Process performance and the absorbent

- The rate of mass transfer, diffusion and chemical reaction kinetics and their impact on column size and cost
- Chemical thermodynamics (CO_2-amine equilibria and absorption enthalpy) and its impact on the process energy requirements
- Operational issues

Effect of mass transfer on column size and cost

- Mass transfer of CO_2 into an absorbent defines the size, and thus the cost, of an absorption column
  - The slower the mass transfer the larger the surface area of contact required between gas and liquid to absorb the same amount of CO_2
  - The surface area (A) is a function of the packing (structured vs. random), the liquid flow rate and the liquid physical properties
  - The flux (N_{CO2}) is a function of the driving force and of the absorbent and its physical and chemical properties

$$\frac{dn_{CO2}}{dt} = N_{CO2} A$$

rate, mol.s^{-1}

flux, mol.$m^{-2}s^{-1}$

area, m^2

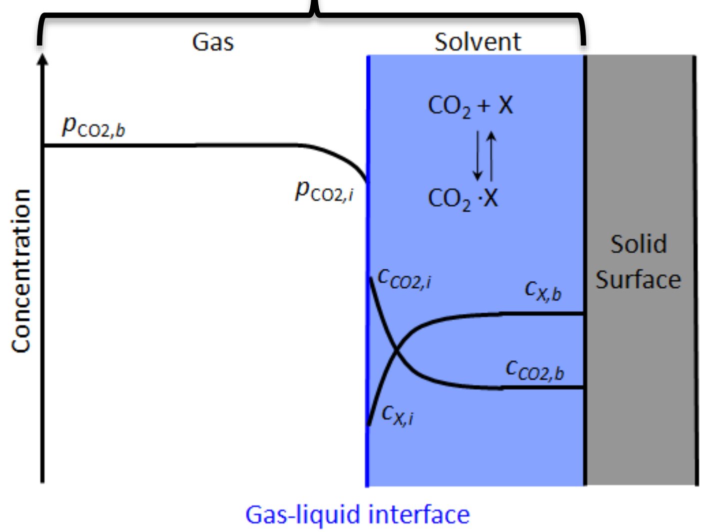
Effect of mass transfer on column size and cost

Driving Force

$$N_{CO2} = \boxed{K_g}\left(p_{CO2,b} - k_{h,CO2}c_{CO2,b}\right)$$

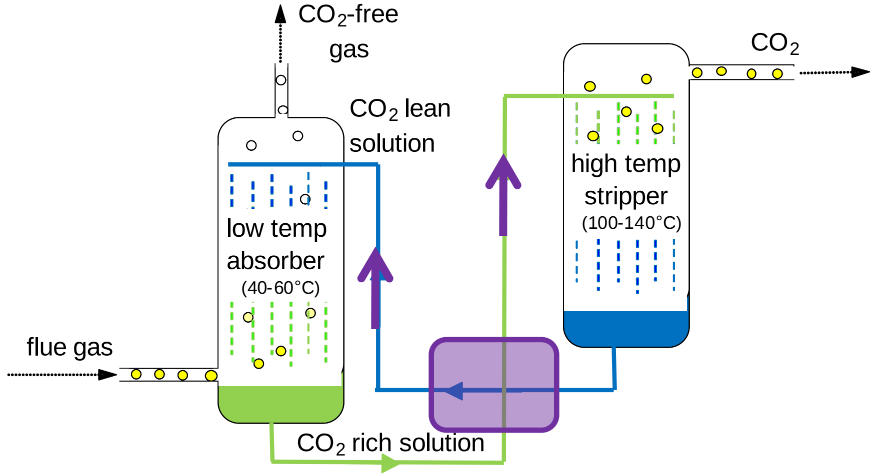
A function of diffusion coefficients and chemical reaction

