Rate-based modelling and simulation of CO_2 absorption and desorption columns using piperazine promoted potassium carbonate

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Introduction

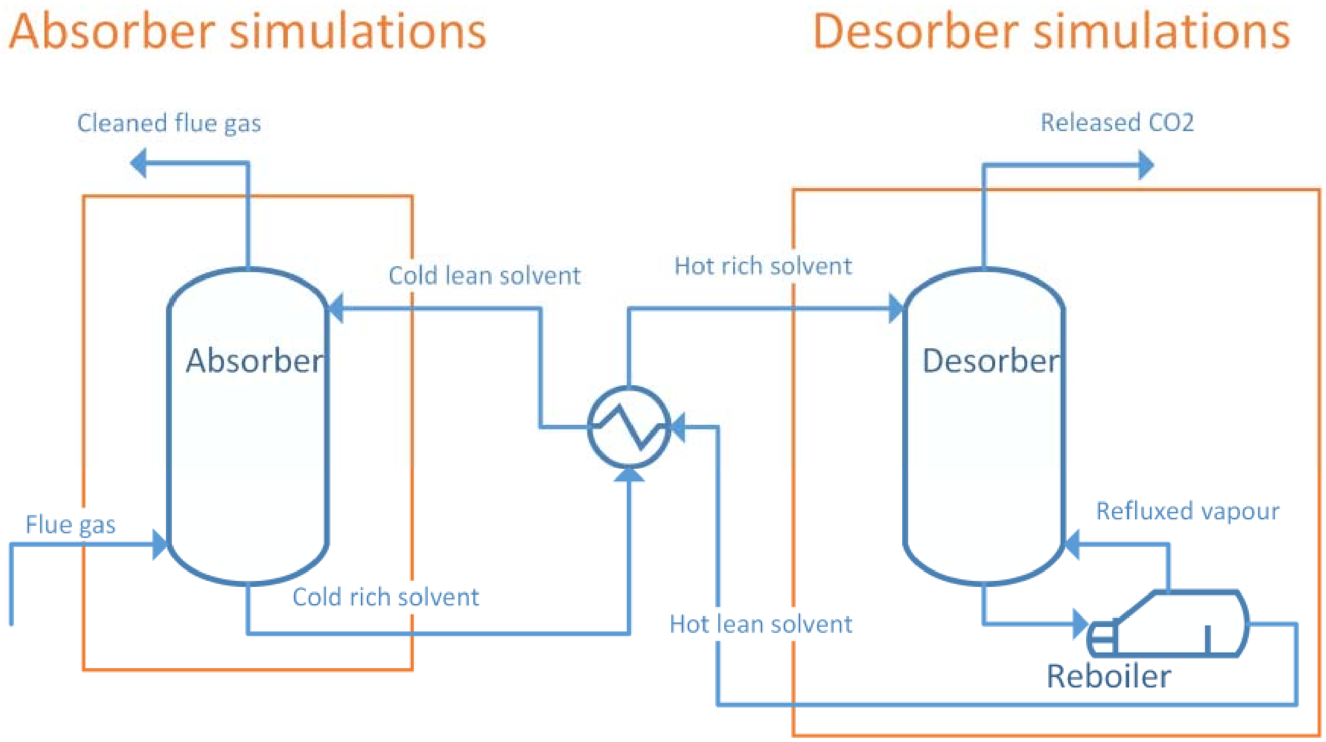
- Challenging to find solvent systems with high capacities, fast absorption rates and low energy requirements
- Aqueous solutions of potassium carbonate (K_2CO_3) promoted by piperazine (PZ) is a promising solvent
  - Pilot experiments show better absorption rates than 7m MEA
- Risk of precipitation at high solute concentrations
  - Potentially causing operational challenges
  - Causing modelling challenges as well

Purpose

- Develop a rate-based model for CO_2 absorption and desorption of columns using aqueous mixtures of PZ and K_2CO_3
- Analyse the effect of different solvent compositions on the column performance variables
  - Absorber: L/G ratio, column height, rich loading
  - Desorber: reboiler energy consumption, lean loading

Process description

- Absorption and desorption processes are simulated independently
  - Heat integration not analysed



Modelling

- The DTU in-house CAPCO2 rate-based model is used for simulations
  - Equilibrium and thermal properties calculated by the Extended UNIQUAQ thermodynamic model
  - Allows solid precipitation to be included in calculation of thermodynamic properties
- General Method (GM) enhancement factor model for parallel reactions*:

