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Process concepts for combined CO2 and SO2 removal

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Aim:

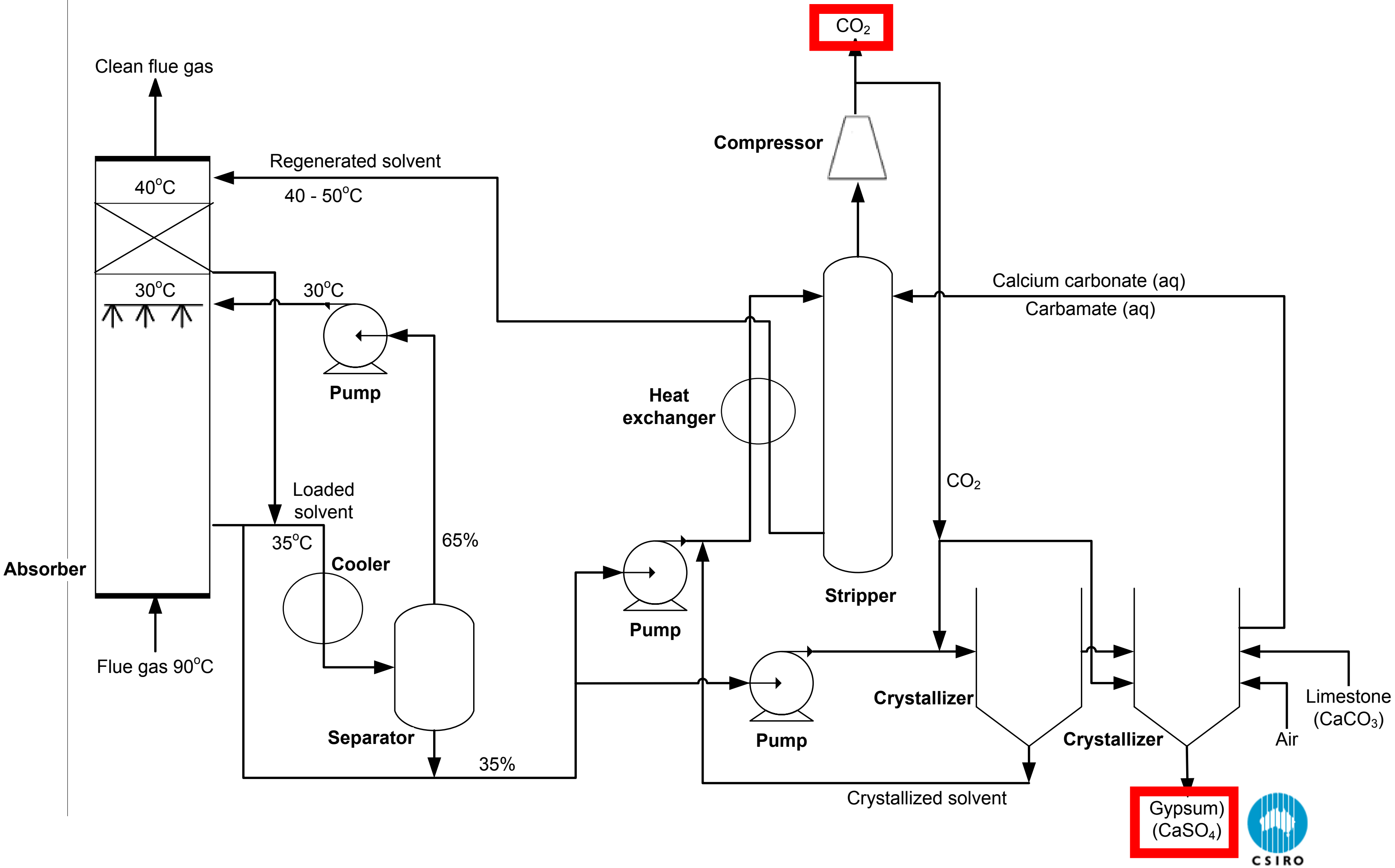
Traditional powerplant with CCS versus co2/so2 integrated system

pictures illustrating this will be made

Process Design routes

- DECASOX
- DOUBLE LOOPED CAPTURE PROCESS
- Modified DECASOX

DECASOx Conceptual Process Design



CO_2

Clean flue gas

Compressor

Regenerated solvent

40 - 50°C

40°C

30°C

30°C

Pump

Calcium carbonate (aq)

Carbamate (aq)

Heat exchanger

CO_2

Loaded solvent

35°C

Cooler

65%

Absorber

Pump

Stripper

Flue gas 90°C

Crystallizer

Separator

Pump

Crystallizer

Limestone ($CaCO_3$)

Air

35%

Crystallized solvent

Gypsum) ($CaSO_4$)

DECASOx Experimental Results & Conclusions

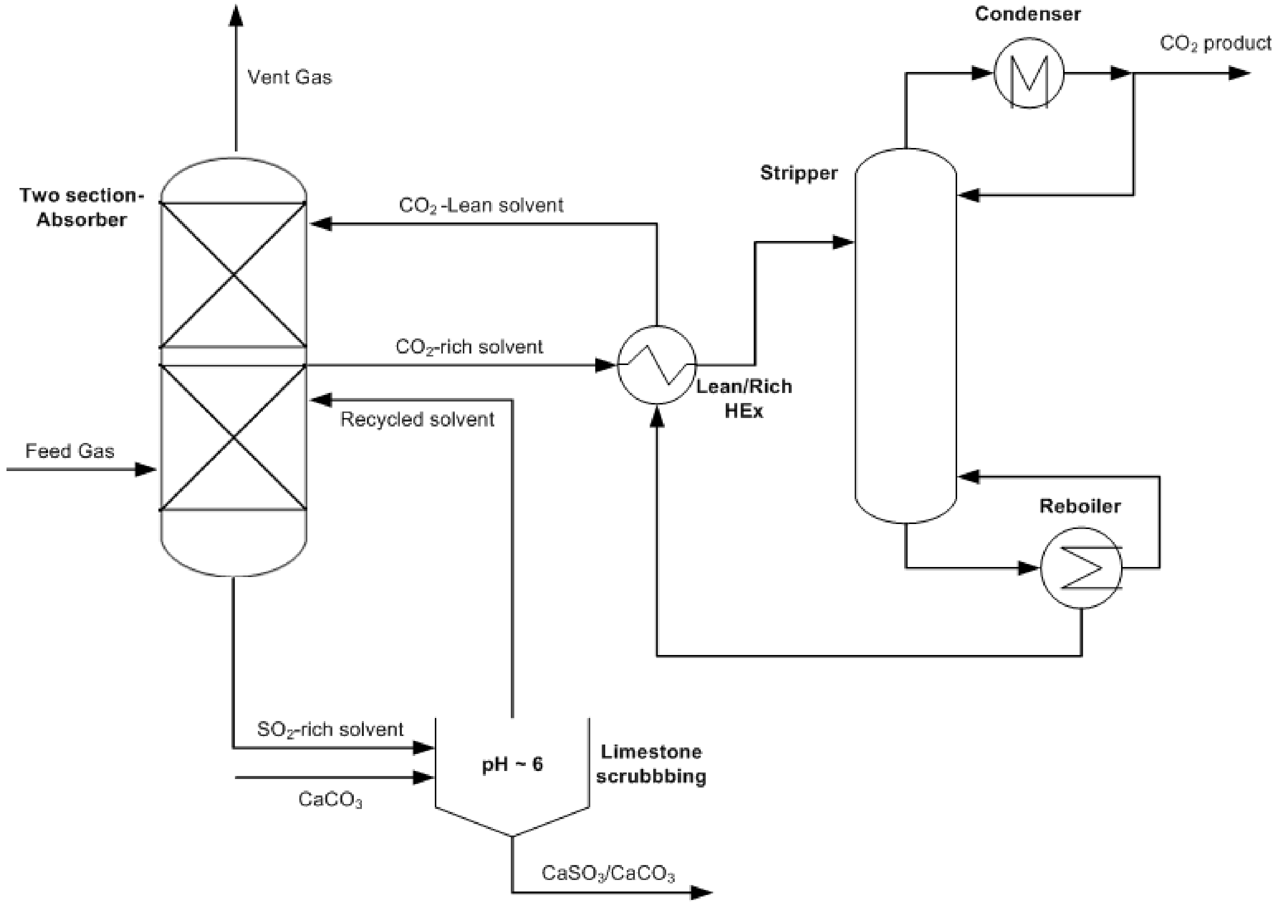
Experimental results of $CaCO_3$ recrystallization to $CaSO_3/CaSO_4$ by applying pressurized CO_2