Driving Force



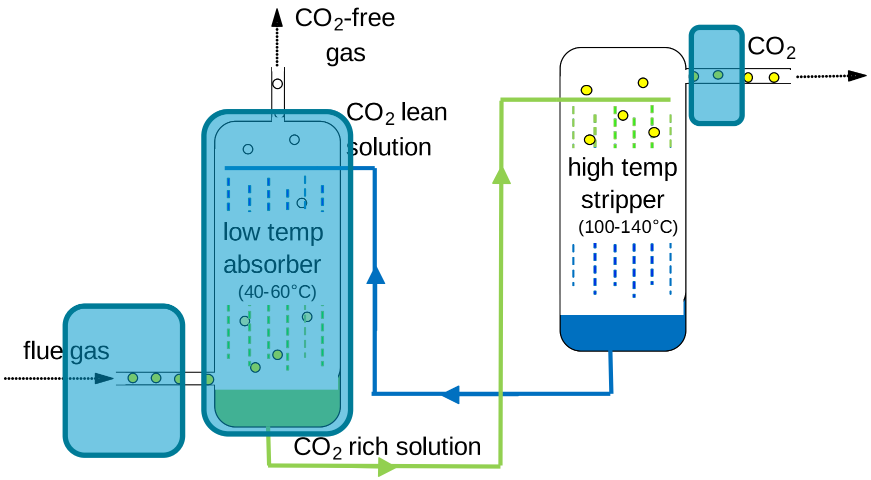
Process energy consumption - pumps

- The overall energy requirement for the production of a unit of pure CO_2 has several components:
  - Energy to pump the absorber solution between absorber and stripper.



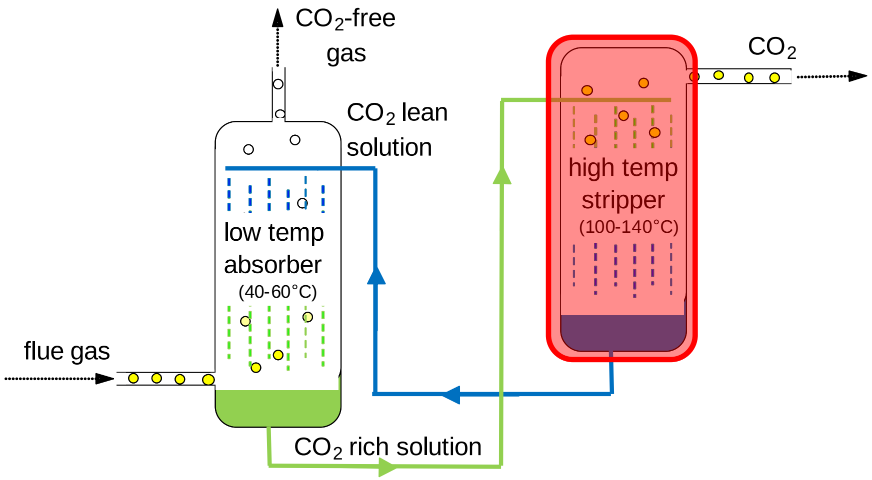
Process energy consumption - cooling

- The cooling of the flue gas to reduce its temperature to the level required in the absorber. (this is easy in Canada in winter but difficult in Australia in summer)
- Additional cooling of the absorber column due to reaction enthalpies
- Cooling of the CO_2 stream to avoid water and amine carry-over



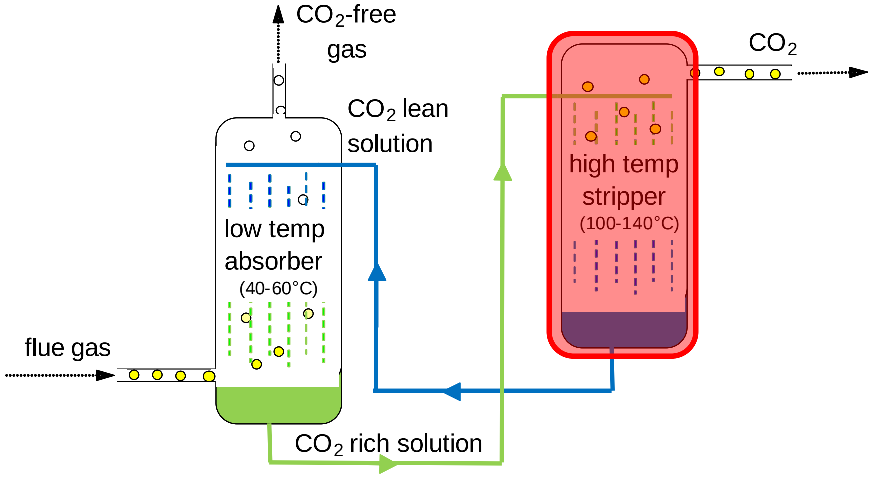
Process energy consumption - heating

- The largest energy component is required for the heating of the stripper column. There are several components:
  - Heat capacity of the solvent
  - Reaction enthalpies
  - Enthalpy of vaporisation



