

CO₂ Capture
by Aqueous Absorption/Stripping
Opportunities for Better Technology

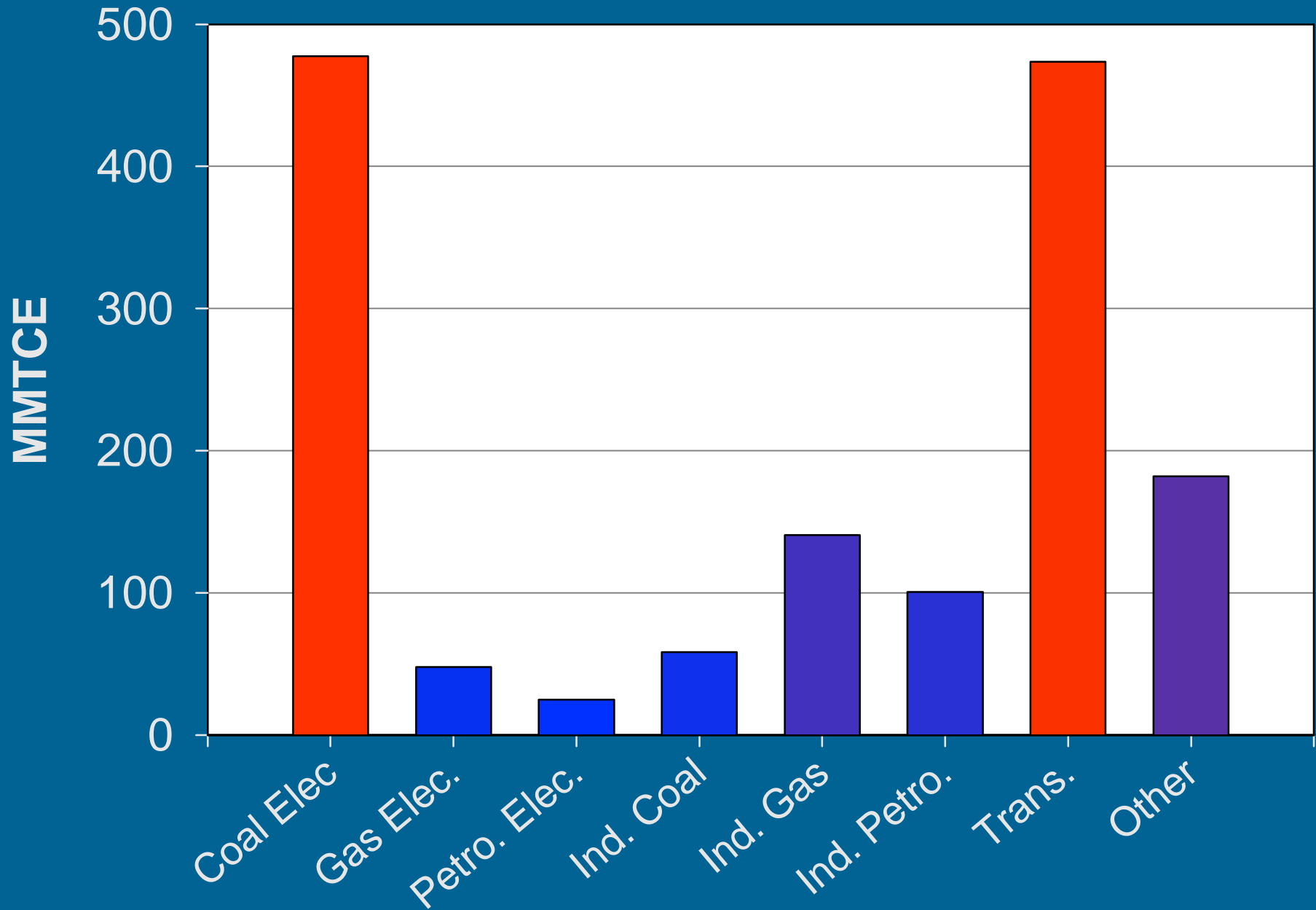
by

Gary Rochelle

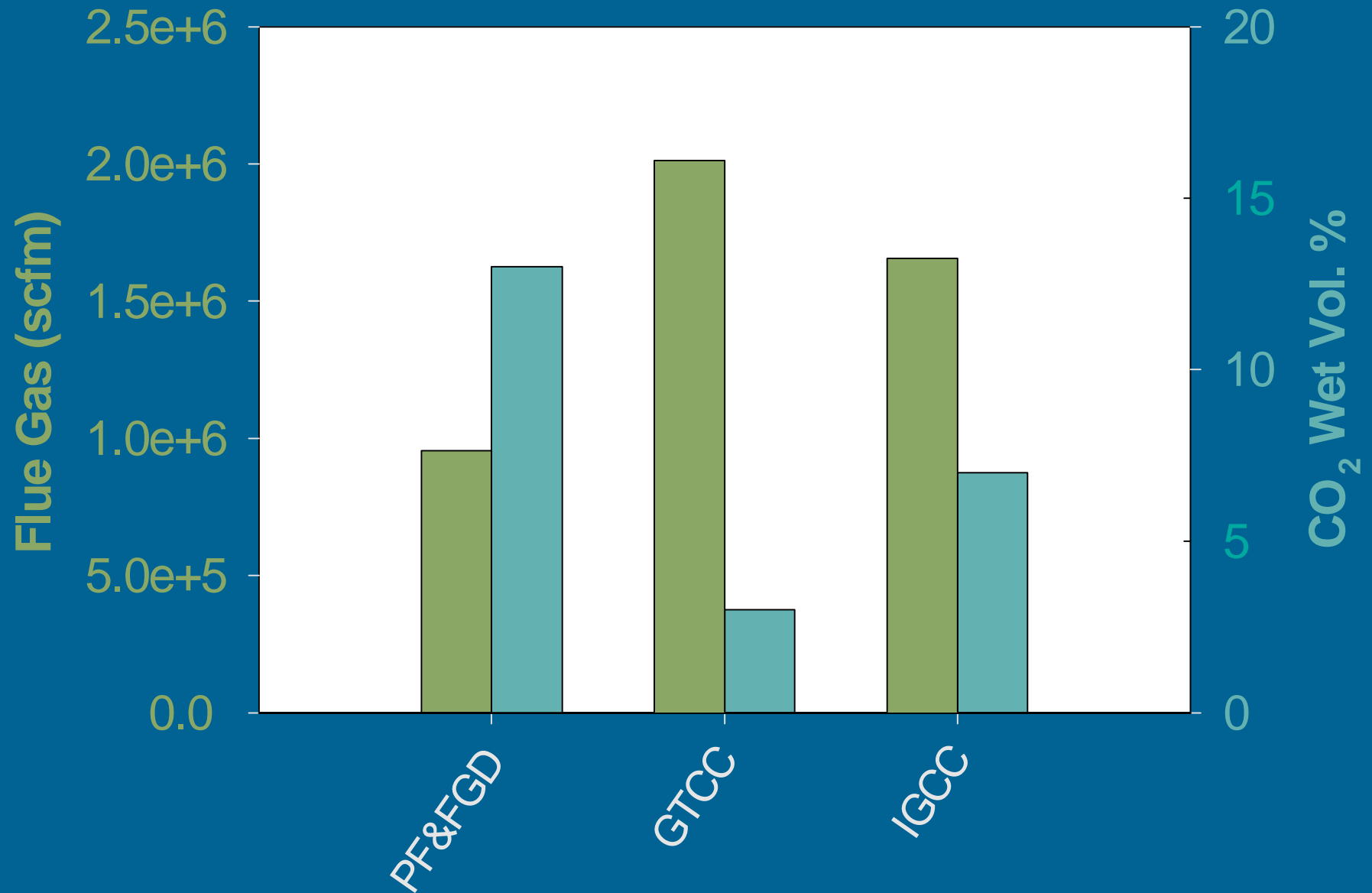
Department of Chemical Engineering

University of Texas

CO₂ Emissions by Source (1998)



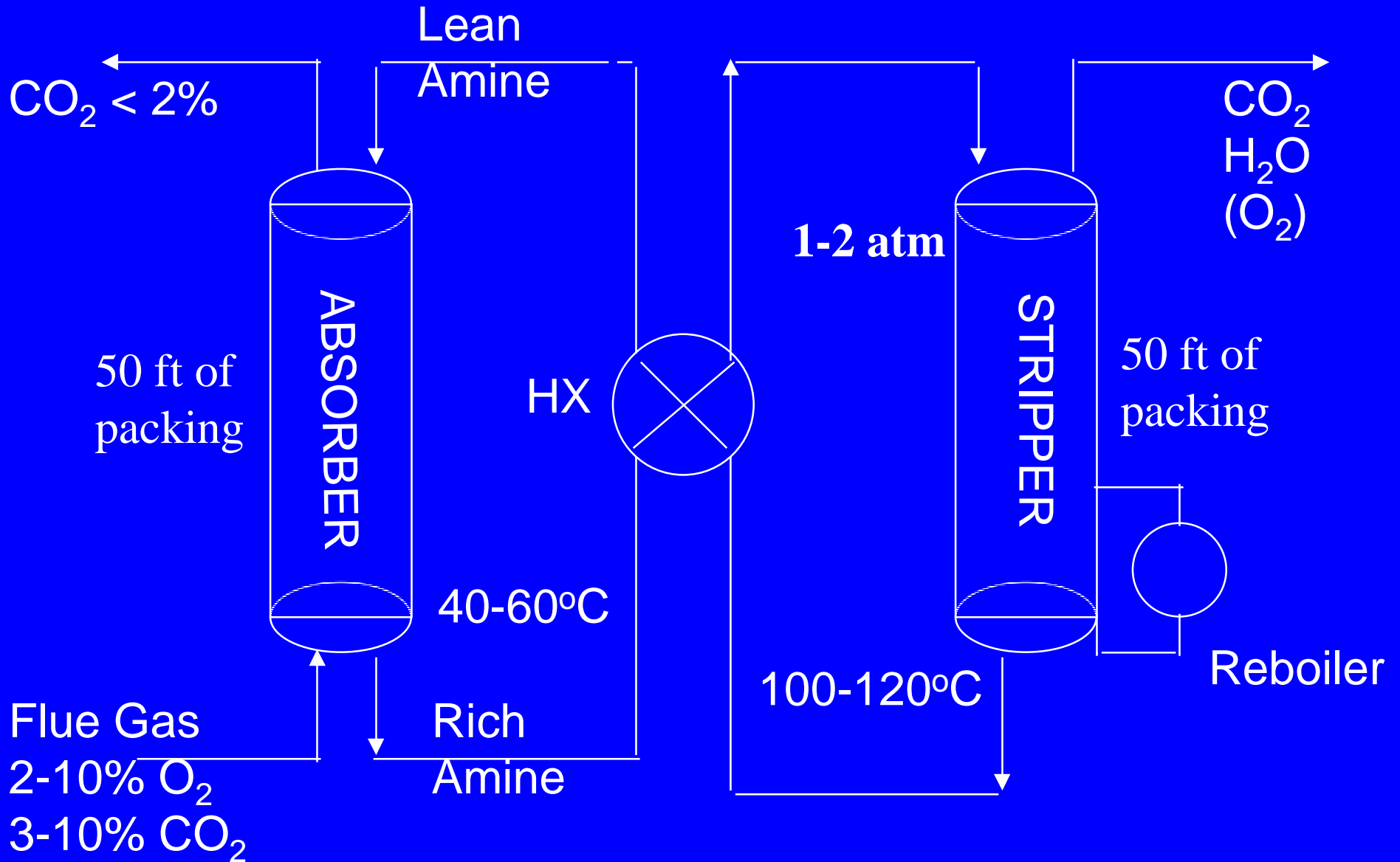
Comparison of Power Technologies (500 MW Power Plant)



The Plan

- Base Case MEA
- Thermodynamics: Solvents for Reduced Energy:
- CO₂ Kinetics: Solvents for Increased Rates
- Energy Integration
- Amine Makeup: Degradation, Corrosion
- Contactor Innovations
- Four Promising Solvent Systems

Typical Absorber / Stripper



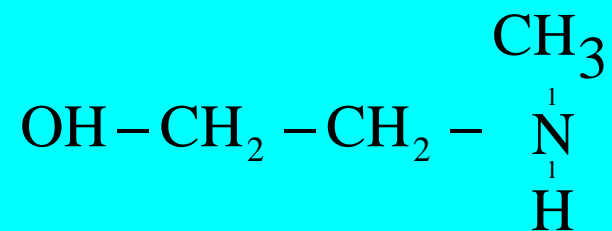
Solvent Alternatives

- Functions
 - Capacity by reversible reaction
Thermodynamics and stoichiometry
 - Fast mass transfer: kinetics at interface
- Three types of chemistry
 - $\text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow 2 \text{HCO}_3^-$
 $\Delta H = 5 \text{ kcal/gmol}$, very slow
 - $\text{R}_3\text{N} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{R}_3\text{NH}^+$
 $\Delta H = 14 \text{ kcal/gmol}$, slow
 - $2\text{R}_2\text{NH} + \text{CO}_2 \leftrightarrow \text{R}_2\text{N-COO}^- + \text{R}_2\text{NH}_2^+$
 $\Delta H = 22 \text{ kcal/gmol}$, fast