exp.	Potassium taurate (kmol.m^{-3})	K_2SO_4 (kmol.m^{-3})	K_2SO_3 (kmol.m^{-3})	$CaCO_3$ (kmol.m^{-3})	CO_2 pressure (bar)	Final pH	Reaction time (hh:mm)	$CaCO_3$ converted (%)
A	0.10	0.35	0.35	0.25	7.15	6.27	2:22	22.56%
B	0.03	0.13	0.13	0.25	7.20	6.37	2:29	3.14%
C	0.03	0.13	0.12	0.25	38.86	5.88	18:19	30.83%

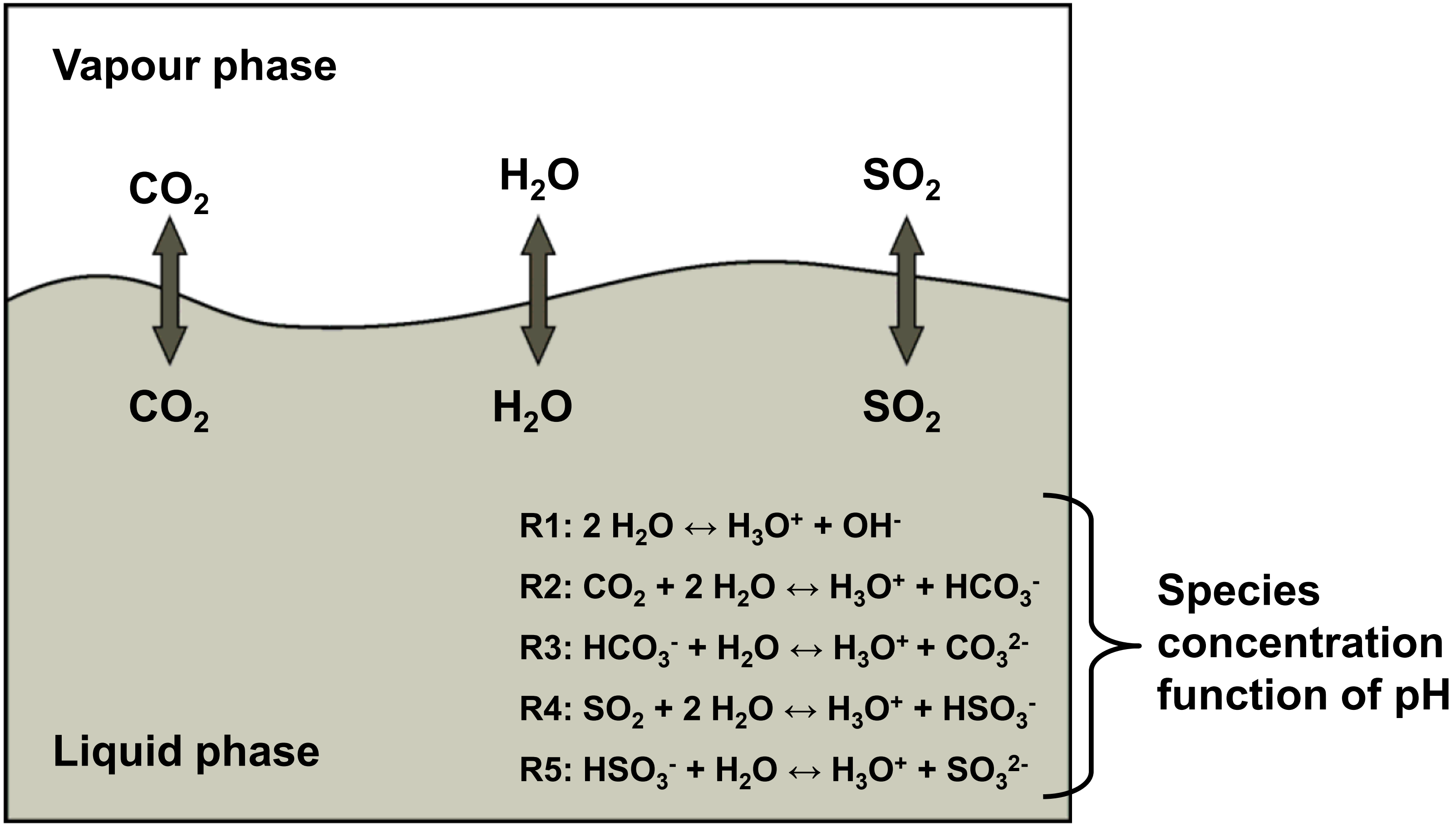
- **Feasible $CaCO_3$ recrystallization to $CaSO_3/CaSO_4$ by CO_2 pressure, but $CaCO_3$ conversion not very high due to:**
  - **At pH ~6, most sulphite converted to bisulphite → calcium bisulphite soluble compound has higher solubility than sulphite.**
  - **$CaCO_3$ extremely low solubility.**