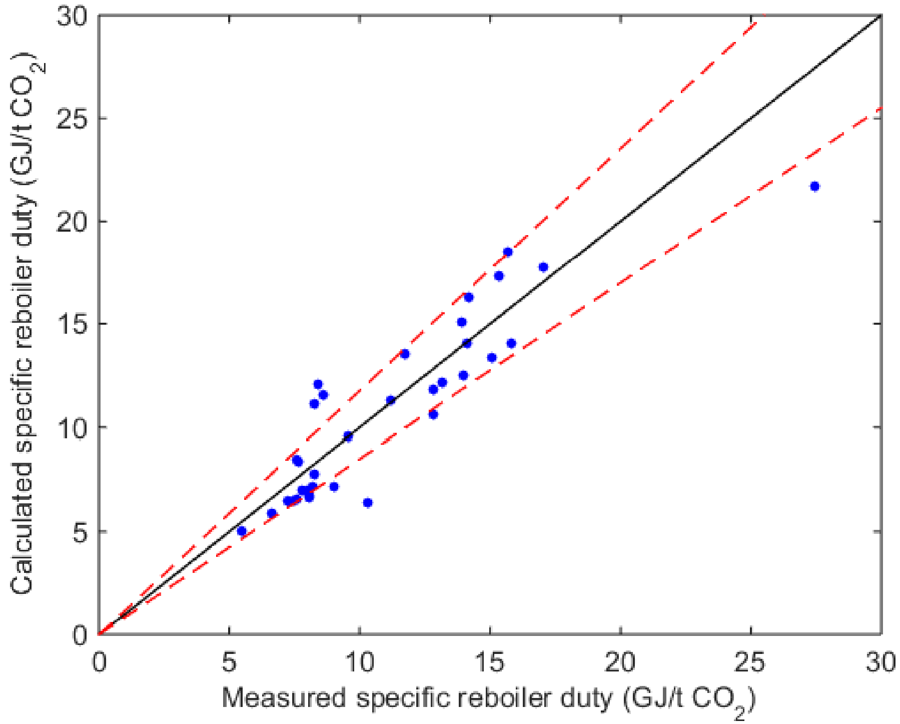
$$CO_2 + PZ + H_2O \rightarrow PZCOO^- + H_3O^+$$
$$CO_2 + PZCOO^- + H_2O \rightarrow PZ(COO^-)_2 + H_3O^-$$
$$CO_2 + OH^- \rightarrow HCO_3^-$$

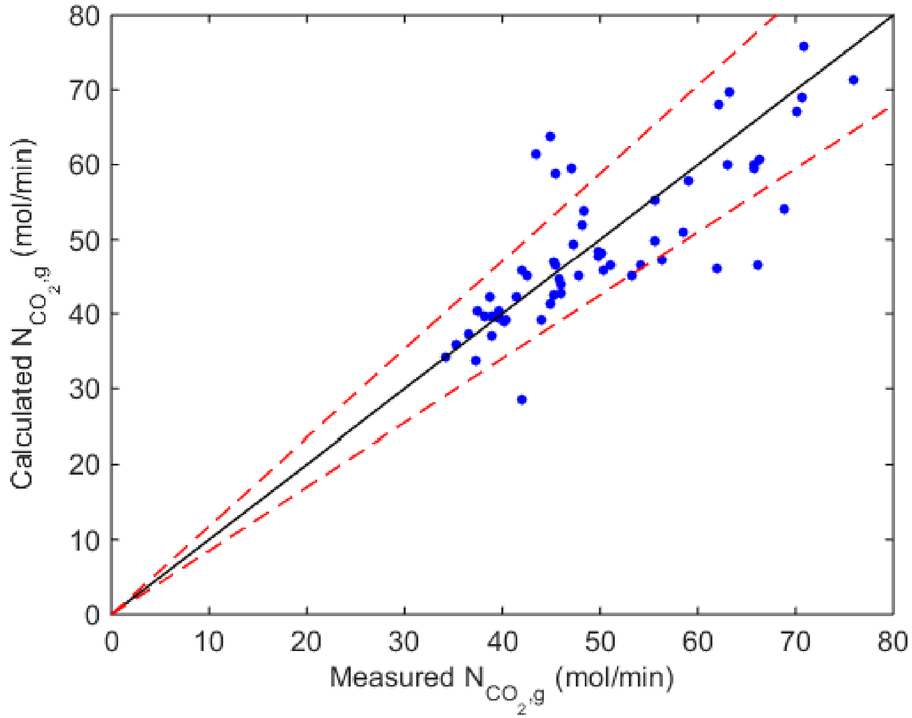
*Gaspar, J., & Fosbøl, P. L.A general enhancement factor model for absorption and desorption systems: A CO2 capture case-study. *Chemical Engineering Science (accepted), 2015*.