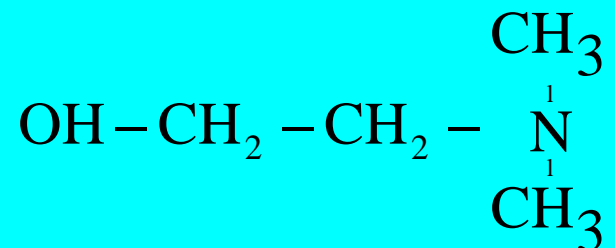
Simple Alkanolamines

Primary - Monoethanolamine (MEA)
(Ethylene Oxide + NH₃)
HO-CH₂-CH₂-NH₂

Secondary – Methylmonoethanolamine (MMEA), [& DEA]

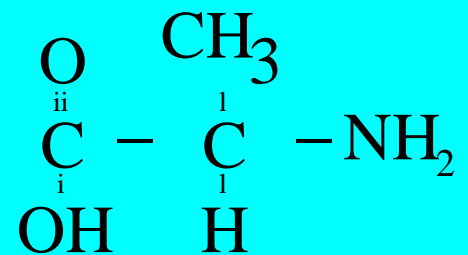


Tertiary – Dimethylmonoethanolamine (DMMEA) [& MDEA]

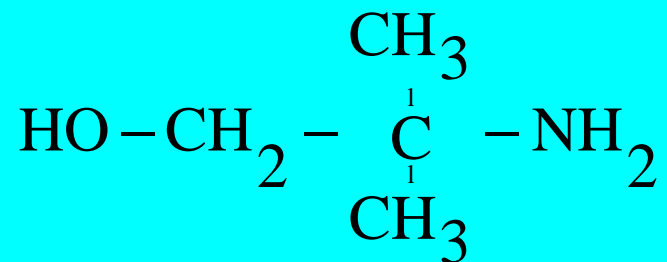


Other Amines

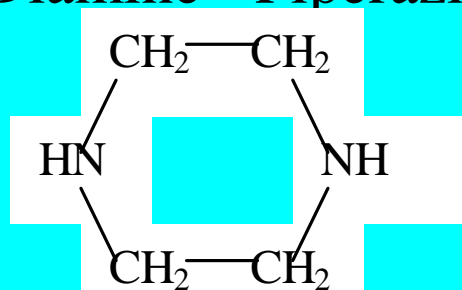
Mildly Hindered Primary– Alanine (ALA)



Moderately Hindered – methylaminopropanol (AMP) [& PE]



Cyclic Diamine - Piperazine



Commercial on H₂ & CH₄

- Generic Monoethanolamine (MEA)
- Hindered Amines
 - Exxon Flexsorb PS
- Promoted Hot Potassium Carbonate
 - Exxon Flexsorb HP
 - UOP proprietary promoter
- Promoted Methyldiethanolamine (MDEA)
 - BASF – Piperazine (PZ)
 - DOW, Huntsman, Arial?? – secondary amines

Comparison to Natural Gas

	Flue Gas	Natural Gas
Total P (atm)	1	10-100
Gas Rate (MMacfm)	1-3	0.001-0.1
P_{CO_2} (atm)	0.1	1-10
P_{O_2} (%)	0.02-0.1	0 – 0.01
Energy/Capital Cost	1	0.1

Offered on Flue Gas

- Monoethanolamine with flue gas
 - Fluor Daniel – 30% with inhibitors
 - ABB Lummus – 20% with inhibitors
 - Praxair – Industrial gas production
- Hindered Amines
 - Mitsubishi K-1 (K-2, K-3)

Nonlinear Equilibrium



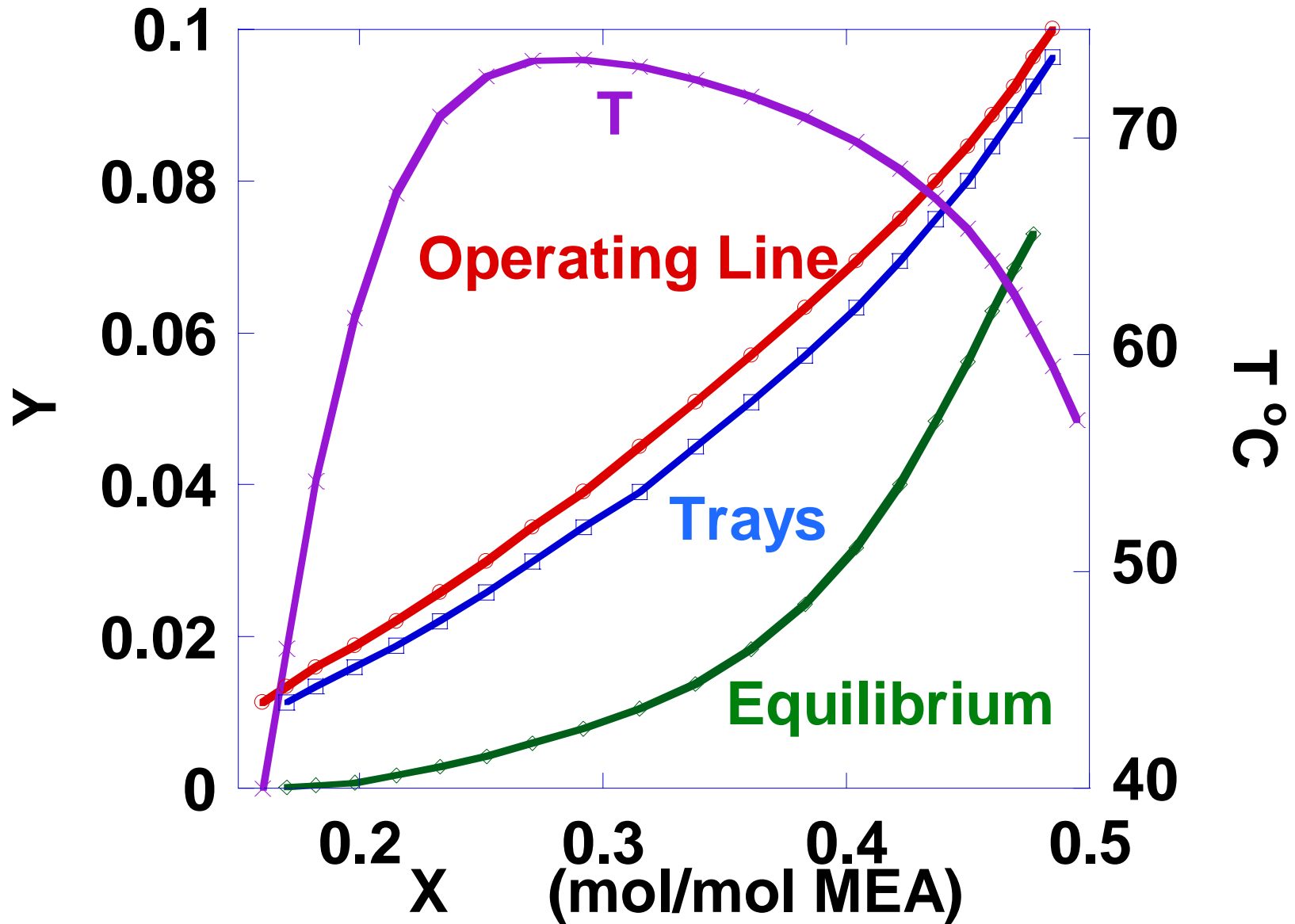
$$P_{\text{CO}_2} = K \frac{[\text{MEAH}^+][\text{MEACOO}^-]}{[\text{MEA}]^2}$$

$$= K \frac{\alpha^2}{(1 - 2\alpha)^2}$$

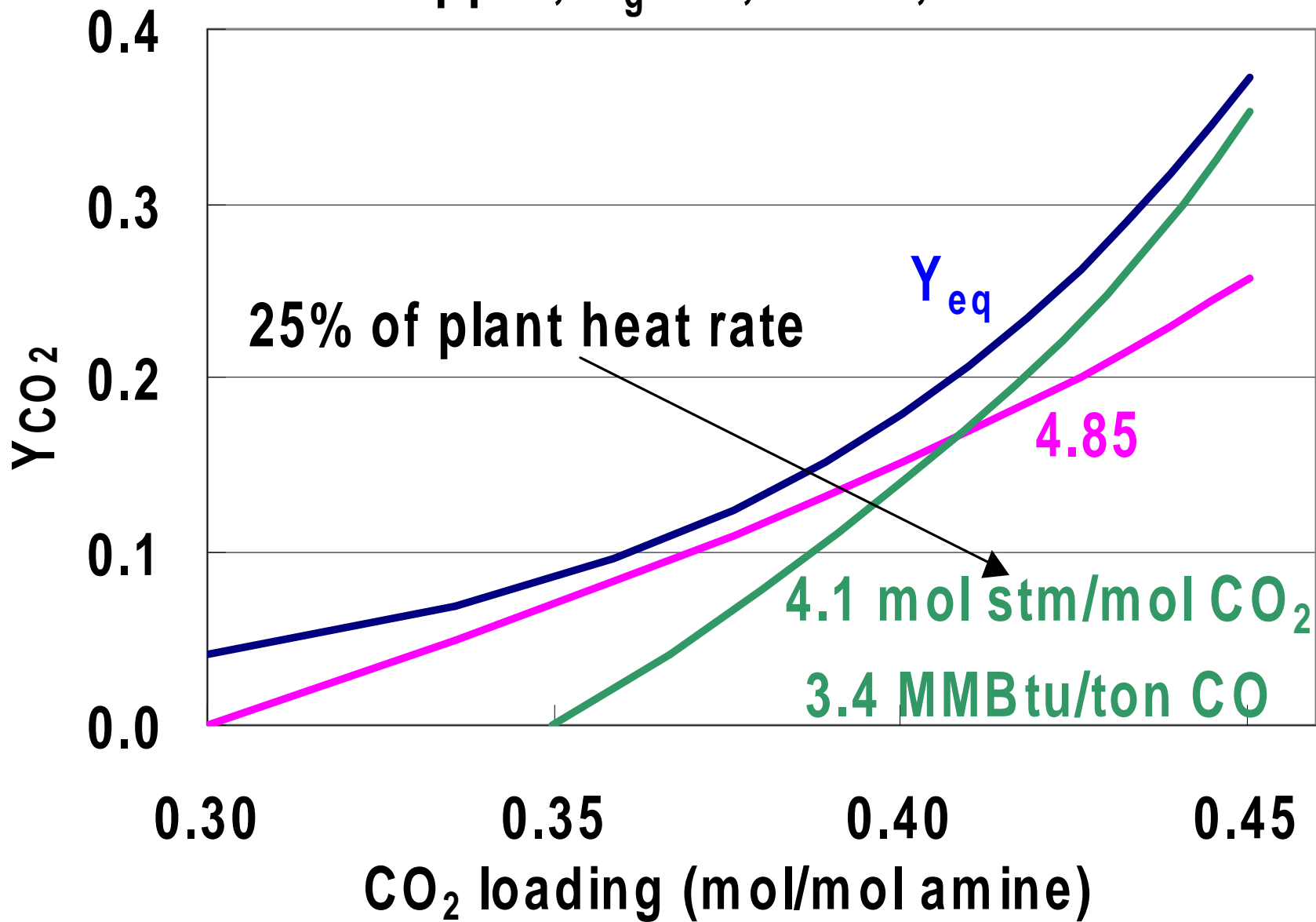
$$\alpha = \text{CO}_2 \text{ _ LOADING} = \frac{\text{Total _ CO}_2}{\text{Total _ MEA}}$$

Absorber McCabe-Thiele

15 wt % MEA, 16% eff, 20 trays



Stripper, $N_g=10$, 1 atm, 5 M MEA



Current MEA Systems

- Demonstrated, commercial technology
 - Transferred from natural gas treating
 - Works, ready for evolutionary improvement
- Energy use almost prohibitive
 - Can use heat at 120°C
- Reasonable rates of absorption/desorption
 - Significant cost of packing and DP
- Corrosion Inhibitors to use carbon steel
- Cheap Amine = Makeup costs acceptable
 - Significant oxidative and thermal degradation
 - Pretreat for SO₂ removal

Components of Stripper Energy (mol stm/mol CO₂)

$$S_{\text{H}_2\text{O}} = \left[\frac{\text{H}_2\text{O}}{\text{CO}_2} \right]_A \text{EXP} \left[\frac{-(H_{\text{CO}_2} - H_{\text{H}_2\text{O}})}{R} \left(\frac{1}{T_A} - \frac{1}{T_S} \right) \right]$$

$$S_{\text{rxn}} = H_{\text{CO}_2} / H_{\text{H}_2\text{O}}$$

$$S_{\text{sens}} = \frac{C_p (T_{S,\text{Bot}} - T_{S,\text{Feed}})}{H_{\text{H}_2\text{O}} A_T \Delta L d g}$$