Conclusion: DECASOx is complex and has a high operational cost

Double Looped Capture Process



Thermodynamics K_2CO_3 – SO_2 – CO_2 System



Vapour phase

CO_2 H_2O SO_2

CO_2 H_2O SO_2

R1: $2\ H_2O \leftrightarrow H_3O^+ + OH^-$

R2: $CO_2 + 2\ H_2O \leftrightarrow H_3O^+ + HCO_3^-$

R3: $HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$

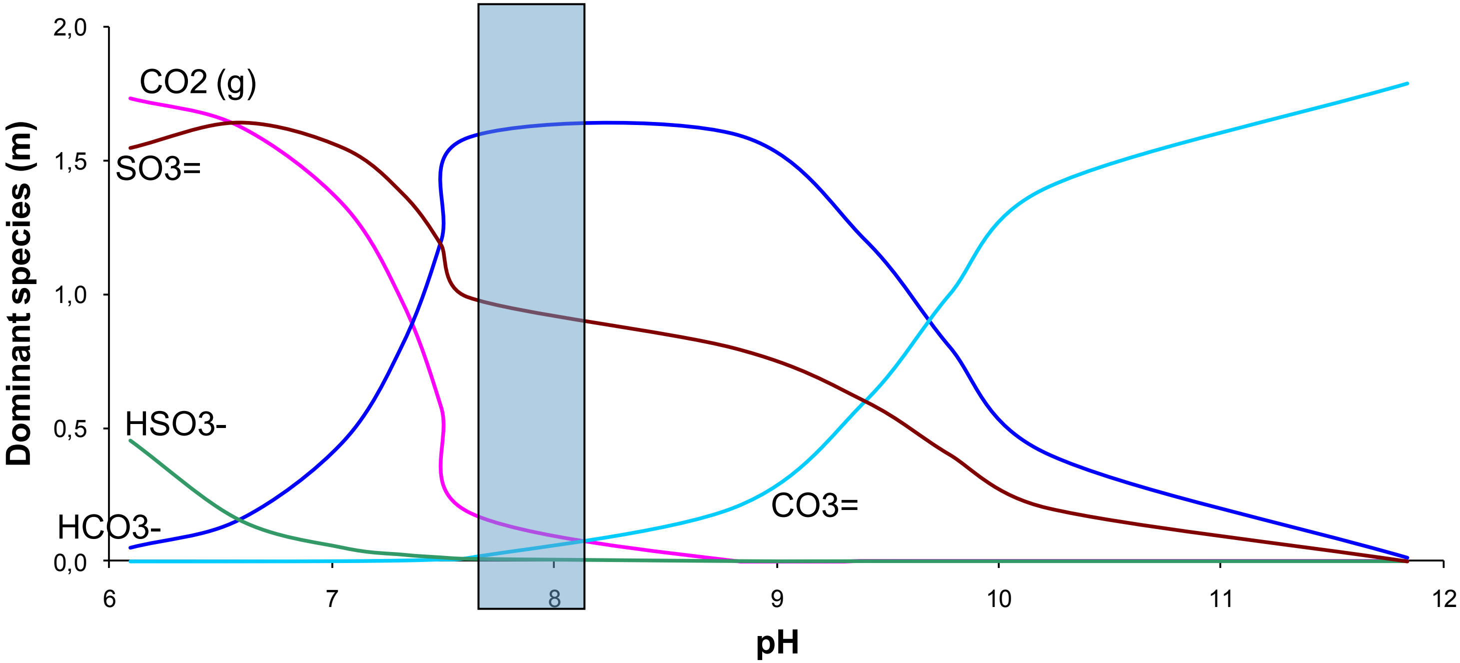
R4: $SO_2 + 2\ H_2O \leftrightarrow H_3O^+ + HSO_3^-$

R5: $HSO_3^- + H_2O \leftrightarrow H_3O^+ + SO_3^{2-}$

Liquid phase

Species concentration function of pH

Sulfite-Carbonate Equilibrium



- At **pH ~ 8** recycled solvent enters absorber → CO_2 mostly found in bicarbonate (HCO_3^-) form.
- **pH < 6** is required for **limestone ($CaCO_3$) scrubbing**.

Limestone scrubbing

- **Limestone Dissolution:**

  $CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$

- **Reaction with Dissolved SO_2:**

  $Ca^{2+} + HSO_3^- \leftrightarrow CaSO_3 + H^+$

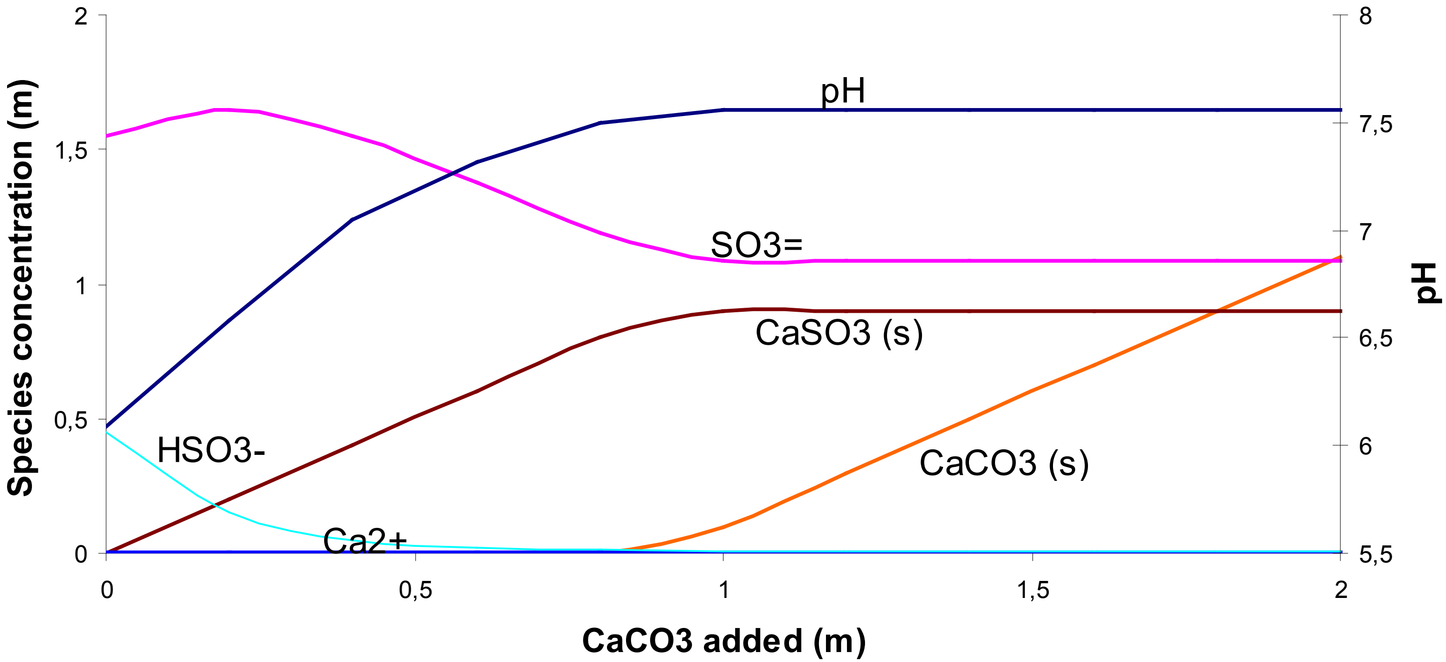
  $Ca^{2+} + SO_3^{2-} \leftrightarrow CaSO_3 (\downarrow)$