Physical properties

- Density and viscosity are correlated and validated against experimental data
- Surface tension, diffusivities and kinetic rate constants are calculated from correlations in literature
- Mixture properties are validated against data or estimated using linear mixing-rules

Rate-based model validation





Red dotted lines showing +/- 15%

	Spec. reboiler duty	CO2 flux
Average deviation	14.3 %	13.3 %

Process specifications

Variable	Value	Unit
Desorber rich solvent temp.	100	° C
Desorber rich solvent rate	12.90	kmol/s
Desorber diameter	7	m
Desorber height	10	m
Desorber pressure	162.0	kPa
Absorber lean temp.	40	° C
Absorber pressure	101.3	kPa
Flue gas rate	3.228	kmol/s
Flue gas temp.	40	° C
Flue gas CO2 mole fr.	0.1325	-
Flue gas H2O mole fr.	0.1211	-
Column packing	Mellapak 250Y	-

- Solvent capacity:
  - K_2CO_3 can absorb 1 mol CO_2 per mol
  - PZ can absorb 2 mol of CO_2 per mol

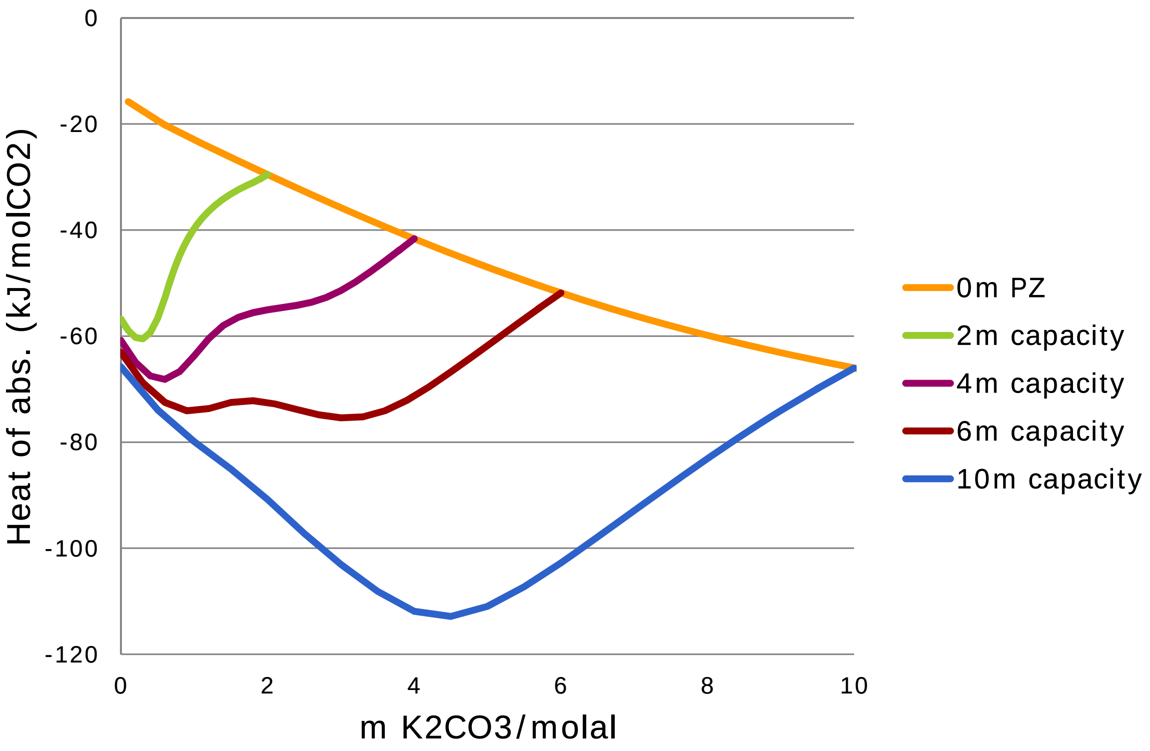
    Total capacity: $mol\ K_2CO_3 + 2\ mol\ PZ$
- Loading:
  - Based on free CO_2 – not bound in K_2CO_3

$$\alpha = \frac{mol\ CO_2^{free}}{capacity} = \frac{mol\ CO_2^{free}}{mol\ K_2CO_3 + 2\ mol\ PZ}$$

