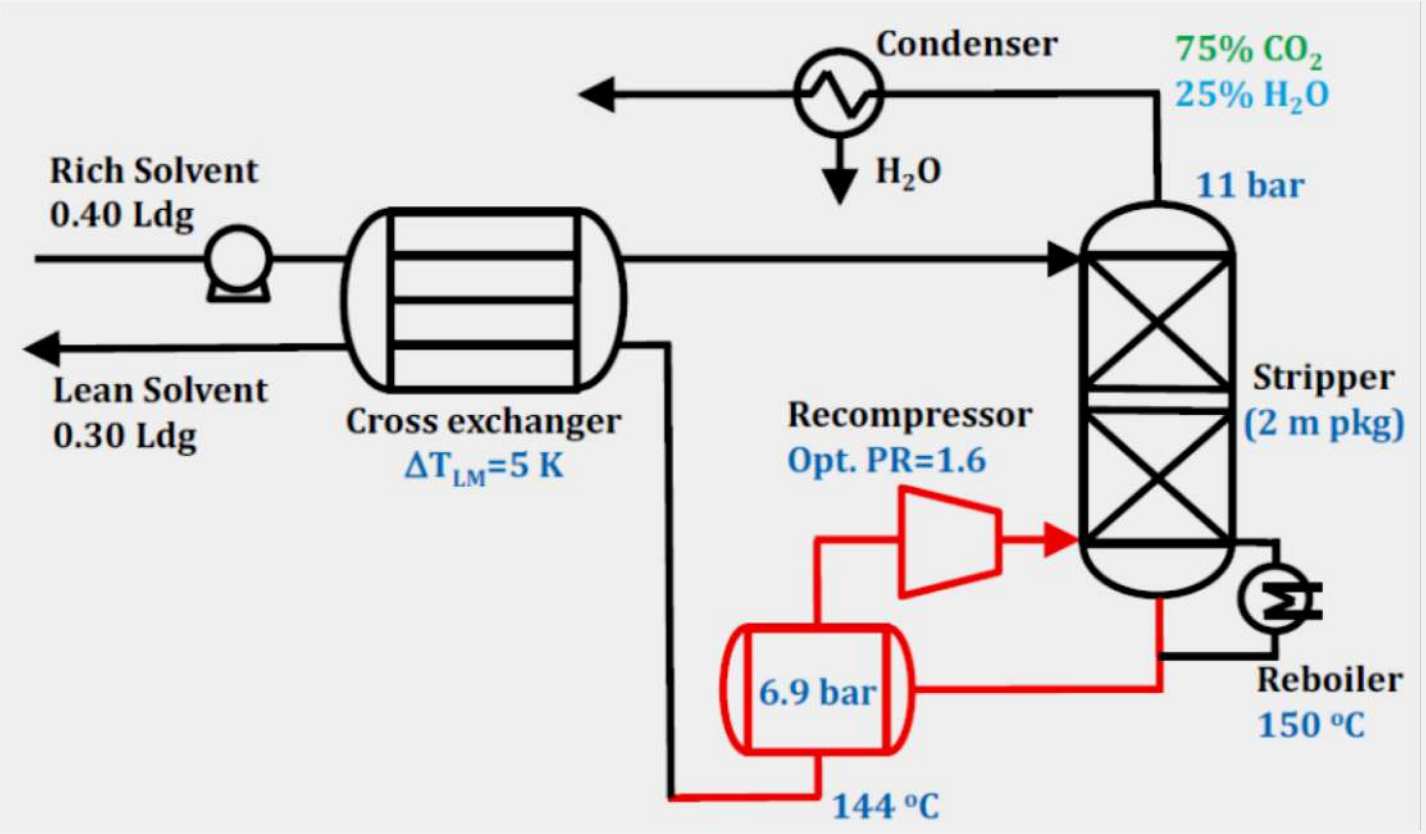


Source: Rochelle, 2014

Lean vapor compression (Cansolv)

- This configuration is included with the Saskpower Boundary Dam project

- It is not as flexible as the advanced flash stripper since the compressor needs to run at a maximum single-stage compression ratio (1.8 to ¬2.2)