- **Precipitation** of solid species governed primarily by solubility:

Salt	**Solubility product (M^2)**
$CaSO_3 \cdot \frac{1}{2}H_2O$	2.76×10^{-7} (40°C)
$CaSO_4 \cdot 2H_2O$	1.20×10^{-6} (40°C)
$CaCO_3$	0.87×10^{-8} (25°C)

Source: Kohl, Nielsen, Gas Purification, 1997.

$CaCO_3$ addition



- $CaCO_3$ starts precipitating above **pH ~ 7.5**.
- Sulfur found in solution in **sulfite** (SO_3^{2-}) form.
- **Almost no Ca^{2+}** remains in solution → no $CaCO_3$ precipitation expected in the absorber.

Expected Recycled Solvent Composition

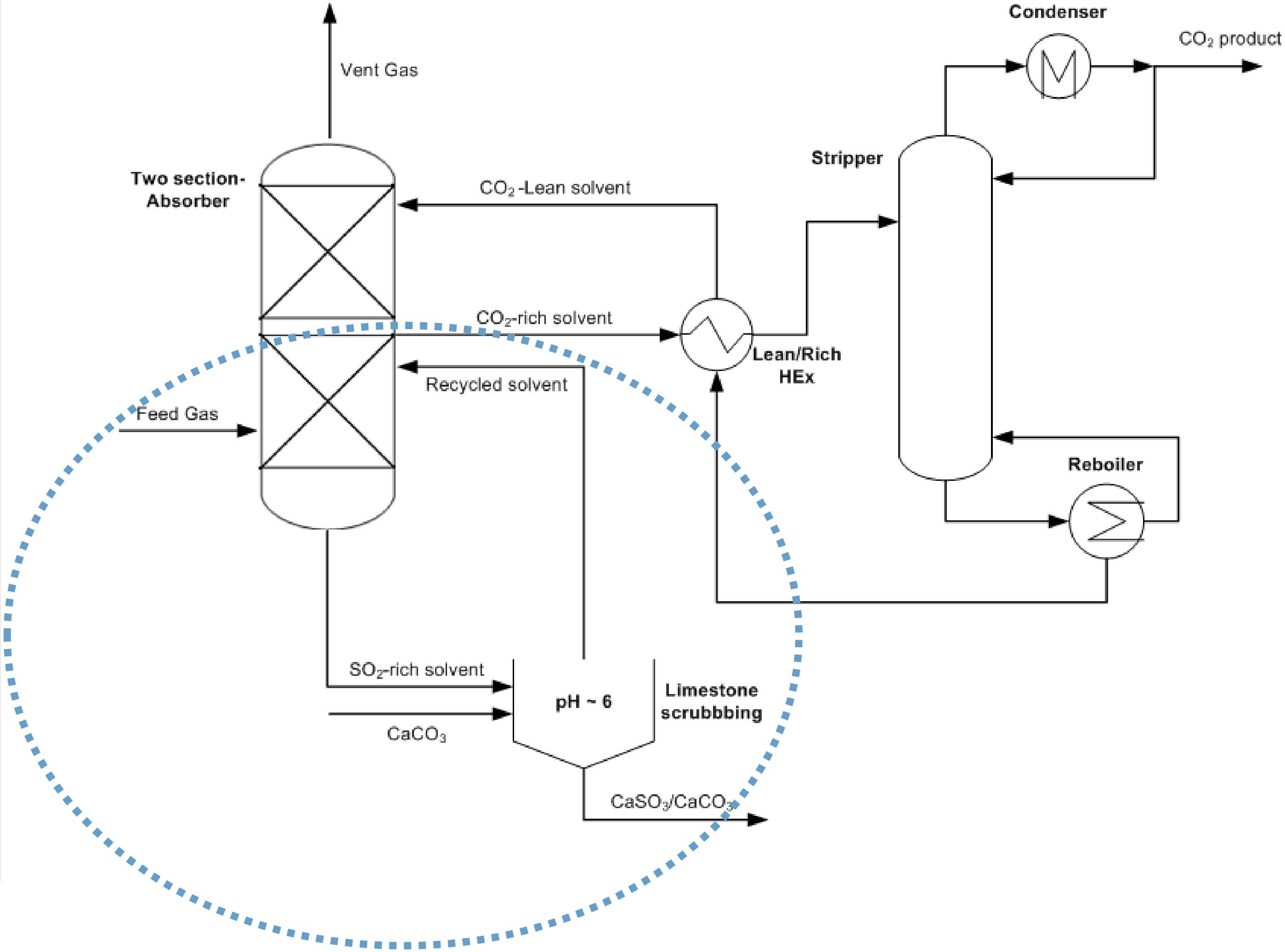
$CaCO_3$ added (m)	pH	HCO_3^- (m)	CO_3^{2-} (m)	SO_3^{2-} (m)	HSO_3^- (m)	Ca^{2+} (m)
0	6.09	0.05	1.3×10^{-5}	1.55	0.45	0
0.2	6.58	0.15	1.2×10^{-5}	1.65	0.15	3.2×10^{-5}
0.4	7.05	0.45	0.001	1.55	0.05	3.4×10^{-5}
0.6	7.32	0.82	0.004	1.38	0.02	3.7×10^{-5}
0.8	7.50	1.20	0.007	1.19	0.01	4.1×10^{-5}
1	7.56	1.40	0.01	1.09	0.01	4.4×10^{-5}
1.2	7.56	1.40	0.01	1.09	0.01	4.4×10^{-5}