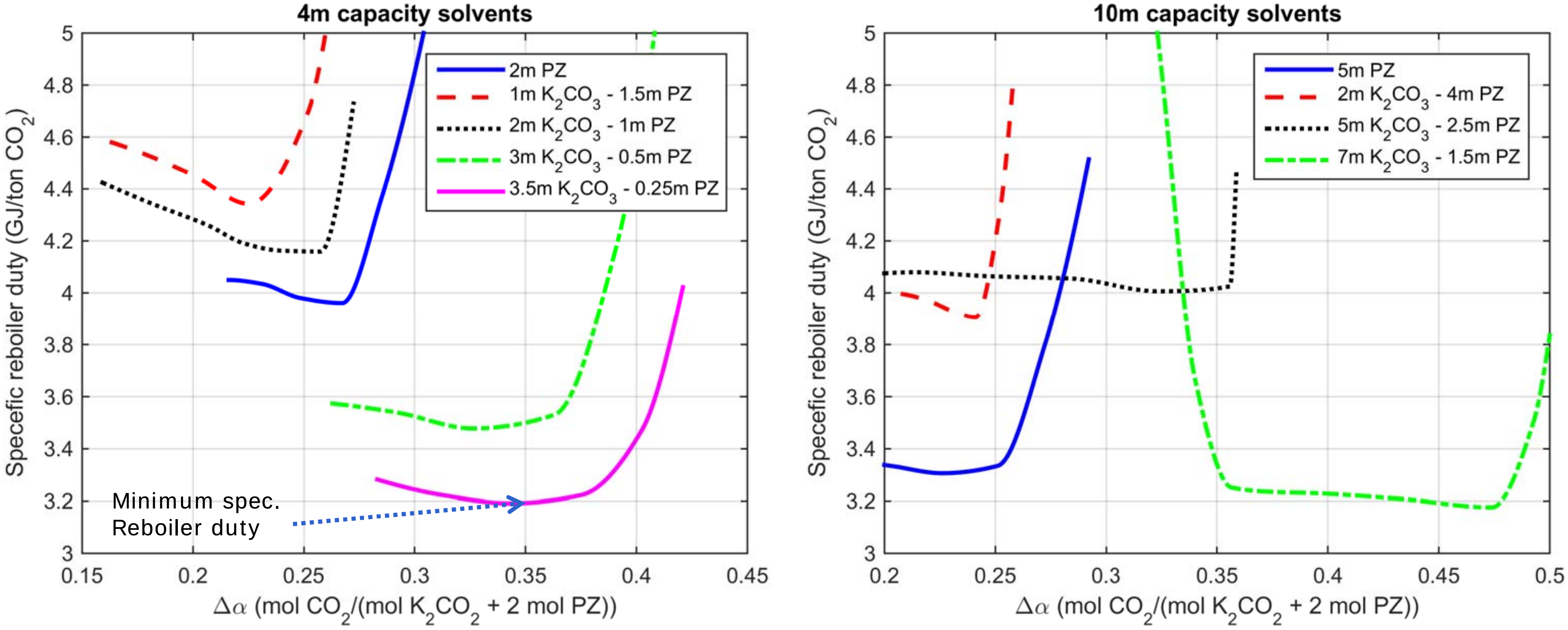
- Desorber inlet rich loading is assumed to be the equilibrium loading at 50 ºC

Heat of reaction between CO_2 and solvent

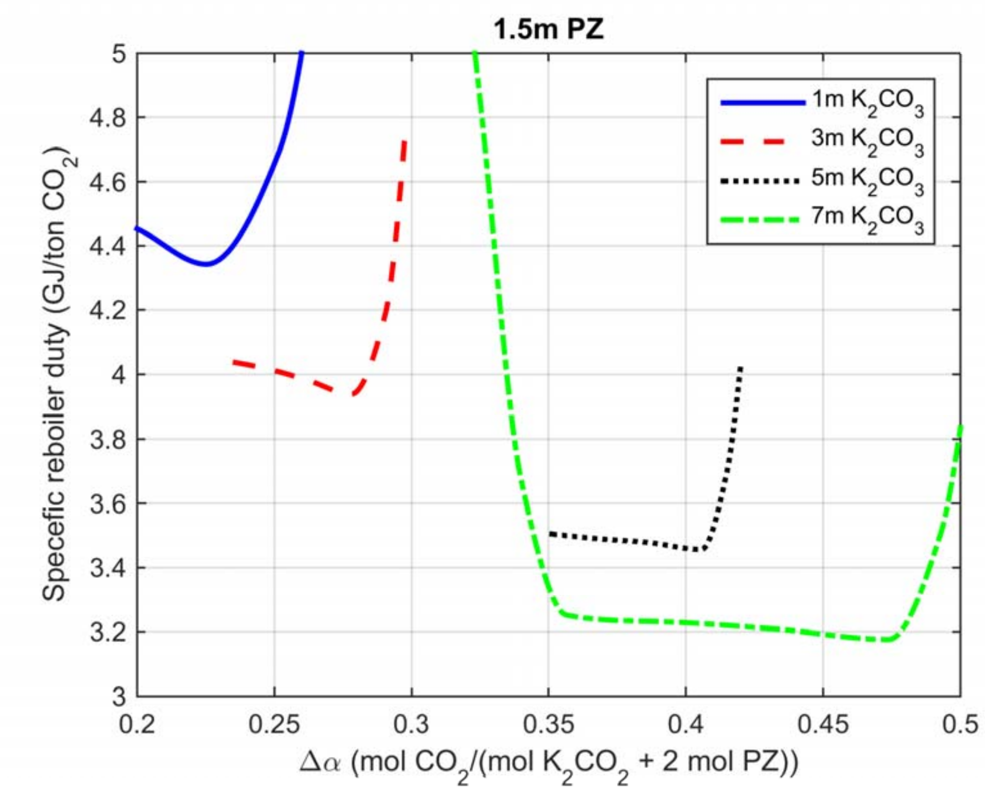
- Basic thermodynamic analysis of energy requirements
  - 2m capacity means that the solvent has a total capacity of 2 molal (mol/kg H_2O) free CO_2
  - Small or moderate amounts of K_2CO_3 tends to increase heat of absorption compared to pure PZ
  - Large amounts may, however, result in a lower heat of absorption