Thermodynamics of Alternatives

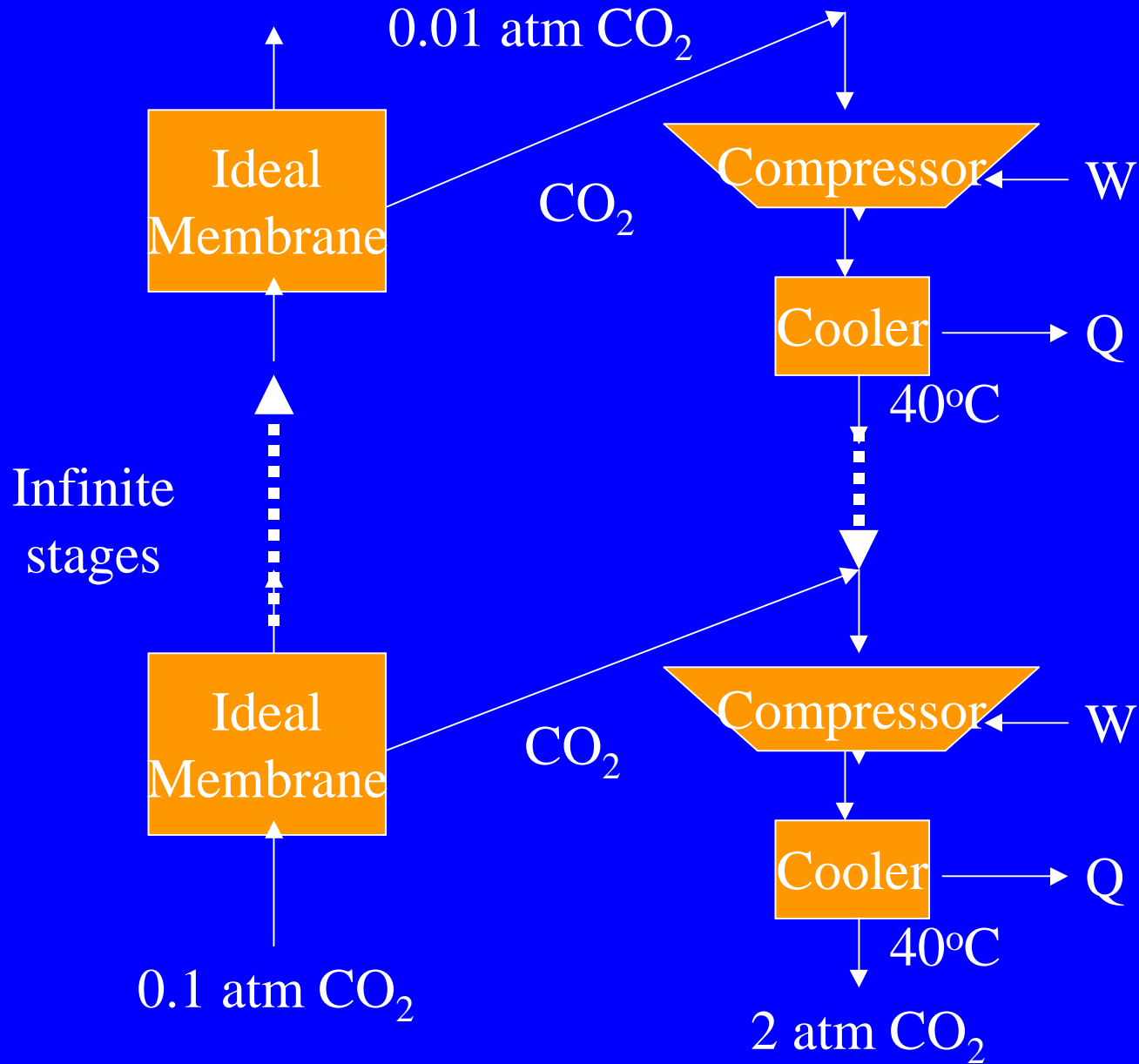
(90% Removal, 0.05 atm, 55°C, 5 M Reagent)

Primary Reaction	ΔH_{rxn} kcal/mol	ΔL_{dg}
Potassium Carbonate $\text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^-$	4.5	0.3
Tertiary or Hindered Amine $\text{AMP} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{AMPH}^+ + \text{HCO}_3^-$	14	0.5
Primary Amine $\text{CO}_2 + 2 \text{MEA} \rightarrow \text{MEACOO}^- + \text{MEA}\text{H}^+$	22	0.15

Stripper Steam Requirement (Mol stm/mol CO₂)

5 M amine	MEA	MDEA/AMP	K ₂ CO ₃
S _{H₂O}	0.6 55/120°C	1.1 55/120°C	3.0 55/55°C
S _{rxn}	2.2	1.5	0.5
S _{sens} 10°C	1.4	0.5	0
S _{total}	4.2	3.3	3.5

The Ideal Process



Carnot Power (kcal/mol CO₂)

40°C Sink, 2 atm Product

10°C ΔT for Reboiler

Power Plant $W = 60$ kcal/gmol

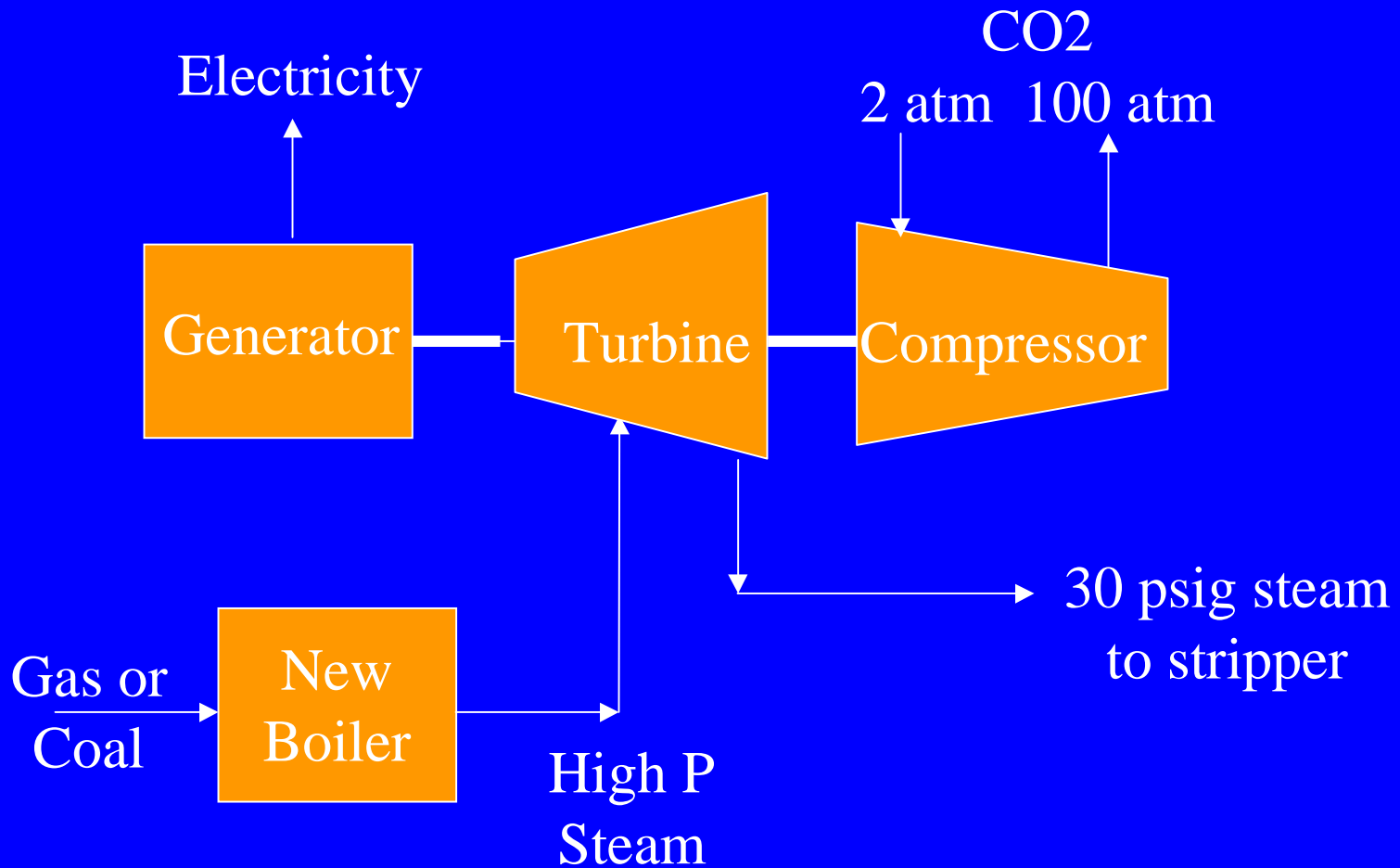
$$W = Q \left[1 - \frac{40 + 273}{T_{\text{reb}} + 10} \right]$$

Ideal	MEA 55/120°C	MDEA/AMP 55/120°C	K ₂ CO ₃ 55/55°C
2.3	9.5	7	5.5

Principles of Energy Integration

- Reduce steam P in turbine to minimize P at stripper
 - Make electricity and/or drive process compressors
- Permit use of offpeak power capacity
 - Avoid derating during peak power use
 - Create additional power capacity to use for peaking
- Utilize waste heat
 - Compressor intercooling
 - Flue Gas
- Ultimately use local coal or electricity from the grid
- Integrate with new gas turbine/waste heat boiler
- Minimize capital cost: Keep it simple
- :