$CaCO_3$ precipitation

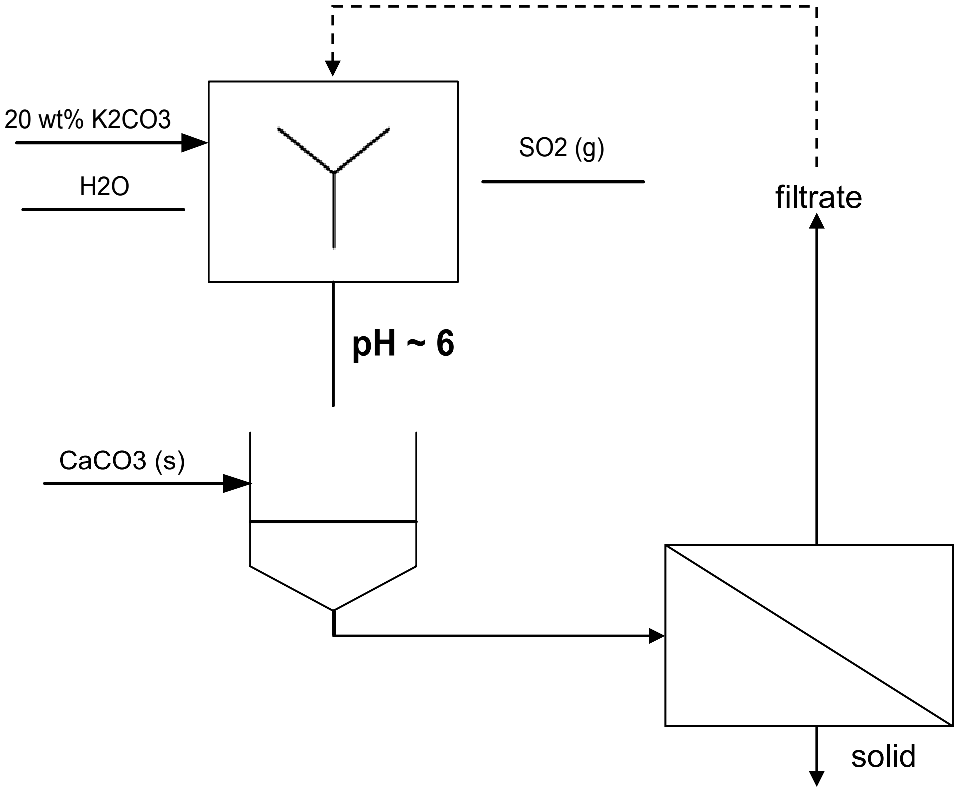
* 1.8 m K_2CO_3; 2 m SO_2 @25 C,1 atm

low Ca^{2+} concentration in recycled solvent


Proof of principle



Proof of Principle K_2CO_3-SO_2 System



Composition of solid sample:

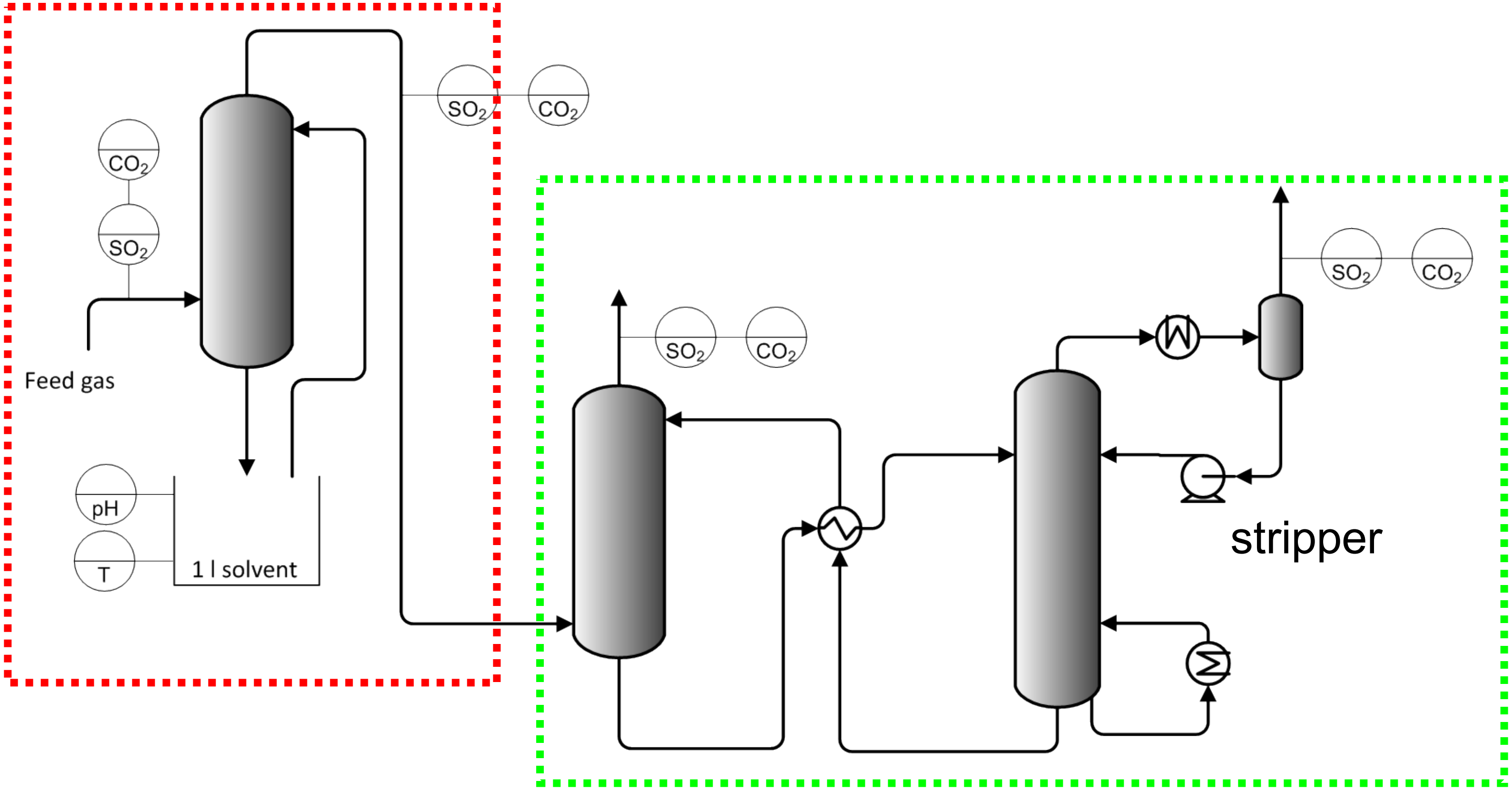
Compound	%
CaCO3	35
CaSO3•0.5H2O	55
K2SO4	10