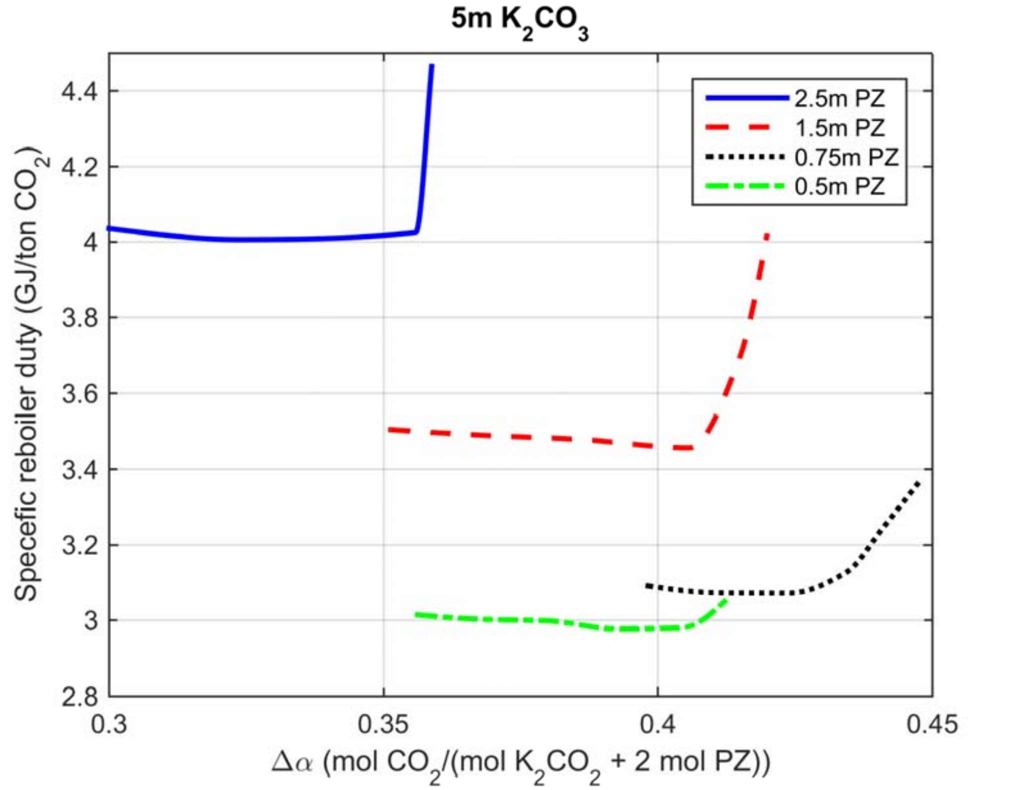


Energy consumption – constant capacity



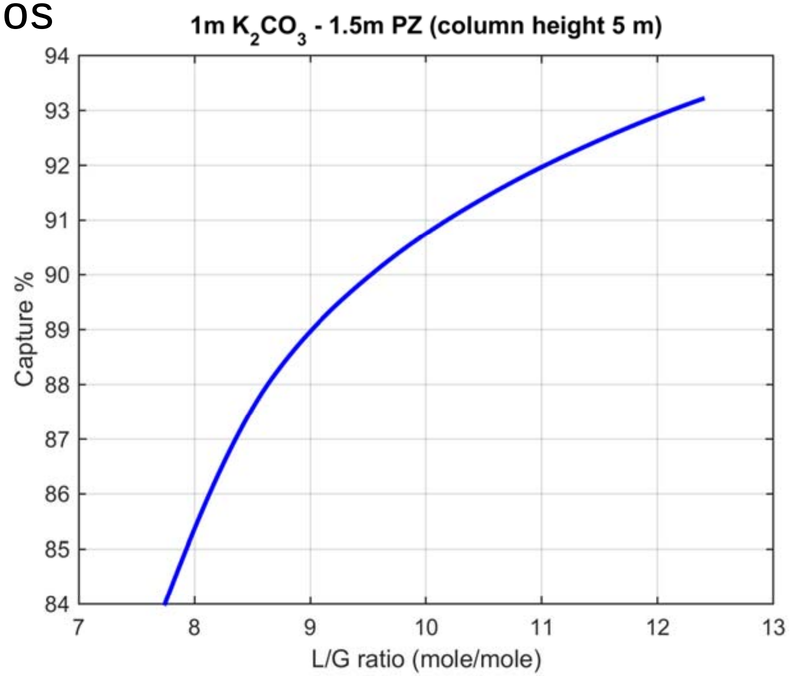
Energy – increasing solvent concentration