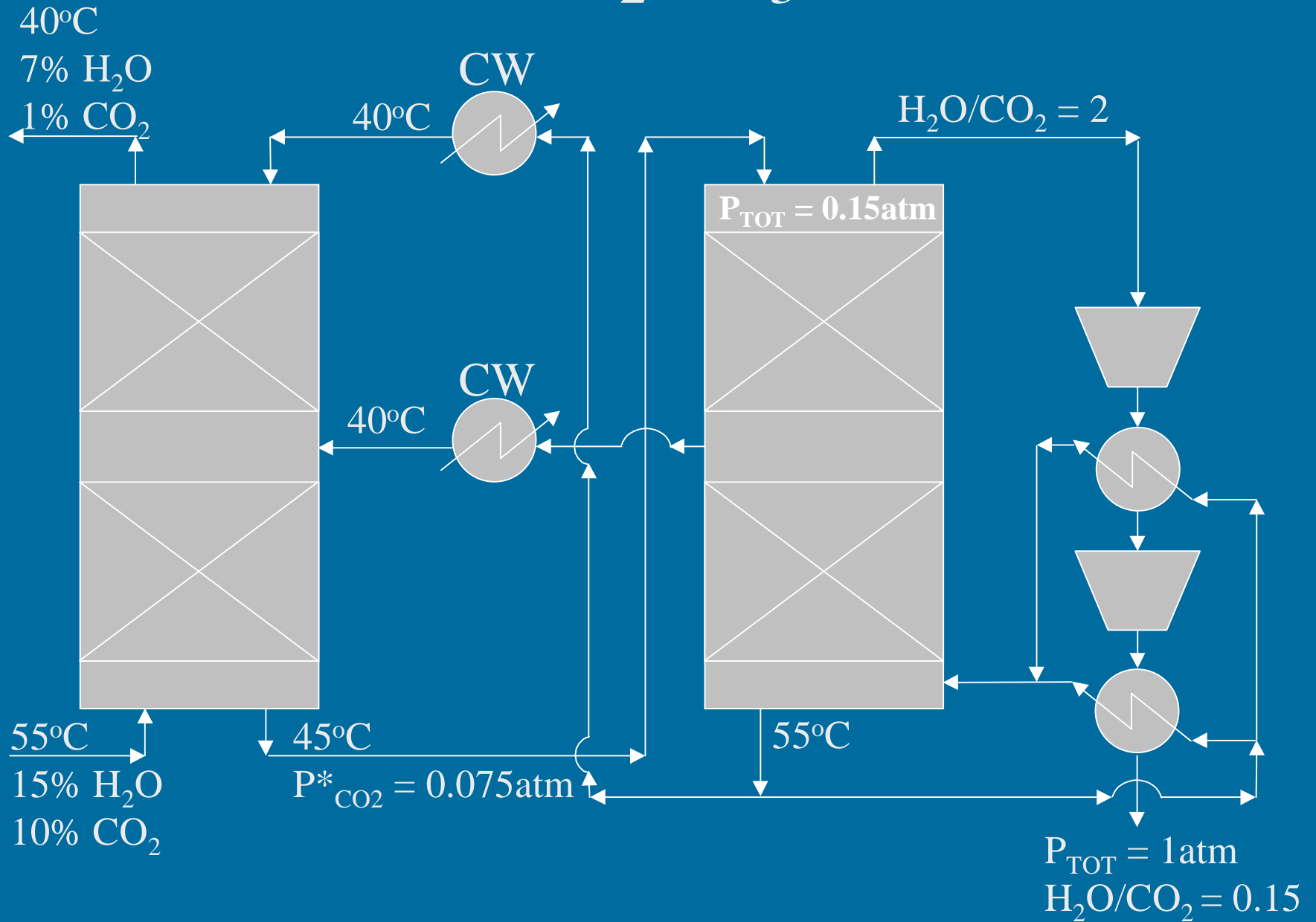
Steam from turbine exhaust



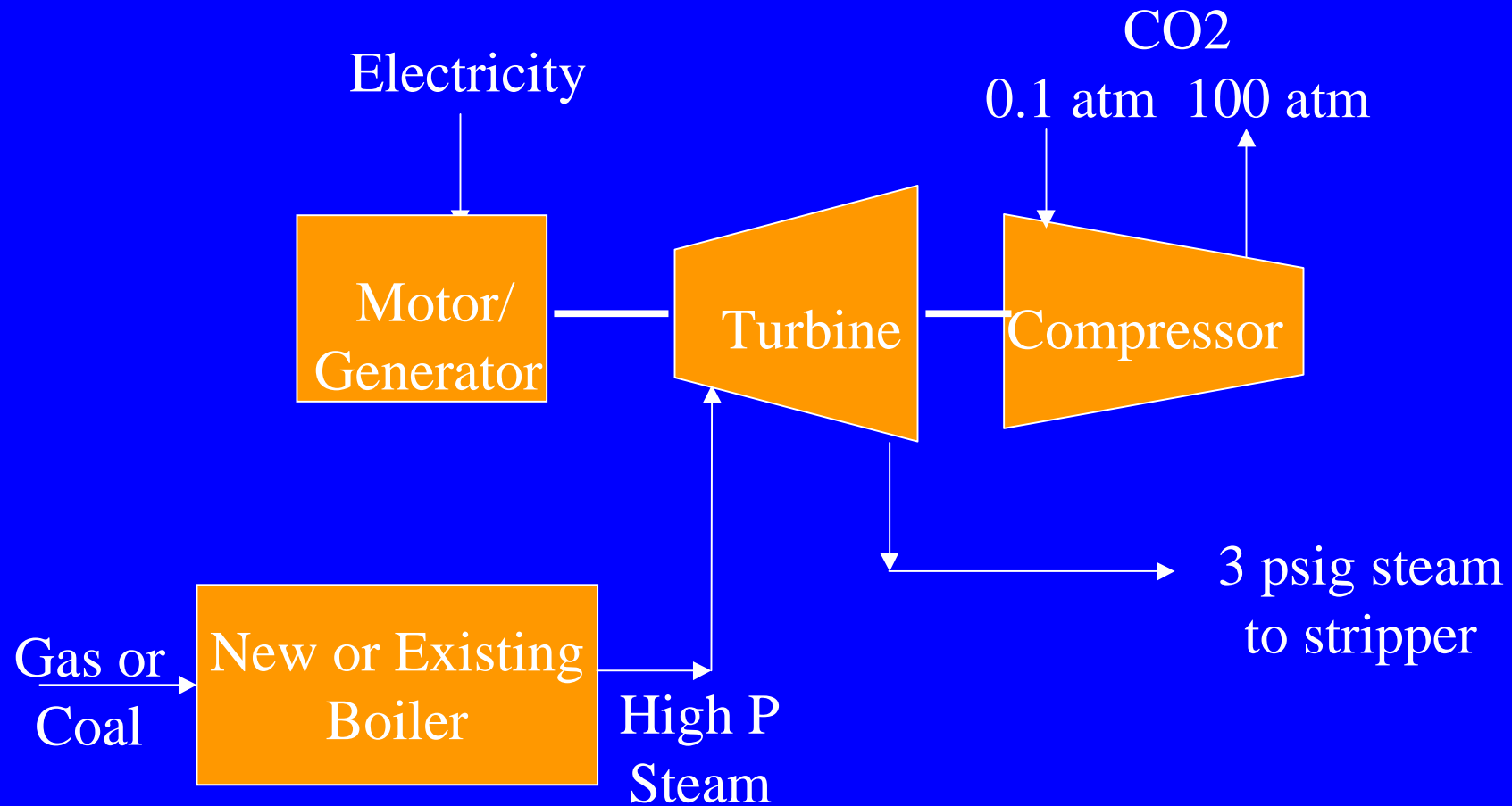
Steam extraction

- Extract low P Steam from Main turbine
 - Inconvenient distances
 - Not available at desired P
 - Derates low P power turbine, may affect efficiency
 - Shut down stripper at peak power loads, derating does not affect system capacity
- Extract low P Steam from new dedicated boiler/turbine, probably high cost gas
 - Net capacity gain, but adds capital cost
 - Use high pressure turbine to drive CO₂ compressor

Advanced K_2CO_3 Process

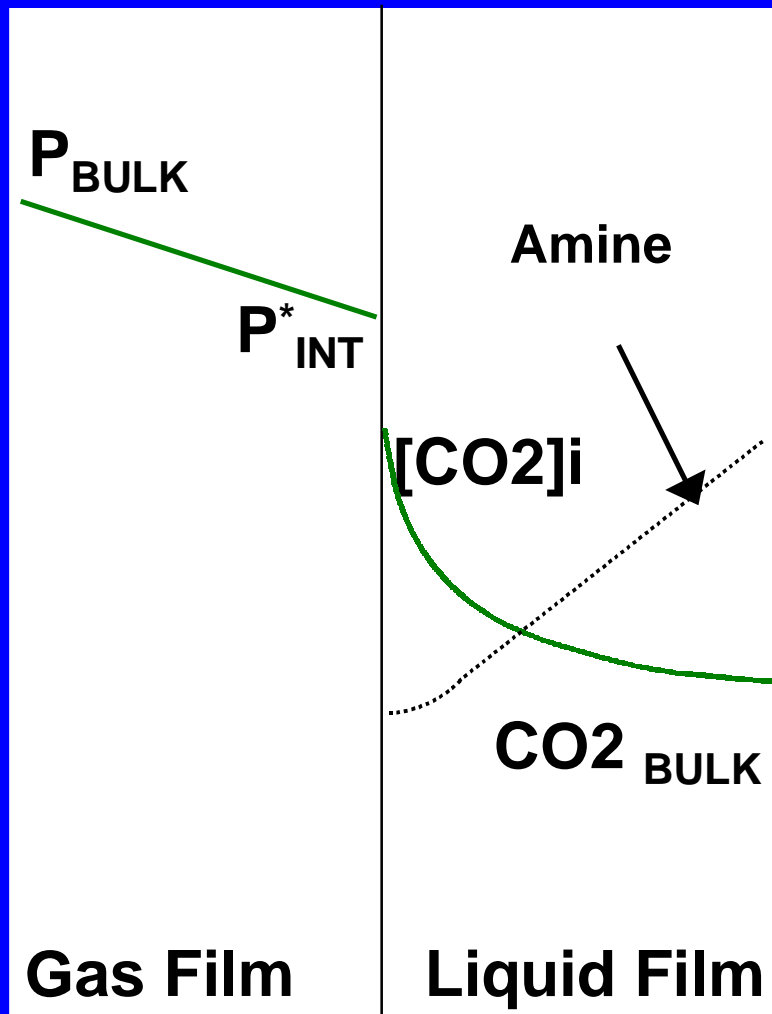


Energy for Vacuum Stripper



Mass Transfer with Chemical Reaction

Important Physical Phenomena



- Vapor Liquid Equilibrium
 - P^* (Define Pinch Conditions)
 - Speciation (Free Amine, CO₂)
- Reaction Chemistry
 - Usually Rate Limiting
 - Mechanism Important
- Mass Transfer Model
 - buildup of reaction products
 - depletion of reactants

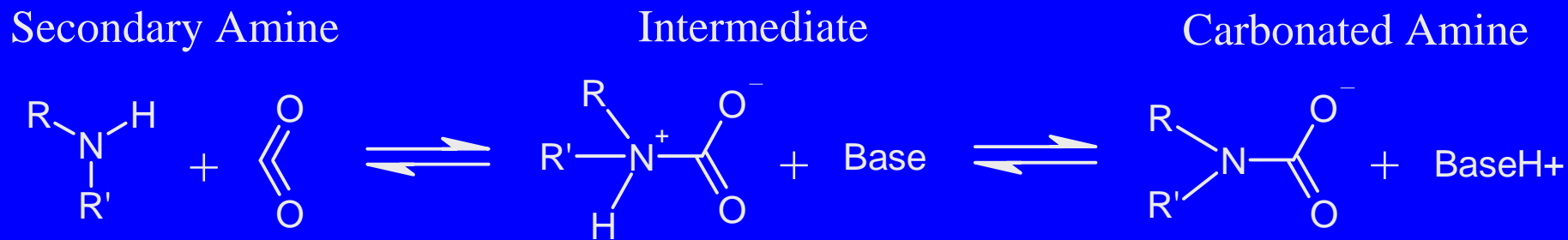
Mass Transfer Design

$$\frac{1}{K_g a} = \frac{1}{k_g a} + \frac{1}{E H_{\text{CO}_2} k_1^0}$$

$$\text{Flux} = E k_1^0 = \sqrt{k_2 [\text{Amine}]_i D_{\text{CO}_2}} \frac{[P_{\text{CO}_2} - P_{\text{CO}_2}^*]}{H_{\text{CO}_2}}$$

- E must be 20 – 100
- k_2 should be 1 – 10 ($\text{m}^3/\text{gmol}\cdot\text{s}$)

Zwitterion Mechanism



Rate limiting step may be due to...

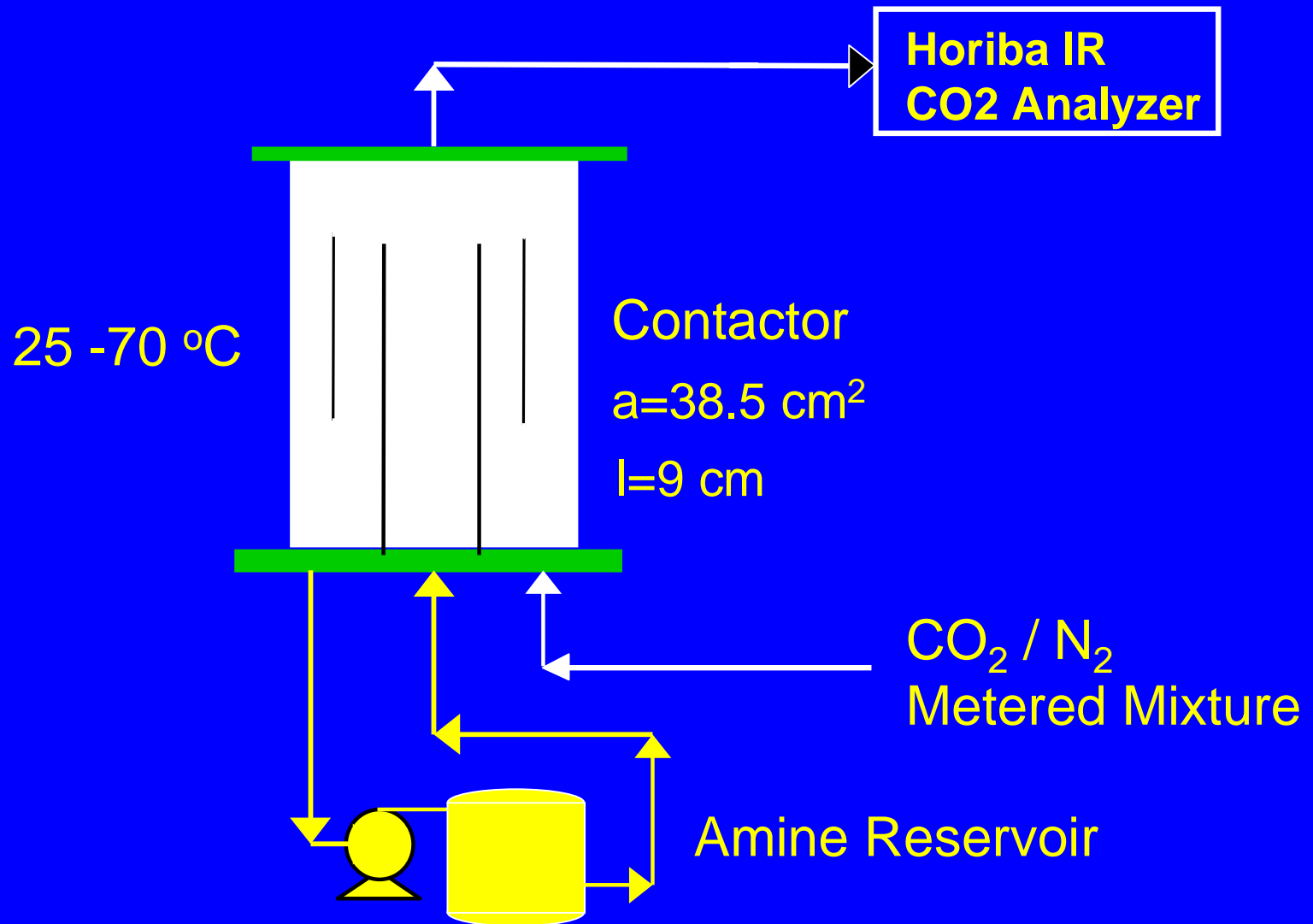
- formation of the zwitterion
- proton extraction from the intermediate