Yield on Sulfur is around 70%

Strong indications that high recovery of sulfurous components is possible

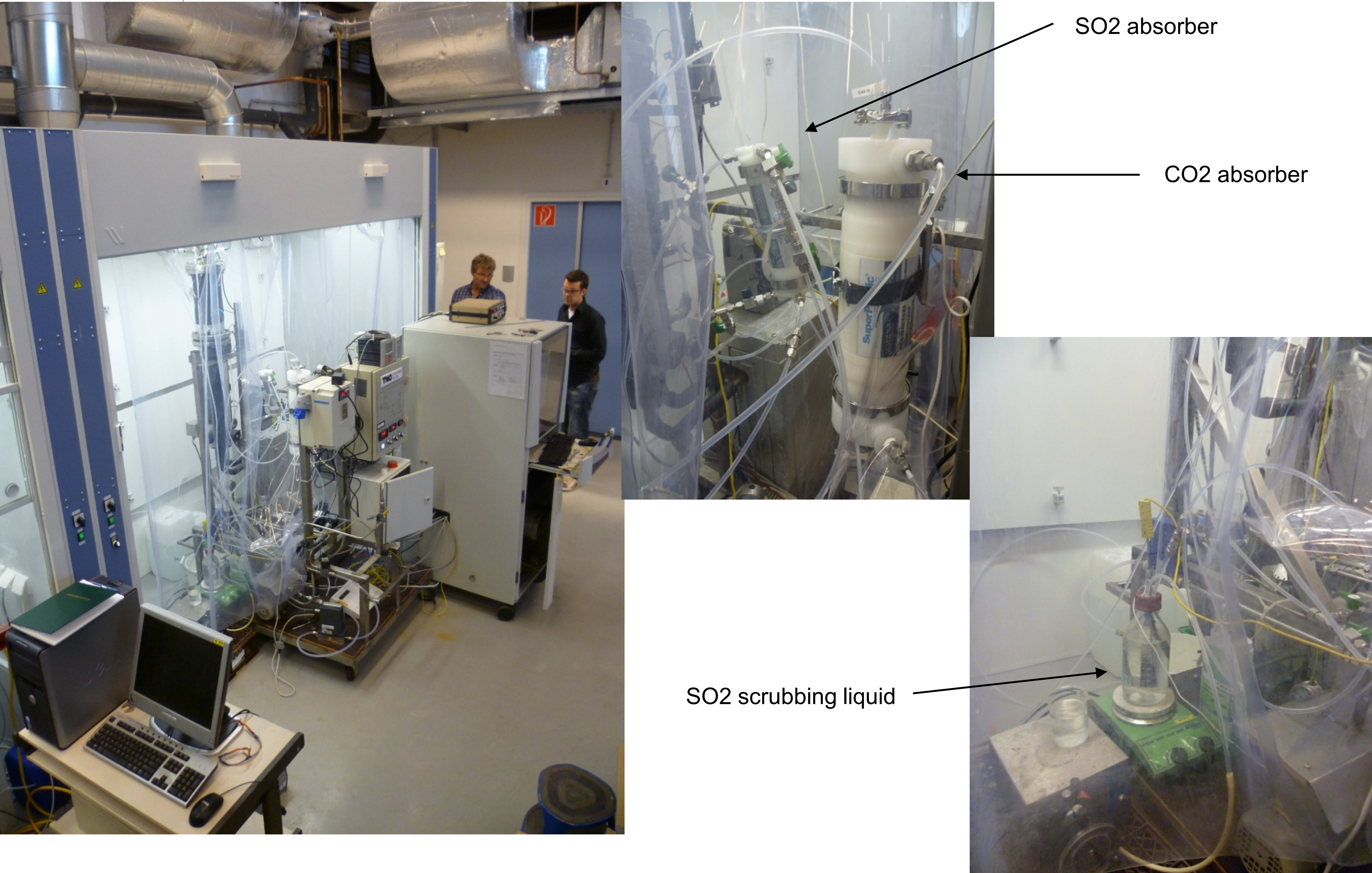
Proof of concept (Continuous processing)

- Microplant experiments



SO2 absorption section

CO2 absorption section

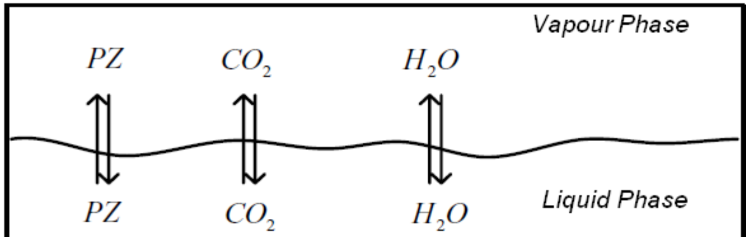


SO2 absorber

CO2 absorber

SO2 scrubbing liquid

Thermodynamics H_2O-K_2CO_3-PZ-CO_2 System



R1: $2H_2O \rightleftarrows H_3O^+ + OH^-$

R2: $CO_2 + 2H_2O \rightleftarrows H_3O^+ + HCO_3^-$

R3: $HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^{-2}$

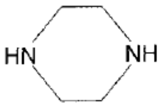
R4: $PZH^+ + H_2O \rightleftarrows PZ(l) + H_3O^+$

R5: $PZ(l) + HCO_3^- \rightleftarrows PZCOO^- + H_2O$

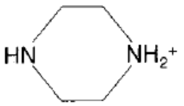
R6: $PZCOO^- + HCO_3^- \rightleftarrows PZ(COO^-)_2 + H_2O$

R7: $H^+PZCOO^- + PZ(l) \rightleftarrows PZCOO^- + PZH^+$

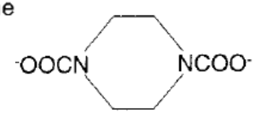
Source: Hilliard M., Thermodynamics of Aqueous Piperazine/Potassium Carbonate/Carbon Dioxide Characterized by the Electrolyte NRTL Model within Aspen Plus, 2005.



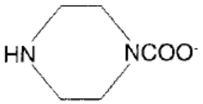
Piperazine
(PZ)



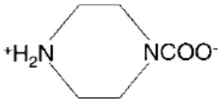
Protonated Piperazine
(PZH^+)



Piperazine Dicarbamate
(H^+PZCOO^-)



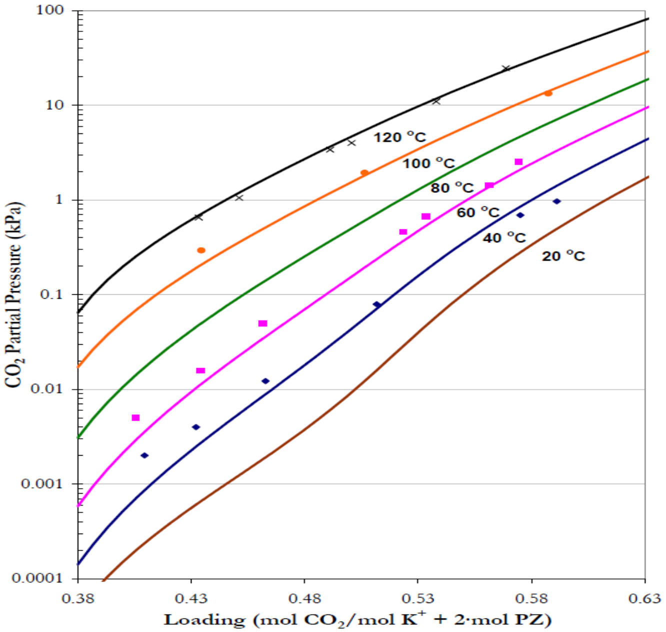
Piperazine Carbamate
($PZCOO^-$)