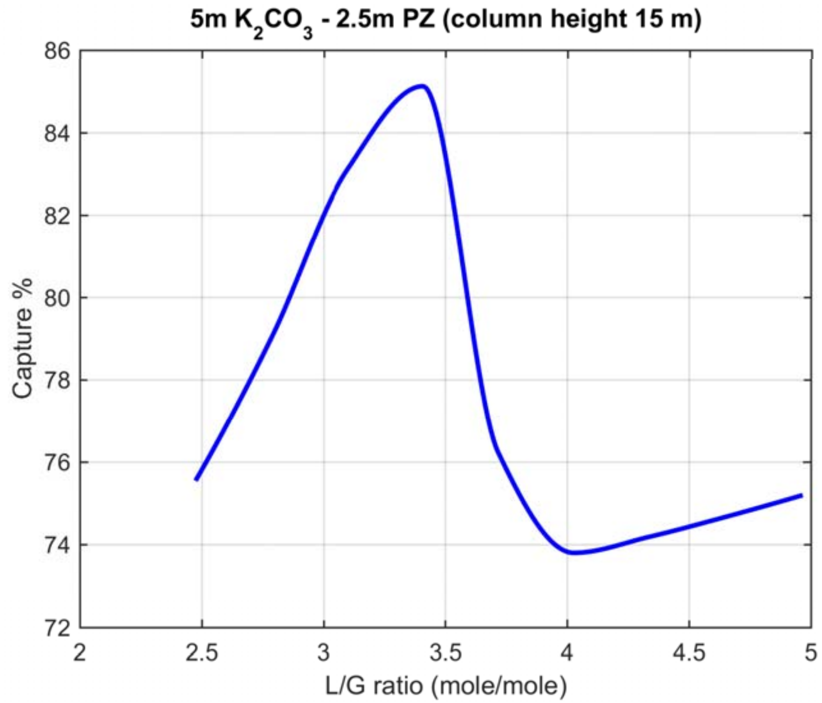




Absorber – capture rate behaviour

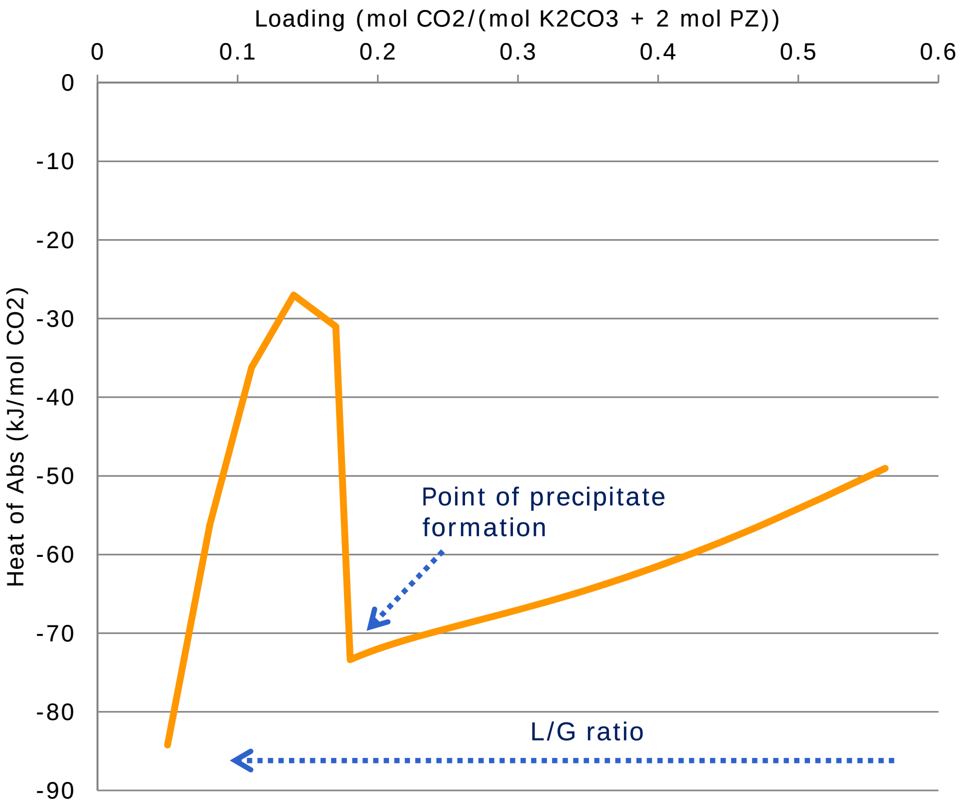
- Drop in capture rate observed for some precipitating high-concentration solvents
  - Fixing the capture rate can result in more than one solution at different L/G ratios