Piperazine rates faster than predicted

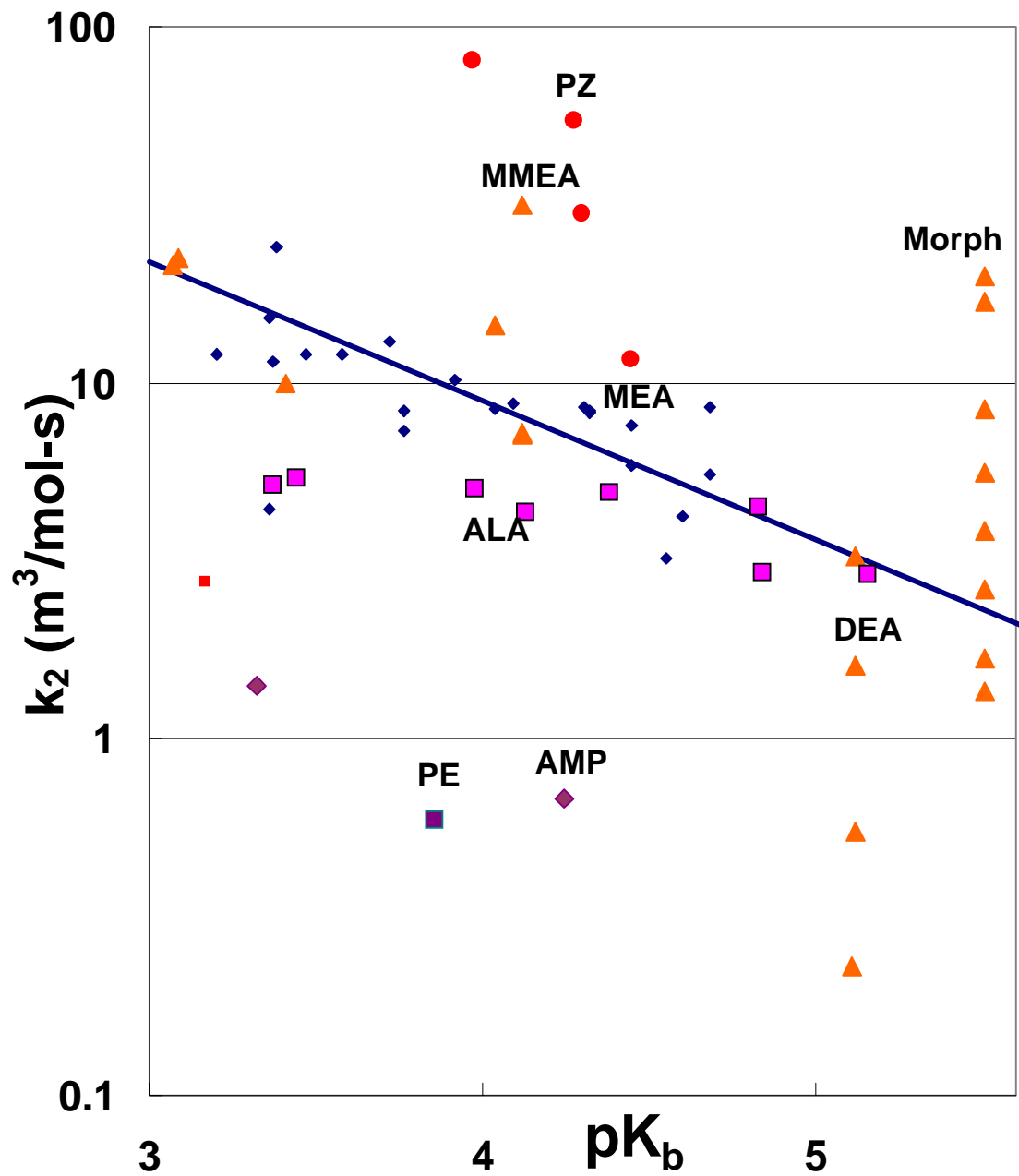
- less steric hindrance
- proton extraction from the intermediate by PZ or $\text{CO}_3^{=}$