Protonated Piperazine Carbamate
(H^+PZCOO^-)

Molecular structures of piperazine species

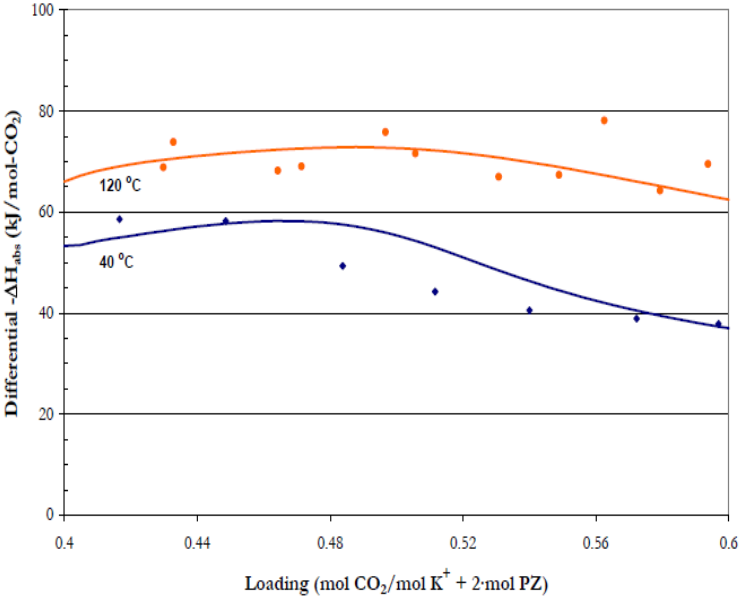
VLE data H_2O-K_2CO_3-PZ-CO_2 System



CO_2 Solubility in 6 m K^+ + 1.2 m PZ from 20 – 120°C. Points: 40°C, 60°C, 80°C, 100°C, 120°C.

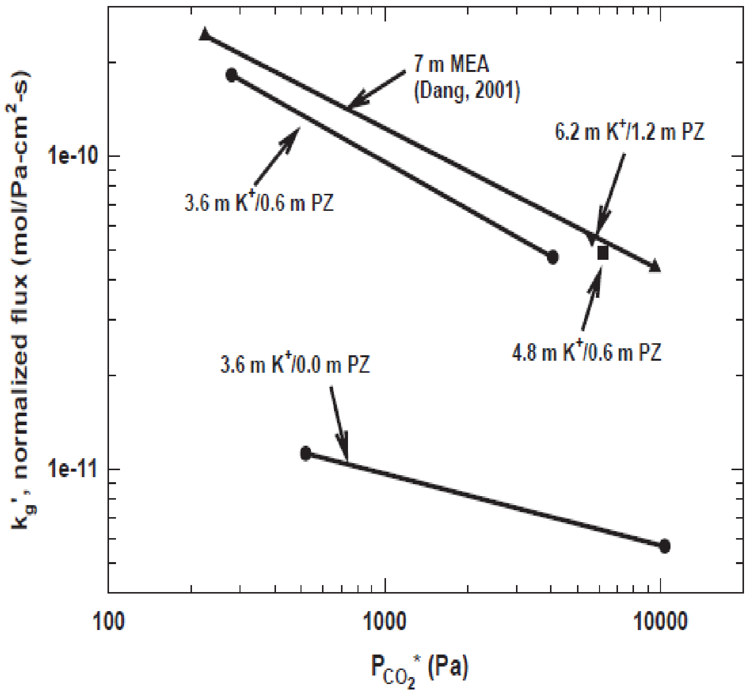
Lines: elecNRTL Model Predictions.

Enthalpy of CO_2 Absorption

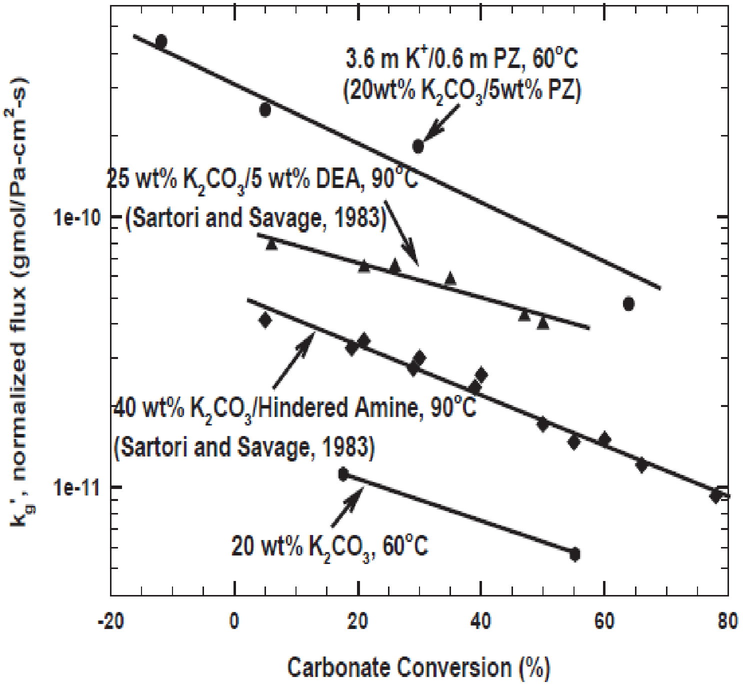


Comparison of the Enthalpy of CO_2 Absorption in 6 m K^+ + 1.2 m PZ at 40 and 120°C from Kim (2007) to Predictions from this work.


CO_2 absorption rates in different solvents



CO_2 absorption rates in K_2CO_3 and MEA solutions at 60 C.