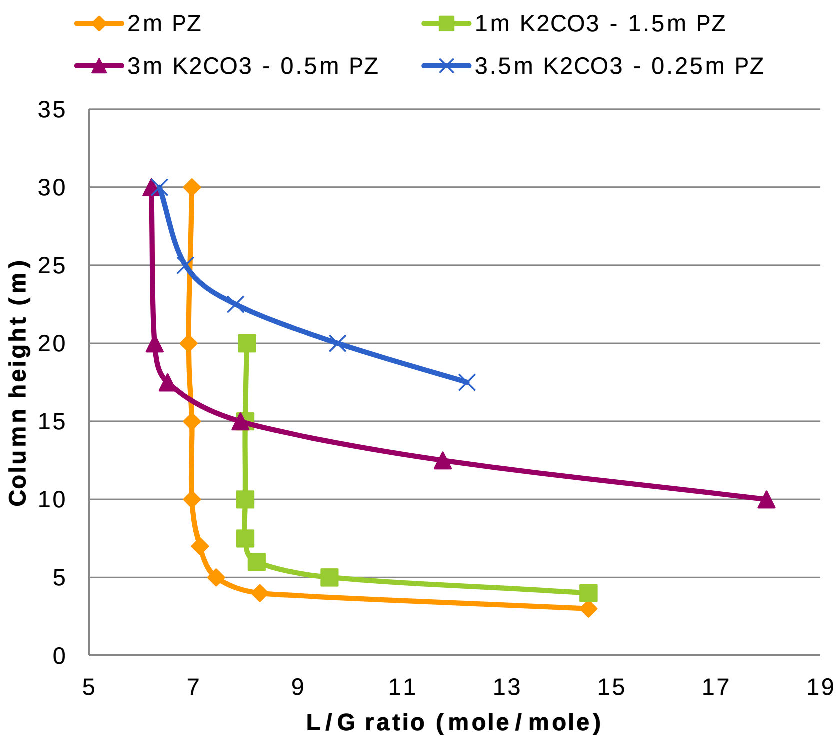
Solid precipitation effect on heat evolvement

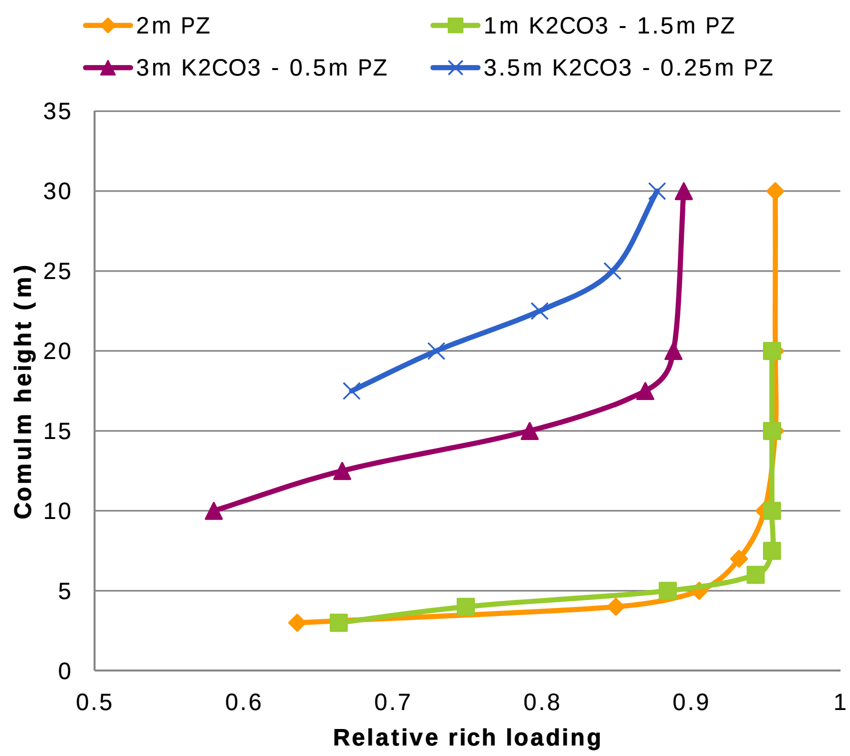
- Drop in capture rate caused by drop in heat of absorption
  - At increasing L/G ratio, the CO_2 loading gets lower and solids (mainly $KHCO_3$) dissapear
  - Causes a sudden jump in heat of absorption
  - Column temperature gets lower and reaction rates are slowing down
  - Expected phenomenon: like heat evolved on ice formation. Now seen for precipitation in CO_2 solvent