Experimental Techniques

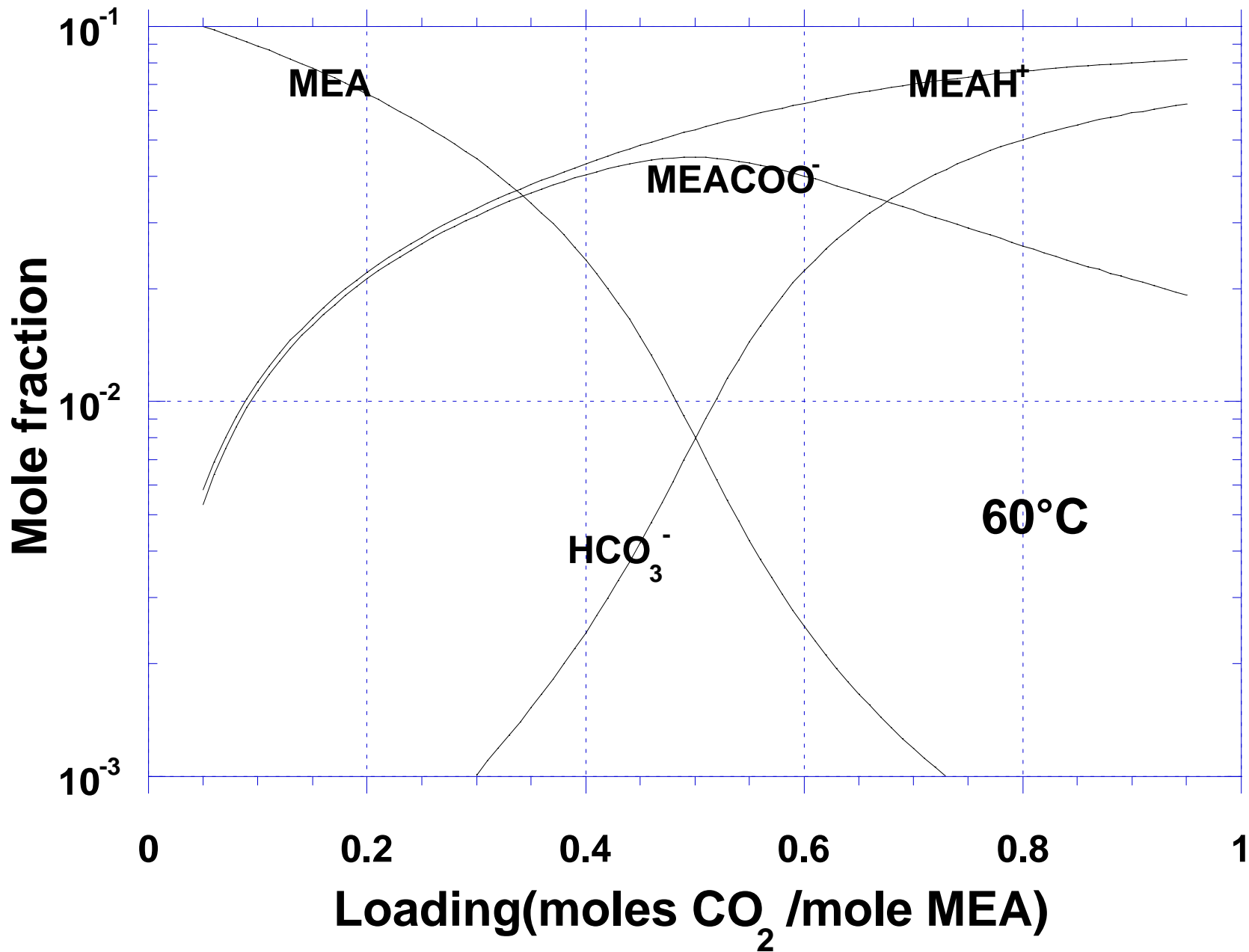
Wetted Wall Column



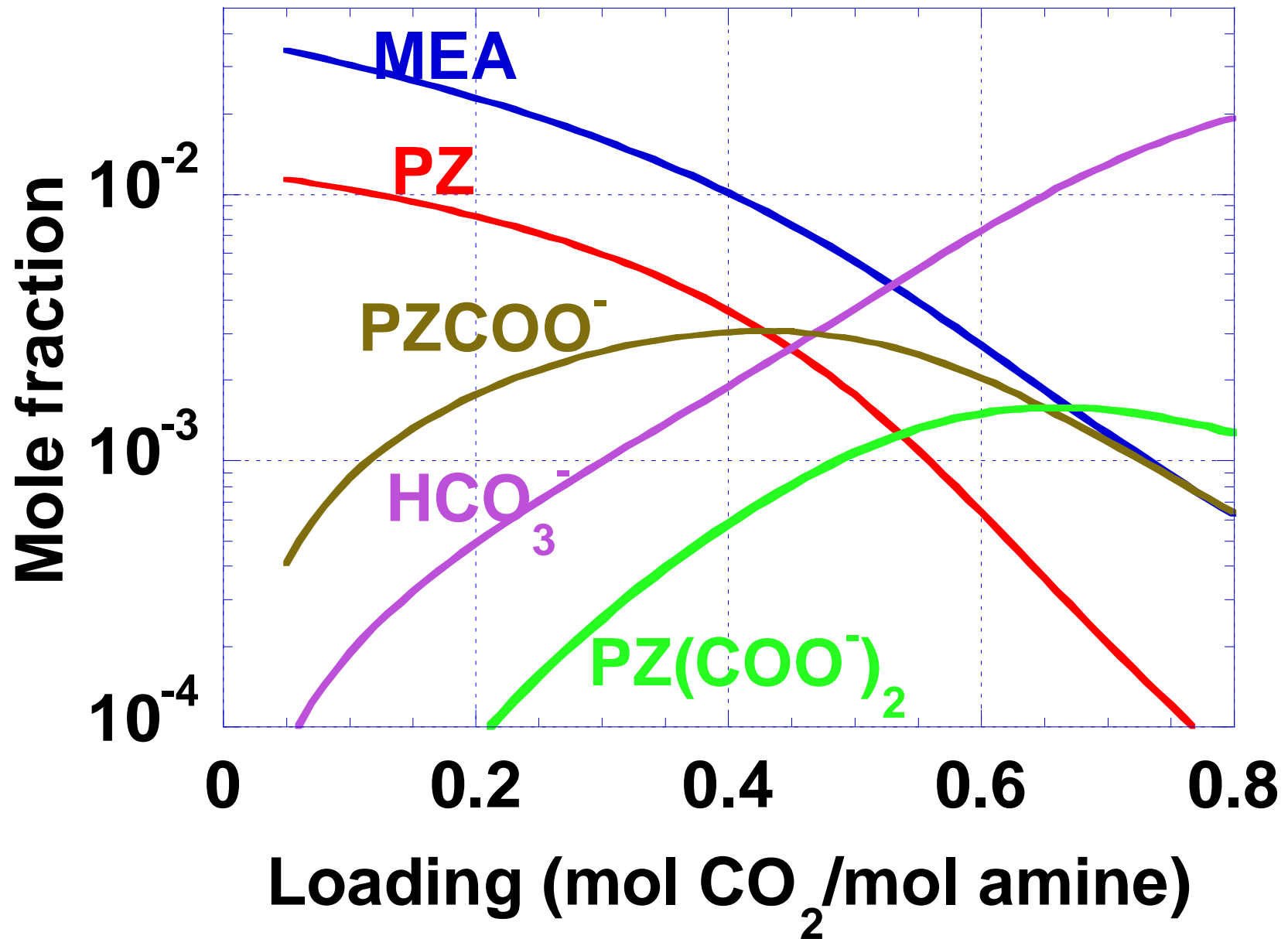
CO₂ Kinetics of Alternatives



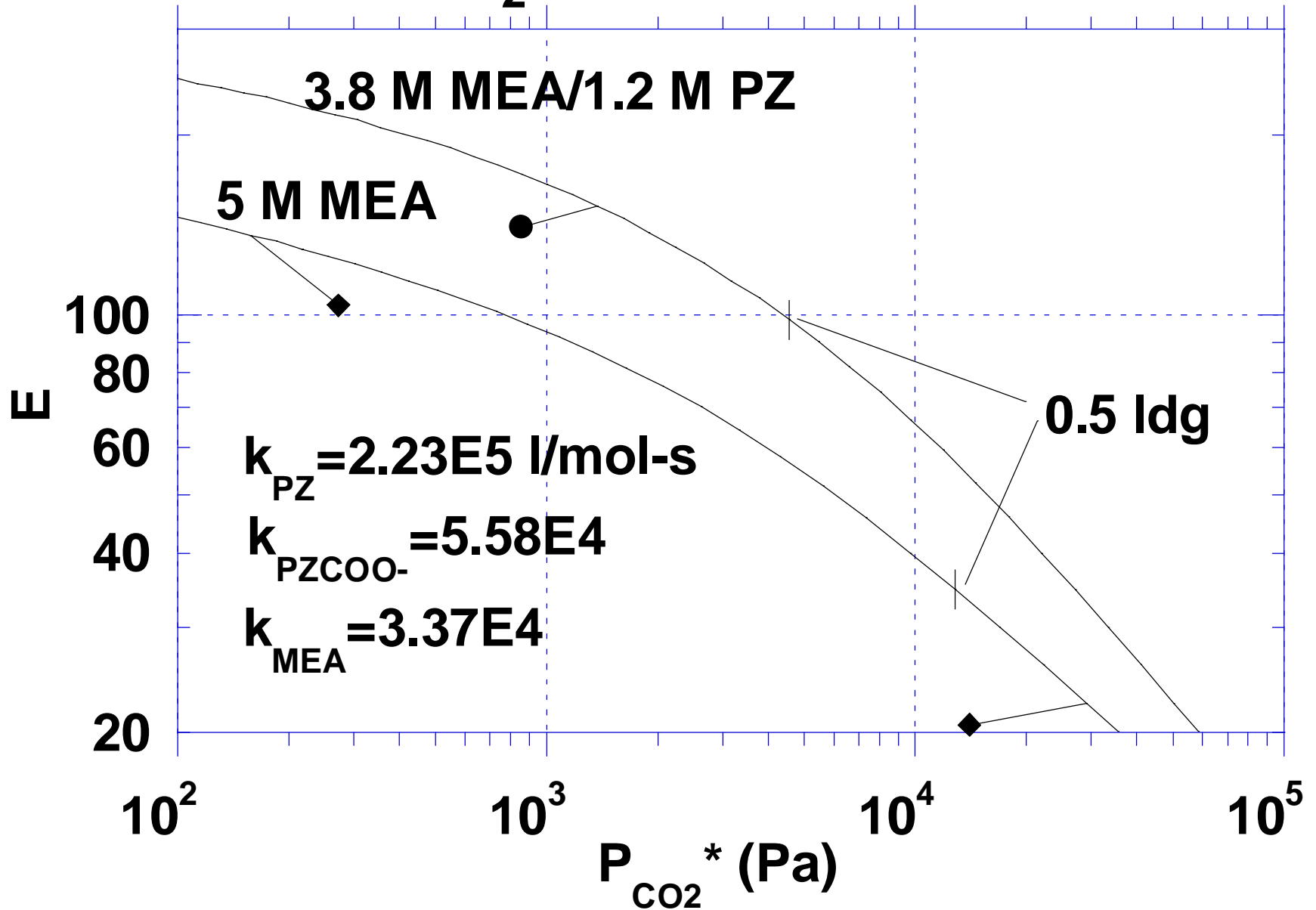
5M MEA speciation



Speciation in 0.6 M PZ/1.9 M MEA at 60°C

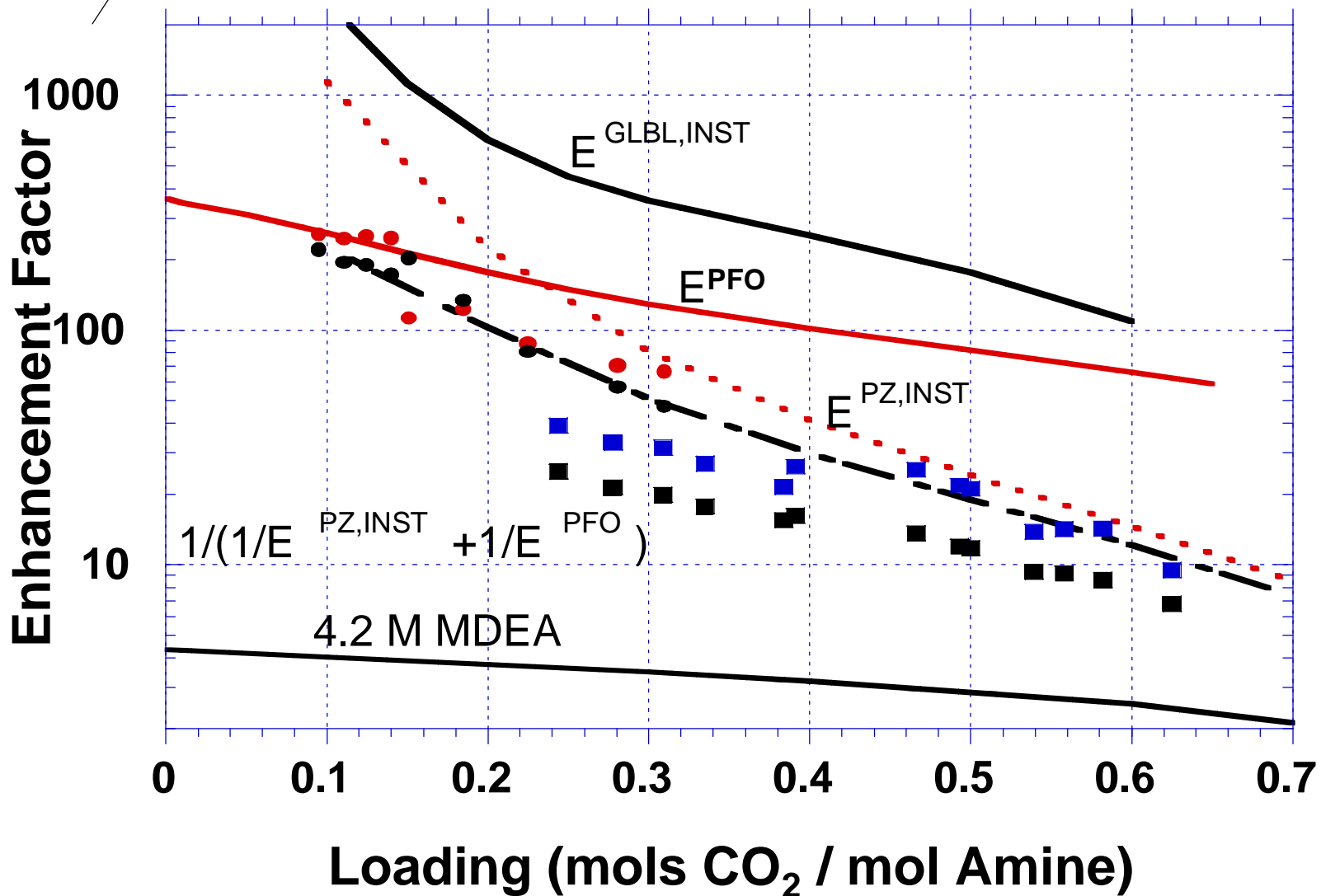


CO₂ Absorption, 60°C

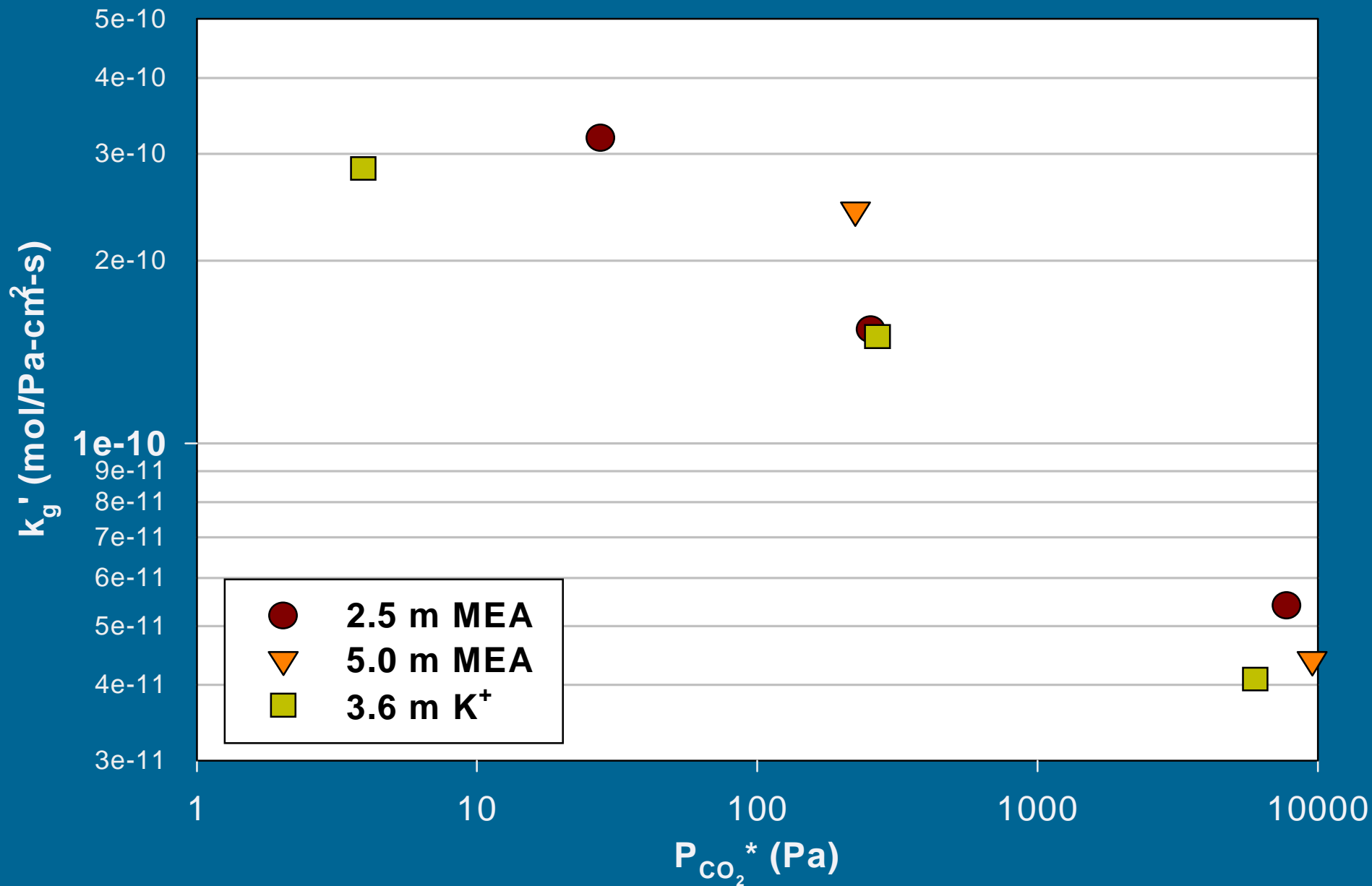


Data and Model Predictions

0.6 M PZ, 4 M MDEA 313K, $k^{\circ}_l=3.3E-5$ m/s



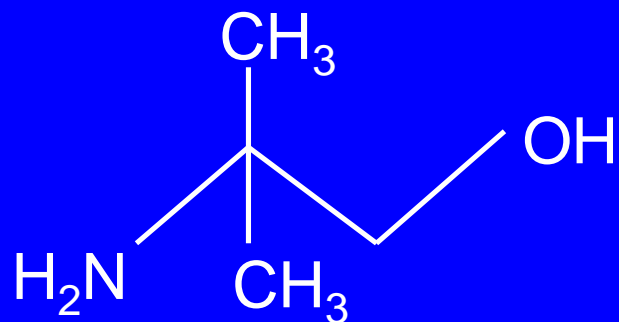
Comparison of MEA/K₂CO₃ Systems



Four Ideas for Reducing Packing Height

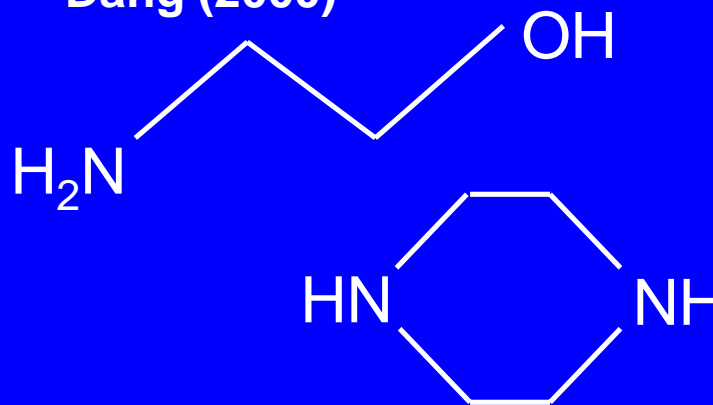
Base Case is 5M MEA

Hindered Amine (5 M AMP)

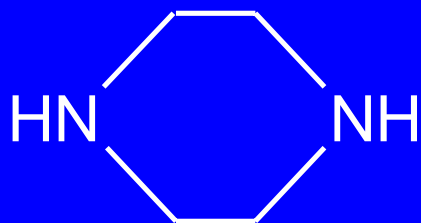


4.4 M MEA / 0.6 M PZ

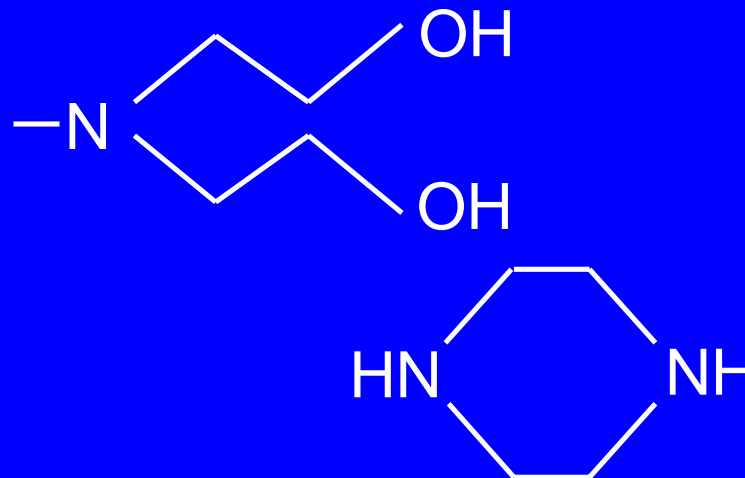
*Dang (2000)