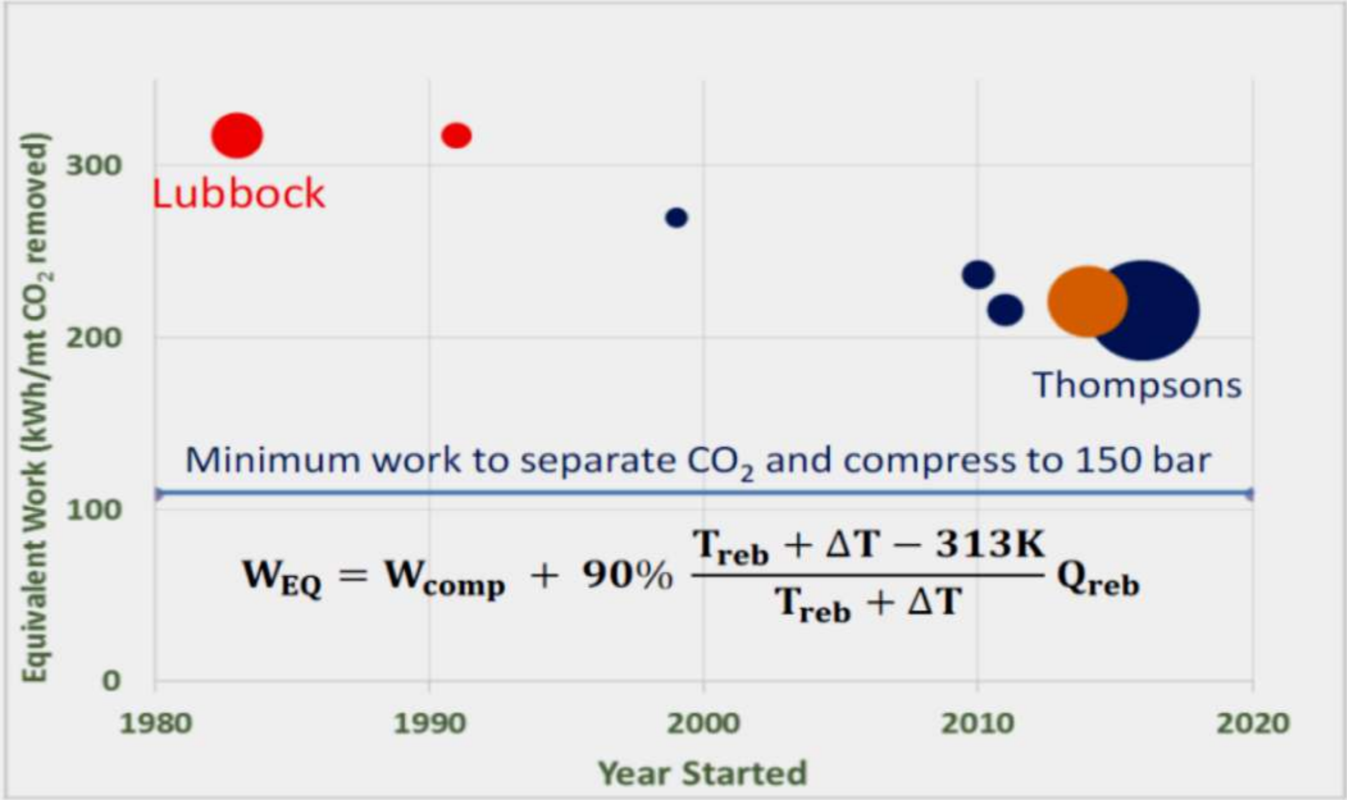


Source: Rochelle, 2015

Electricity burden of commercial units

- The electricity burden with advanced amine scrubbing is approaching the minimum work (113 kWh/tonne CO2 removed)

- It is possible to expect ultimate requirement of 200 kWh/tonne CO2, with a thermodynamic efficiency of 56%.



Source: Rochelle, 2014

Energy criteria for amine selection

The primary basis for amine selection is built on four energy properties:

1. Capacity
2. CO_2 absorption rate
3. Heat of CO_2 Absorption
4. T_{max} from thermal degradation

Absorbent management criteria

Other important amine properties include:

- Oxidative degradation
- Nitrosamine
- Amine volatility
- Amine aerosol emissions
- Molecular weight
- Amine cost and availability
- Amine corrosion

PZ is an excellent alternative to MEA

Property	7 m MEA	5 m PZ
Absorption rate[a] (10^{-7}mol/s-Pa-m^2)	4.3	11.3
Capacity[b] (mol CO_2/mol alkalinity)	0.62	0.76
T_{max}[c] (°C)	120	160
P_{max} (bar)	2.2	14
Heat of absorption[d] (kJ/mol)	71	64
Viscosity[e] (cP)	2.5	3
Solid precipitation[f]	No	Yes

a Average liquid side mass transfer rate between 0.5 and 5 kPa of P*CO2 at 40 °C (Dugas, 2009)
b Difference of lean and rich loading between 0.5 and 5 kPa of P*CO2 at 40 °C (Dugas, 2009)
c Corresponds to 2% amine loss per week (Davis, 2009; Freeman, 2011)
d Differential heat of absorption at 1.5 kPa of P*CO2 (Li, Voice, et al., 2013)
e Average between 0.5 and 5 kPa of P*CO2 at 40 °C (Amundsen et al., 2009; Freeman et al., 2011)

Source: G.T. Rochelle, 2016

PZ blends are comparable but with no issues of solid solubility

Property	5 m PZ	2 m PZ/ 7 m MDEA	2 m PZ/ 4 m AMP	2 m PZ/ 3 m HMPD
Absorption rate[a] (10^{-7}mol/s-Pa-m^2)	11.3	6.9	8.3	10.1
Capacity[b] (mol CO_2/mol alkalinity)	0.76	0.82	0.86	0.92
T_{max}[c] (°C)	160	120	128	149
P_{max} (bar)	14	1.4	3.4	8.8
Heat of absorption[d] (kJ/mol)	64	68	73	-
Viscosity[e] (cP)	3	9	5	-
Solid precipitation[f]	Yes	No	NO	NO

a Average liquid side mass transfer rate between 0.5 and 5 kPa of P*CO2 at 40 °C (Dugas, 2009)
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Conclusions

- Conventional amine scrubbing will be a dominant technology for post-combustion capture
- 2nd generation amine scrubbing provides improved energy performance, with electricity burden approaching 200 kWh/ton CO2 in coal-fired application
- 5 m PZ with absorber intercooling and the advanced flash stripper should serve as the baseline for future improvements in post-combustion capture
- Amine aerosol emissions and amine oxidation are not yet completely understood and managed