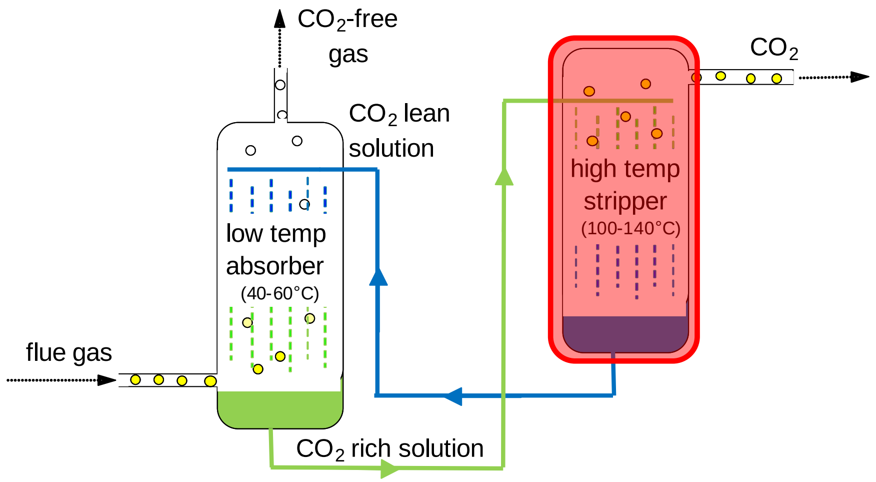
Process energy consumption - heating

- Heat capacity of the solvent:
  - Defines how much energy much be put in/removed to raise/lower the solvent temperature.
  - A high cyclic capacity reduces the amount of solvent that needs to be heated and cooled.



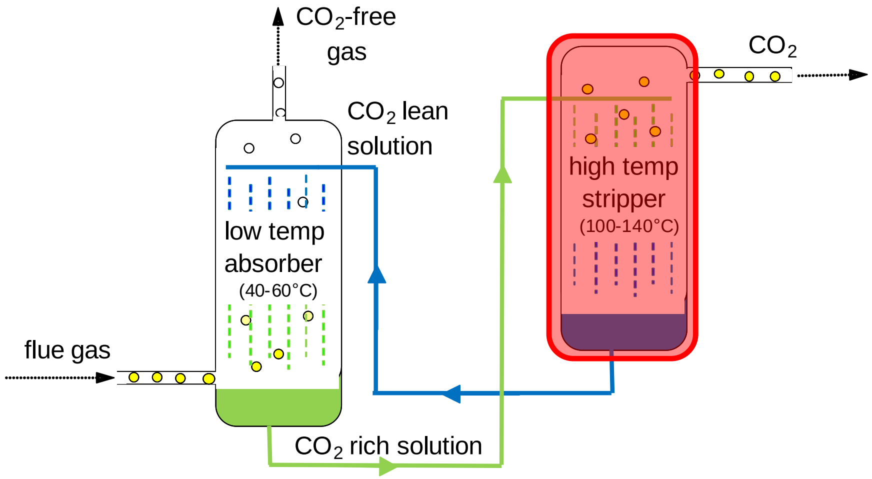
Process energy consumption - heating

- Reaction enthalpies:
  - The enthalpy of absorption (which is made up of contributions from many reactions) defines the energy that much be input to reverse absorption.
  - A larger enthalpy means more energy is required, but it also results in a larger swing in the equilibrium position of the reactions increasing cyclic capacity.