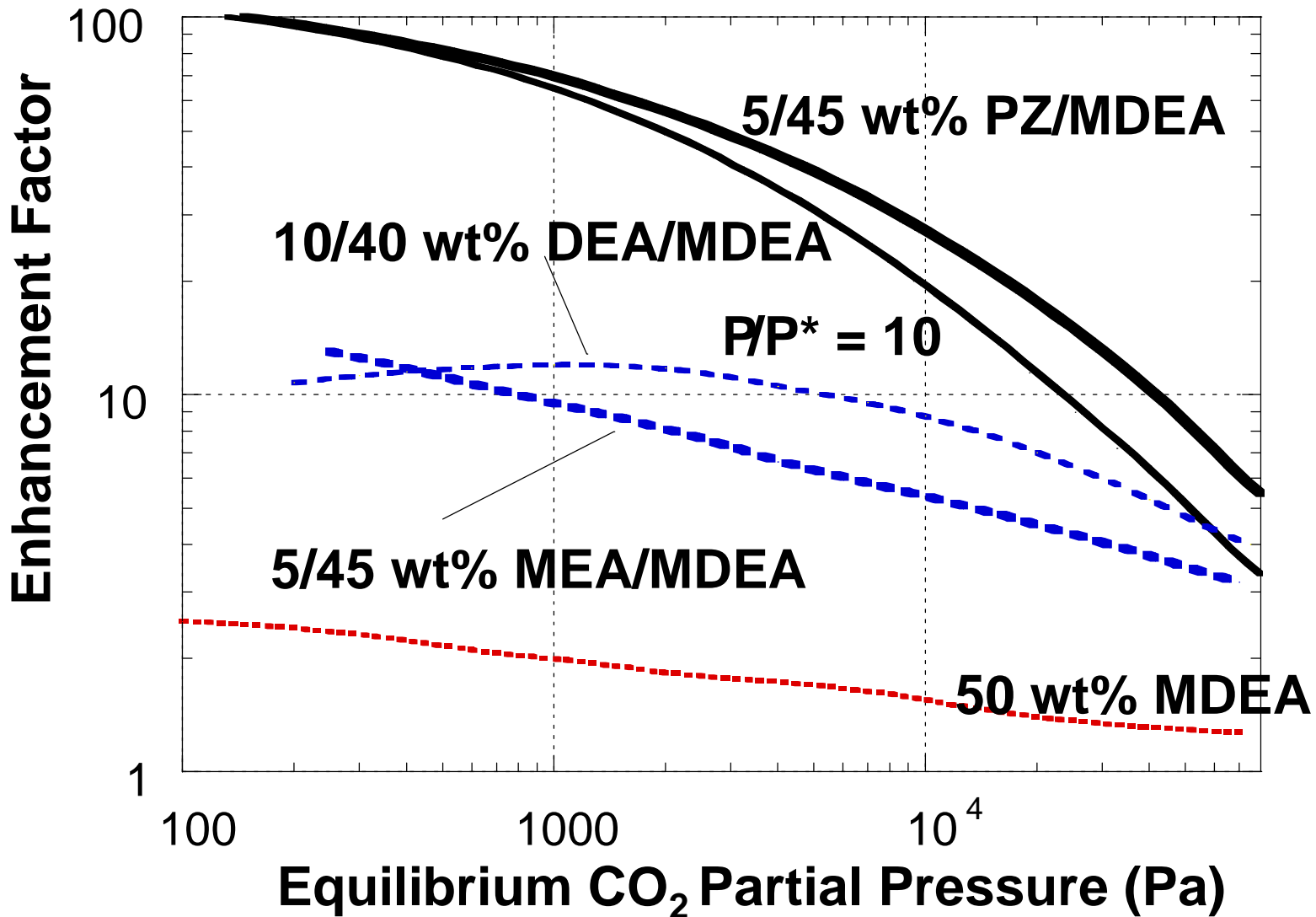
0.6 M PZ / 2.2 M K_2CO_3



0.6 M PZ / 4 M MDEA

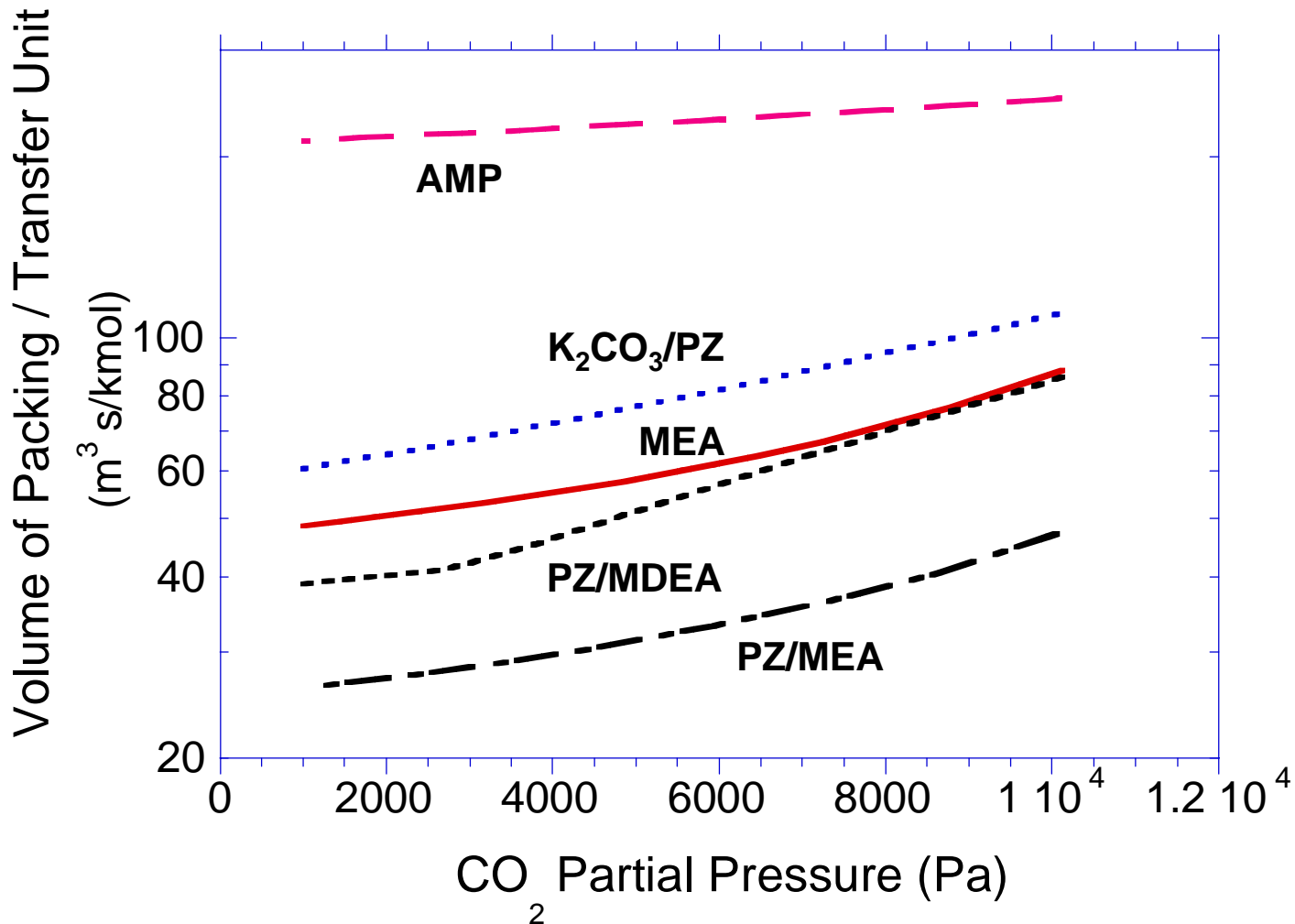


Comparison of Promoters



Model Prediction of Performance

$T = 60^{\circ}\text{C}$, $P^{\text{TOT}} = 1 \text{ atm}$, 10% CO_2 in, 1% CO_2 out



Mass Transfer Design

$$\frac{1}{K_g a} = \frac{1}{k_g a} + \frac{1}{E H_{\text{CO}_2} k_1^0}$$

$$\text{Flux} = E k_1^0 = \sqrt{k_2 [\text{Amine}]_i D_{\text{CO}_2}} \frac{[P_{\text{CO}_2} - P_{\text{CO}_2}^*]}{H_{\text{CO}_2}}$$

- E must be 20 – 100
- k_2 should be 1 – 10 ($\text{m}^3/\text{gmol}\cdot\text{s}$)

Optimized G/L Contactors

- Abs rate limited by fast rxn at Liq surface
 - needs G/L contact area, a
 - k_1a and k_ga are usually insignificant
- To minimize ΔP use dumped packing
 - large openings & high area (Mitsubishi)
 - low gas velocity (same volume of packing)
- Stripper may be limited by k_1a (instant. rxn)
 - packing with low gas velocity
 - trays

Degradation and Makeup

Oxidation (MEA \gg NH_3)

Rxn with O_2 catalyzed by Fe^{++} , Cu^{++} , NO_x

Carbamate Dimerization

High T (stripper), esp with MEA

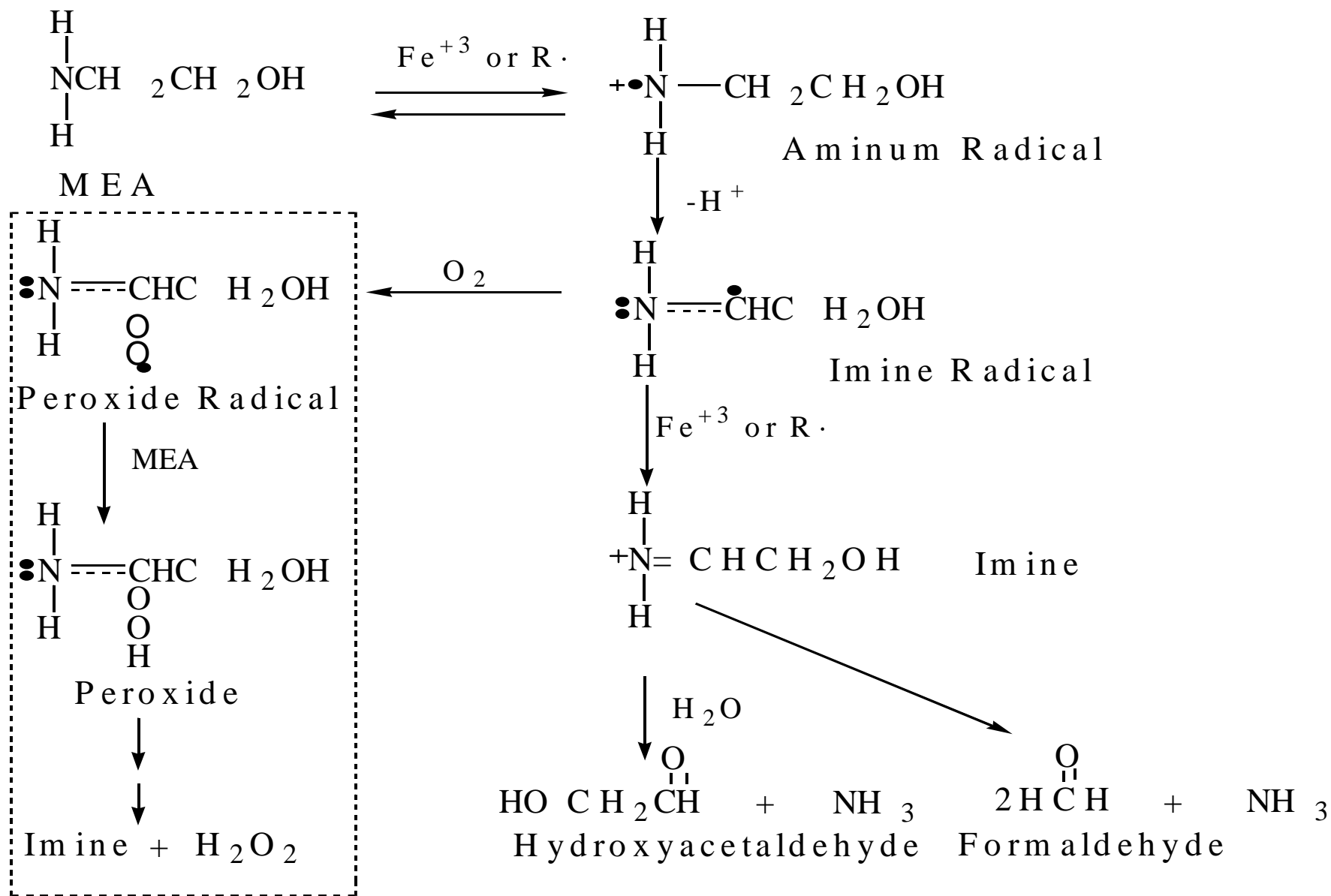
Nitrosamines (secondary amine + NO_x)