Absorber – solvent flow and column height

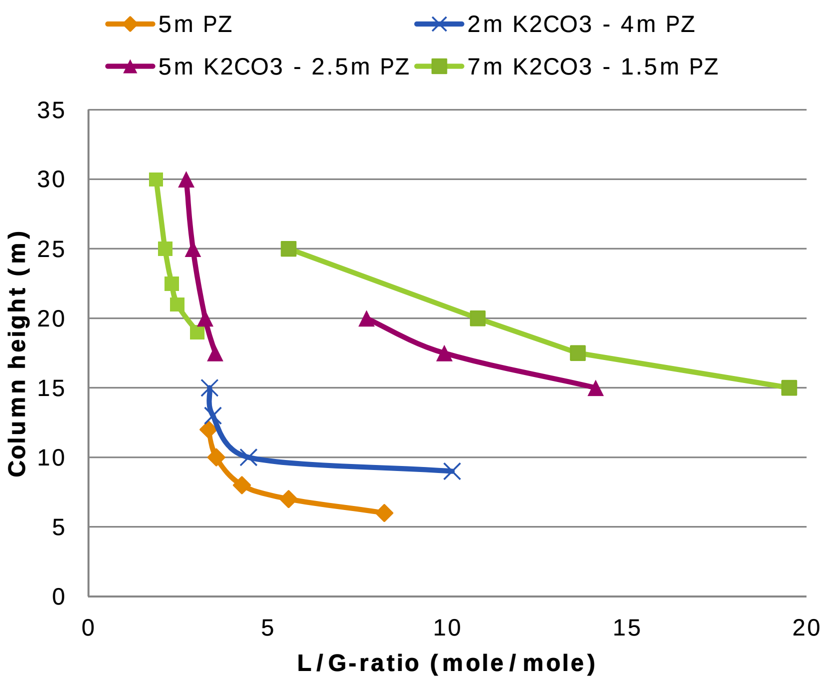
- 4m capacity solvents – capture rate fixed at 90 %

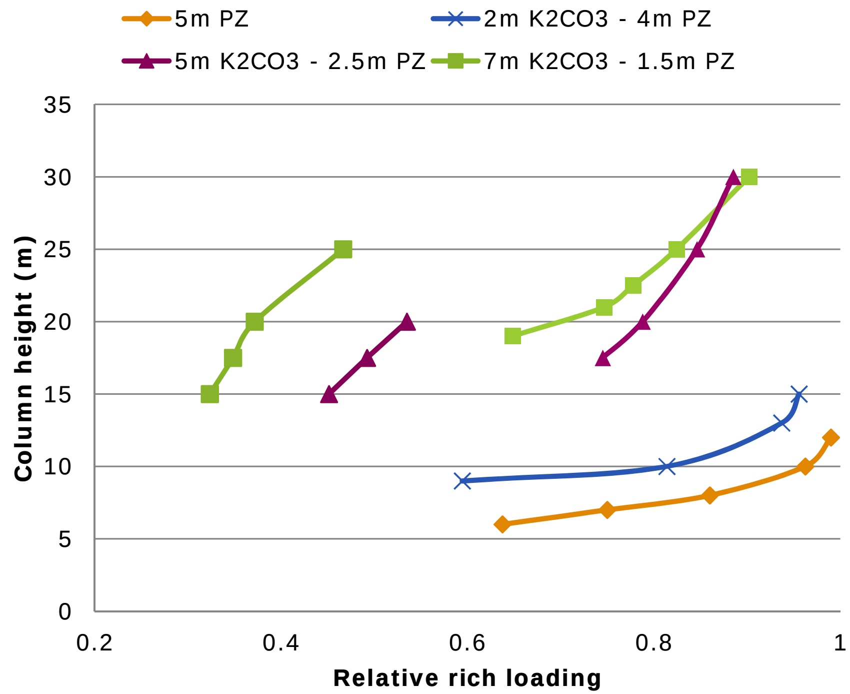




Absorber – solvent flow and column height

- 10m capacity solvents – capture rate fixed at 90 %
  - Due to ”jump” in capture rate, the graphs for 5m and 7m K_2CO_3 solvents are not continuous





Conclusion

- A rate-based column model for CO2 absorption into K2CO2/PZ solvents is succesfully developed and tested
- Desorption analysis
  - The lowest reboiler duties are reached with high K_2CO_3 / low PZ solvents
  - The calculated minimum reboiler duties generally follows the trend of heat of absorption (Figure, slide 9)
  - Addition of K_2CO_3 results in lower reboiler duties
  - Addition of PZ results in higher reboiler duties

Conclusion

- Absorbtion analysis
  - The lowest column height requirements and the highest rich loadings are obtained with low K_2CO_3 / high PZ solvents
  - Jumps in capture rates are caused by precipitation starting to form
- In general, the absorber performance seems to be favoured by a high amount of PZ in the solvent, whereas the desorber performance seems to be favoured by high K_2CO_3 content and a low PZ content
- Further work
  - Dynamic modelling