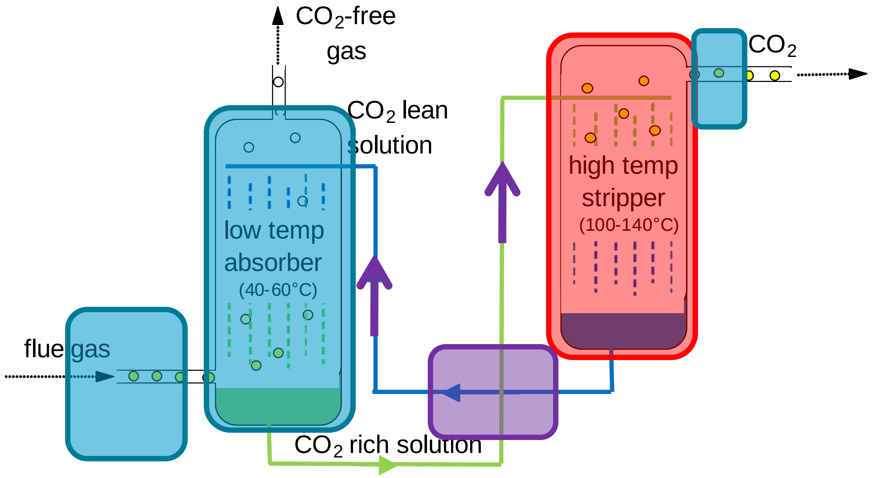
Process energy consumption - heating

- Water vaporisation:
  - Making water vapour requires energy.
  - Water vapour acts as a stripping gas, diluting CO_2 and carrying it from the stripper.
  - Water vapour also acts as an energy vector – as CO_2 is desorbed the solvent cools (endothermic) and water condensation heats the solvent (exothermic) to maintain its temperature.



Process energy consumption

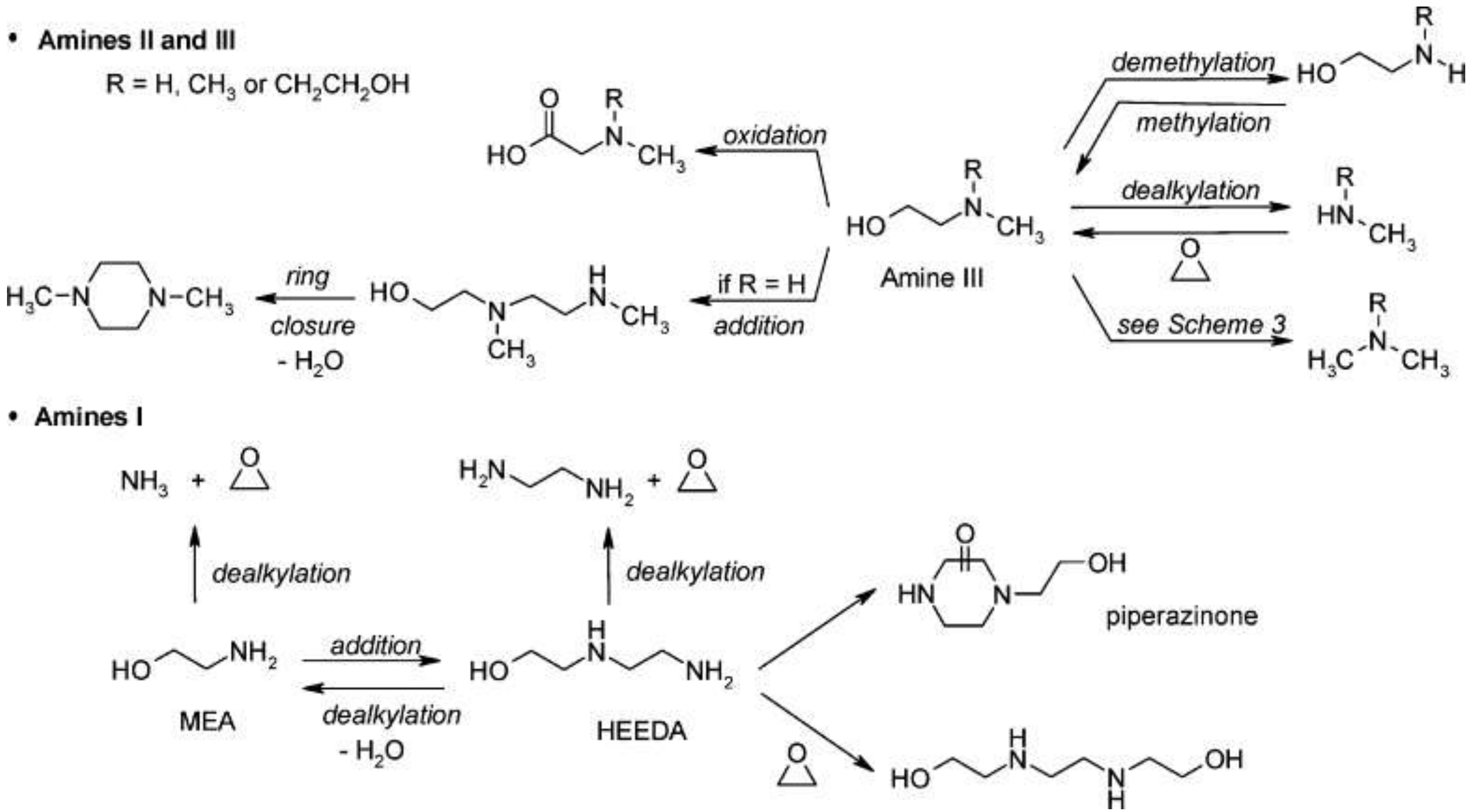
- The complexity of the PCC process requires very careful investigation of many parameters, amongst them the reaction enthalpies. They are important but not well investigated for many amines.