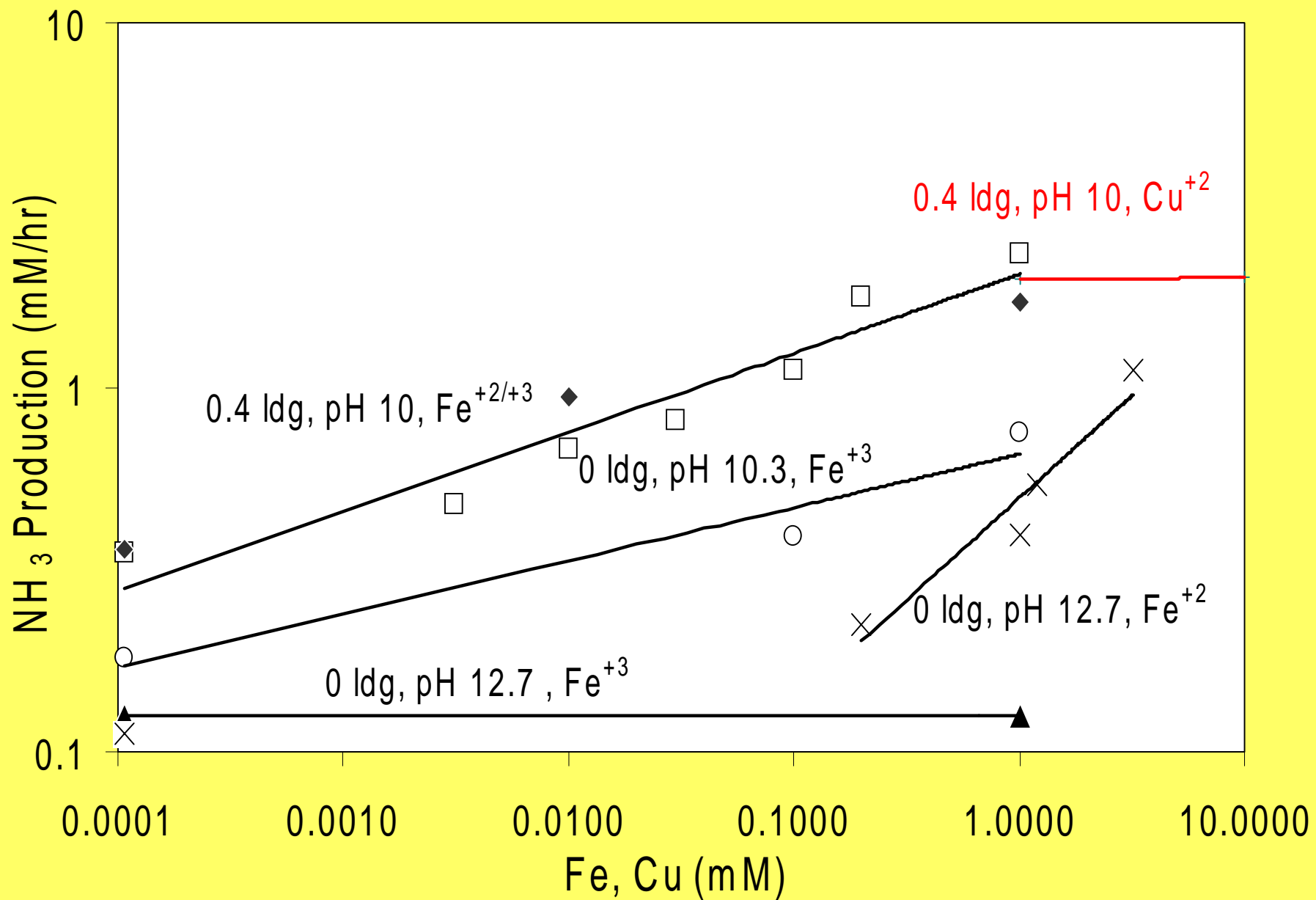
Heat stable salts

Sulfate/Sulfite from SO_2 absorption

Chloride from HCl absorption

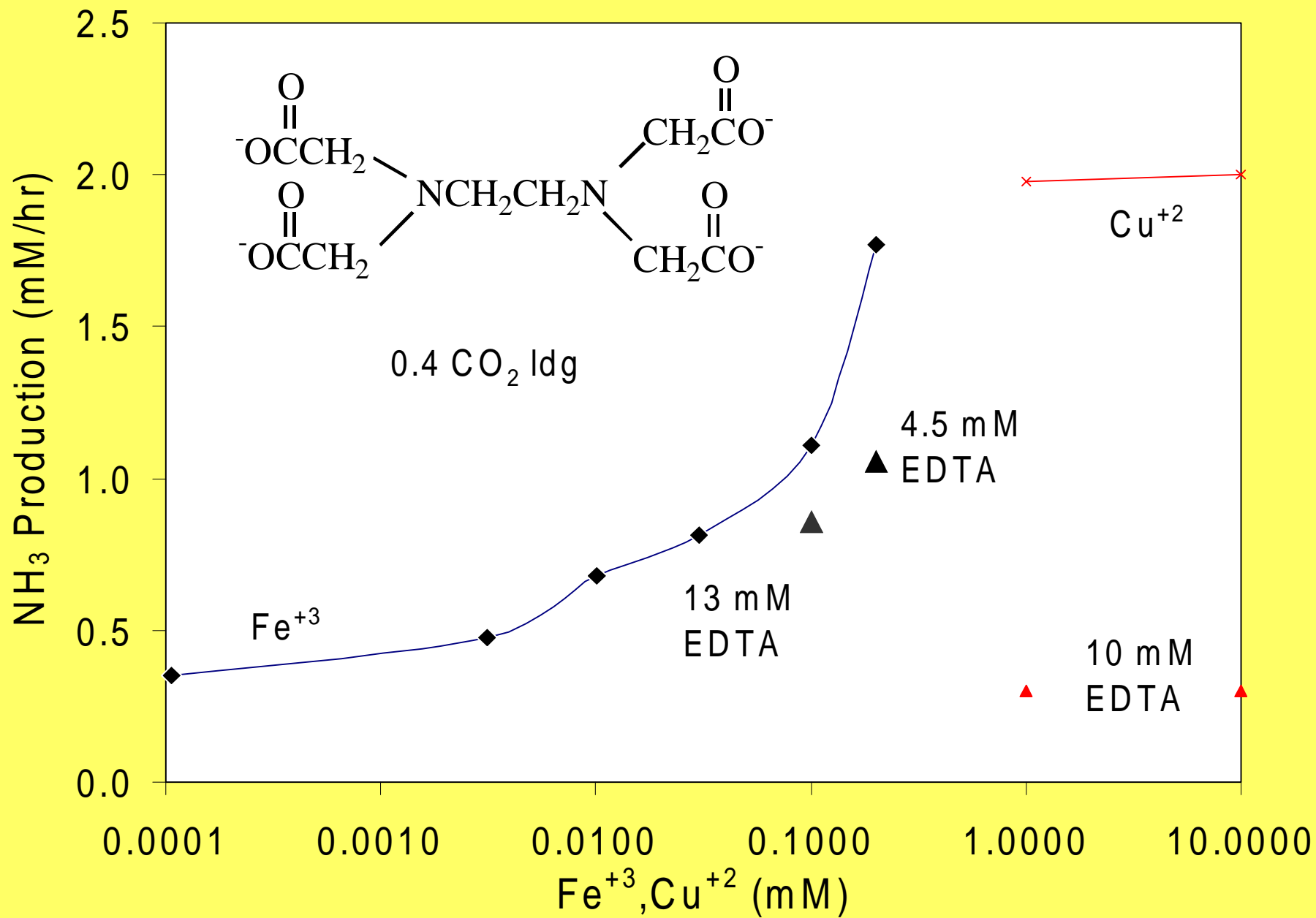
Single Electron Oxidation Mechanism





Avoiding Oxidation

- Minimize contact time with dissolved O_2
- Minimize dissolved metals, NO_x
- Add chelators or free radical scavengers
- Use solvents that oxidize slower
 - hindered amines with tert or quat C's
 - tertiary amines(?)
 - K_2CO_3



Avoiding MEA Dimerization

MEA-carb + H⁺ = MEA carb ester

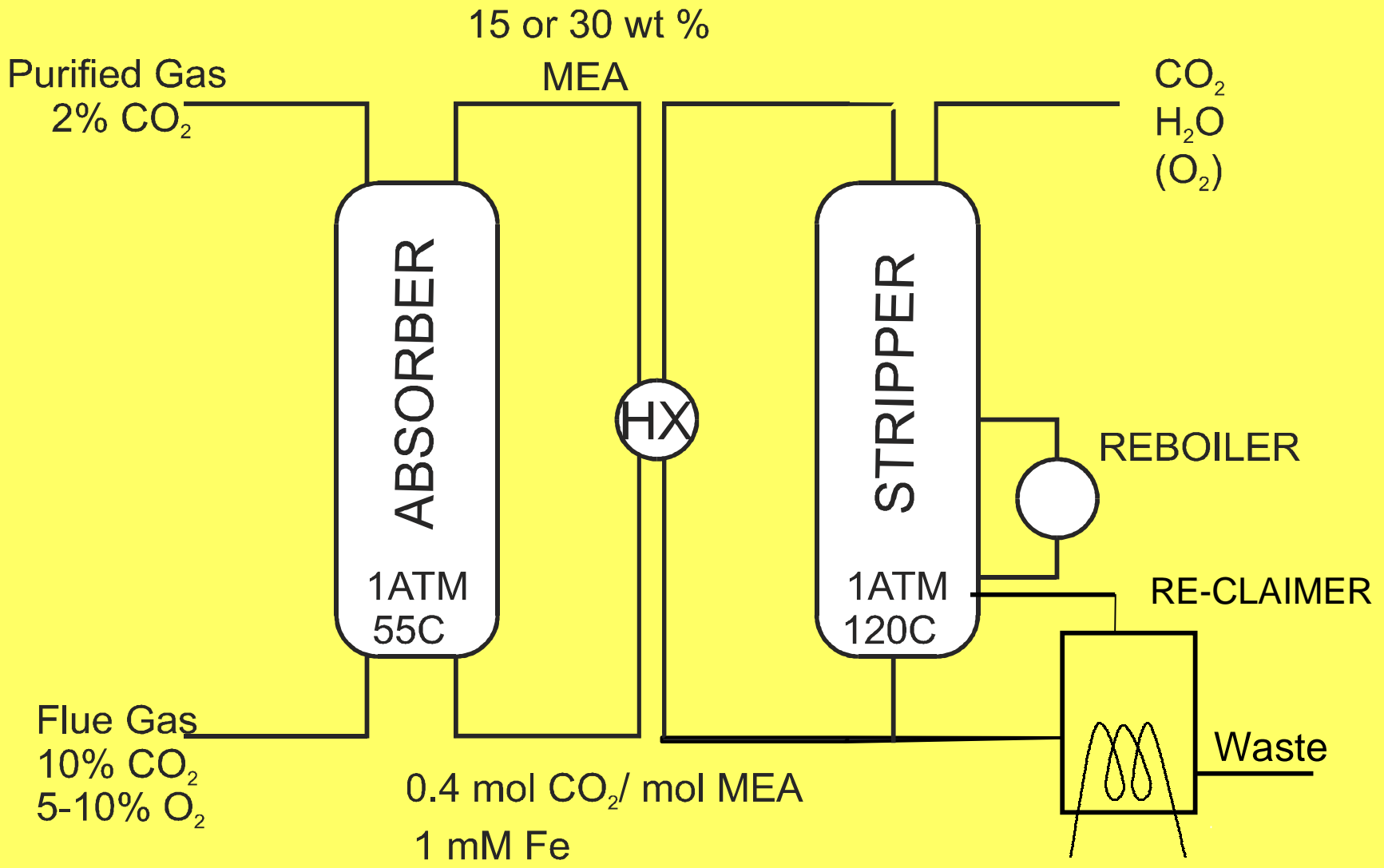
MEA + MEA-carbamate ester = dimer

Occurs at higher T (stripper only)

- Reduce MEA concentration and CO₂ ldg
 - Constrains energy use
- Reduce stripper T/P and residence time
- Avoid alkanolamine (PZ, K₂CO₃)
- Use hindered(?) or tertiary amine

Dealing with Heat Stable Salts

- Prescrub to remove SO_2 & HCl
 - Expensive and incomplete removal
- $\text{Ca}(\text{OH})_2 + (\text{MEA}\text{H})_2\text{SO}_4 = \text{CaSO}_4(\text{s}) + \text{MEA}$
- Reclaim amine, purge $\text{SO}_4^{=}$, Cl^- , etc.
 - Evaporate volatile amine (MEA, PZ)
 - Others by ion exchange, carbon adsorption
- Precipitate K_2SO_4 , KCl



Materials

- CH₄ & H₂ Systems use Carbon Steel
 - High pressure & capital costs dominate
 - Corrosion by loaded solns and degradation products
- Corrosion inhibitors are effective with CS
 - for < 30% MEA, <0.45 ldg, small salt conc.
 - Metals (Cu⁺², V⁺⁵) give oxidized Fe₂O₃ film
 - But catalyze degradation
- Corrosion resistant materials of construction
 - FRP, SS, lined CS: as in FGD systems
 - Cost effective with larger systems at 1 atm
 - Relaxes constraints on solvent conc and CO₂ loading

Enhanced MEA

- Enhanced Mass Transfer
 - Add PZ (reclaimable with MEA)
 - Use advanced packing or reduced gas velocity
 - Get reduced ΔP , less packing
 - Closer approach, reduced heat rate
- Energy Integration, low P steam from turbine
 - Reduced Stripper P to facilitate energy integration
 - also reduces degradation and corrosion
- Materials – FRP or stainless
 - Greater MEA conc & CO₂ loading = reduced energy
- Simultaneous SO₂ removal - Add lime to Crystallize CaSO₄

Promoted Potassium Carbonate

- K_2CO_3 + Piperazine (or other promoter)
 - $\Delta\text{H} = 5\text{-}10$ kcal/gmol
 - Low cost solvent
 - Minimal degradation
- Isothermal Solvent loop – no cross exchanger
 - High solvent rate OK, no sensible heat requirement
- Vacuum Stripper with energy integration
 - Vapor recompression by electricity or steam turbine
 - Use of Waste Heat
 - Net energy = 50% of MEA

Promoted Hindered or Tertiary Amine (Mitsubishi Process)

- Hindered amine (probably promoted)
 - 20% less Q
 - greater capacity, $\Delta H_{\text{CO}_2}=18$ kcal/mol
 - Greatly reduced degradation & corrosivity
 - Greater amine cost
- Enhanced Packing – reduced ΔP
- Auxiliary boiler to provide Q and W
 - Reduces energy use another factor of 2-3
 - Avoids derating power plant

Lesson from FGD

Put \$\$ on the Process that Works

- 1938: Battersea Lime scrubbing
- 1970: Test of Limestone Slurry Scrubbing
- 1974-80: Shawnee test facility
- 1984-94: High sulfur test facility
- 1970 –99: Many \$\$\$\$ to develop and demo
“Advanced Processes”
- 2000: > 150 limestone slurry scrubbing
- 2000: < 15 Other , < 5 “Advanced”

Support Aqueous (MEA+) Absorption/Stripping