Operational issues: oxidative degradation

- Flue gas contains around 5-15% O_2
- This can lead to oxidation of the absorbent
- Oxidation inhibitors are typically used to prevent this (e.g. vanadium, diethylene triamine pentaacetic acid)
- Oxidation is catalysed by dissolved metals and involves a complex mechanism that varies with amine and operating conditions
- A common product of oxidative degradation for all amines is ammonia

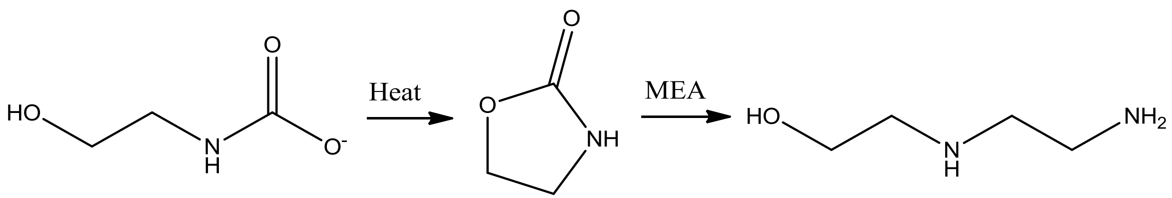
Operational issues: oxidative degradation



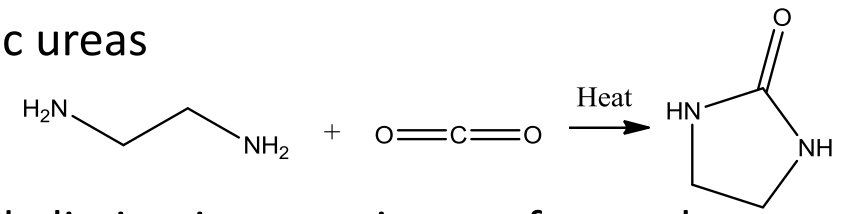
H. Lepaumier, D. Picq, P.-L. Carrette; *Ind. Eng. Chem. Res.* **2009,** 48, 9068-9075.

Operational issues: thermal degradation

- Thermal degradation limits the temperature that can be used for desorption
- Tertiary and cyclic amines are typically most resistant to thermal degradation
- The thermal degradation mechanism varies depending upon amine structure:
  - Primary and secondary alkanolamines undergo cyclic polymerisation of the carbamate



  - Primary and secondary diamines form cyclic ureas



  - Tertiary amines undergo arm-switching and elimination reactions to form other secondary and tertiary amines
  - Cyclic amines undergo ring opening

Operational issues: corrosion

- Corrosion in PCC plants is caused either by wet acid gas (that is a saturated CO_2 containing gas stream) or amine solution
- Wet acid gas corrosion typically occurs near the flue gas inlet and at the top of the desorber
- Amine solutions are only corrosive when they contain some CO_2 and at elevated temperature
- Amine corrosion occurs on the hot side of the lean-rich absorbent heat exchanger, the bottom of the desorber and the reboiler

Operational issues: corrosion

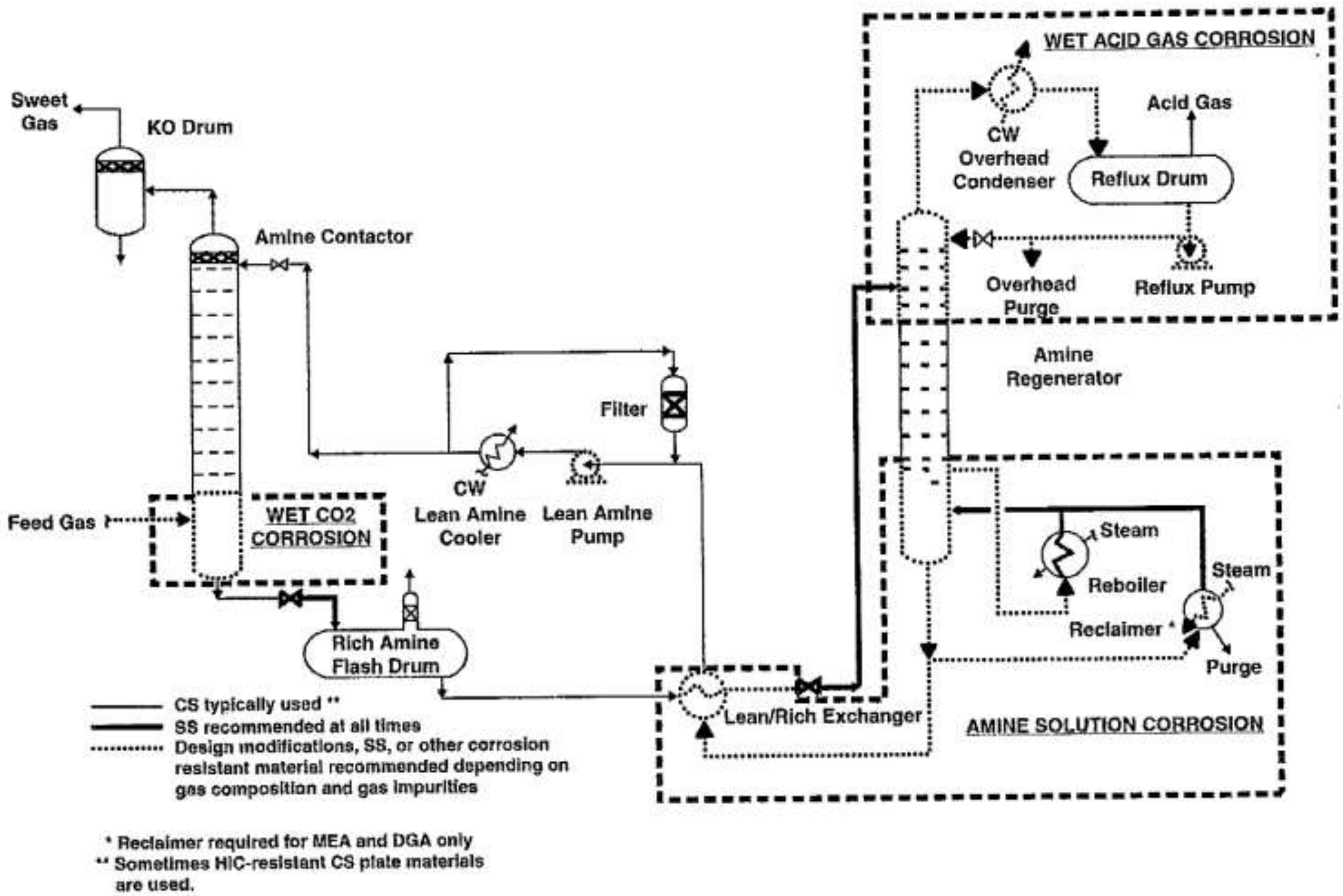


Figure 3-1 from A. L. Kohl and R. B. Nielson, *Gas Purification (5th Ed.)*, Gulf Professional Publishing, Houston (1997).

Acknowledgements

The authors wish to acknowledge financial assistance provided through 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.