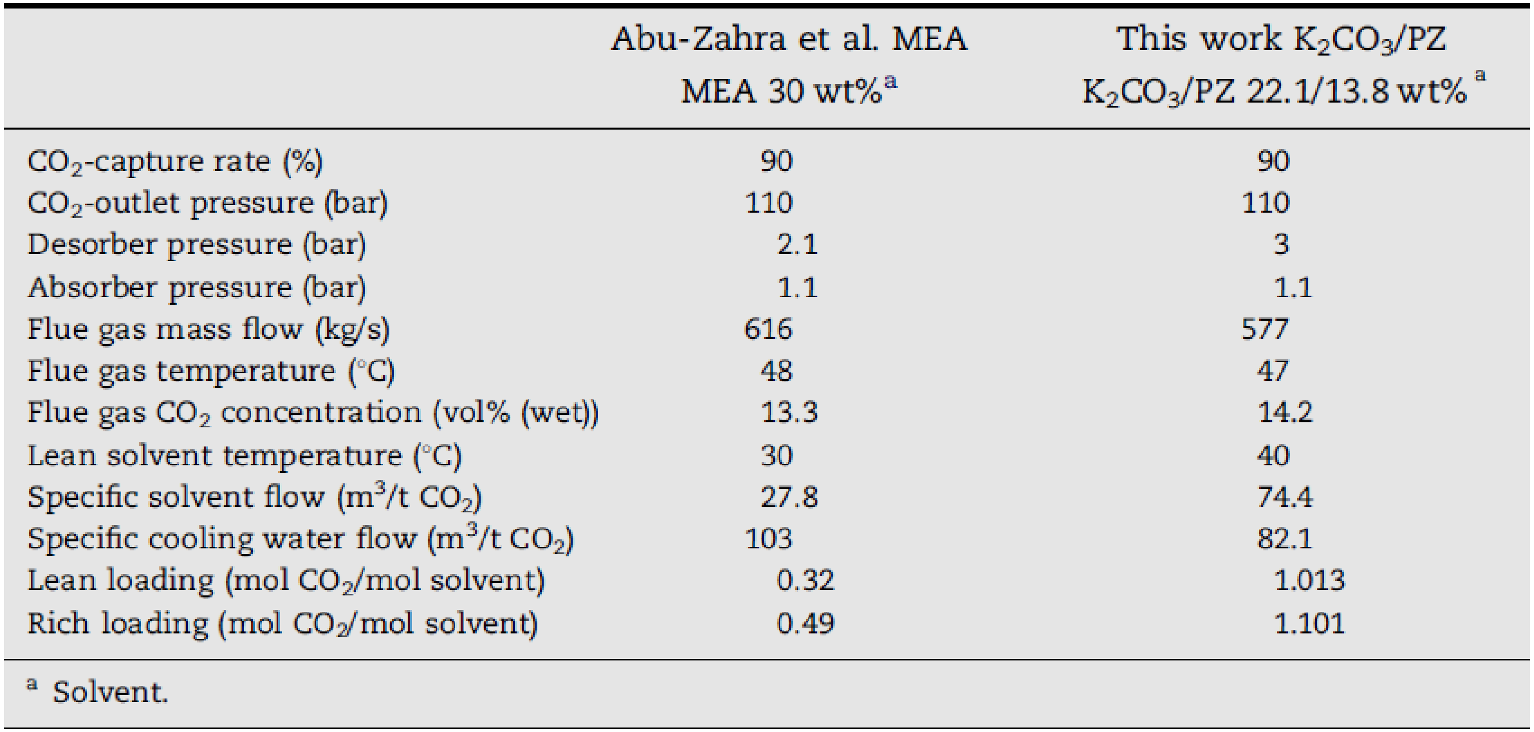


Comparison of promoted K_2CO_3 solutions

Source: Cullinane J.T., Rochelle G.T., Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine, 2004

Comparison to MEA process: Conditions

- Boundary conditions for MEA and K_2CO_3/PZ CO_2-capture process comparison



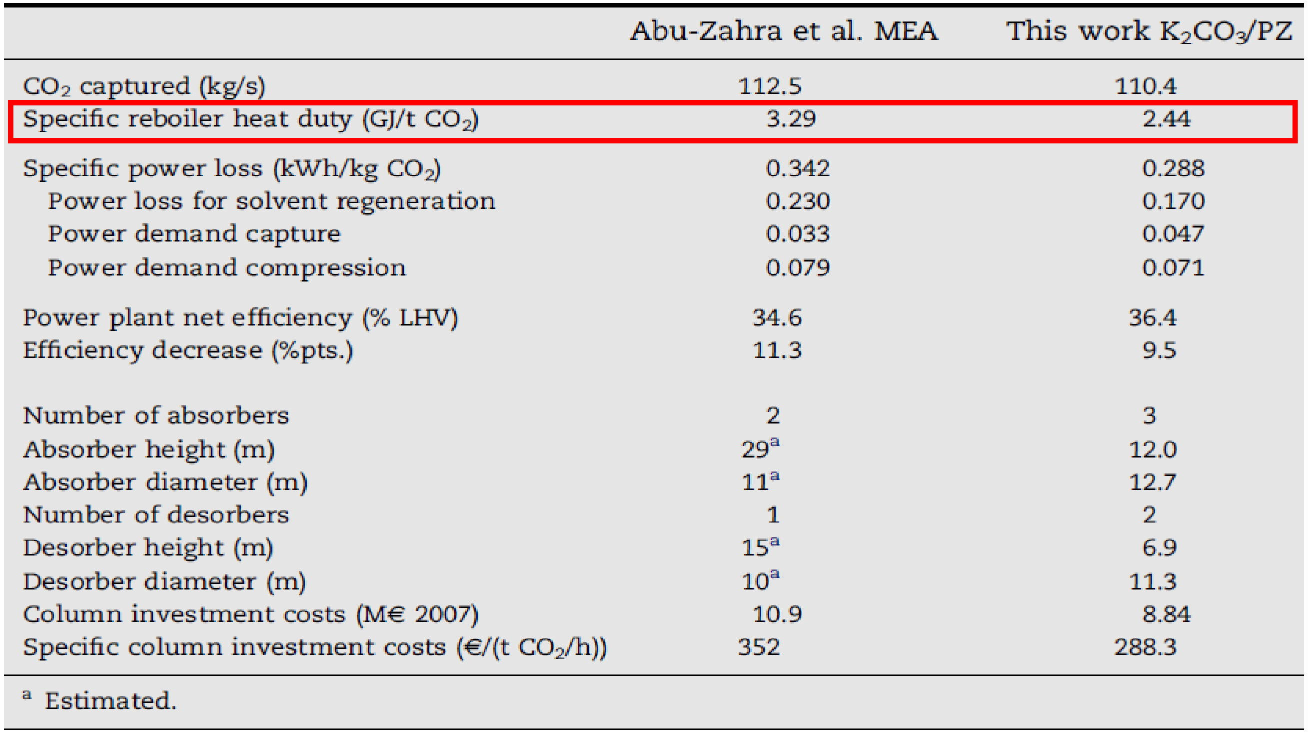
	Abu-Zahra et al. MEA MEA 30 wt%[a]	This work K_2CO_3/PZ K_2CO_3/PZ 22.1/13.8 wt%[a]
CO_2-capture rate (%)	90	90
CO_2-outlet pressure (bar)	110	110
Desorber pressure (bar)	2.1	3
Absorber pressure (bar)	1.1	1.1
Flue gas mass flow (kg/s)	616	577
Flue gas temperature (°C)	48	47
Flue gas CO_2 concentration (vol% (wet))	13.3	14.2
Lean solvent temperature (°C)	30	40
Specific solvent flow (m^3/t CO_2)	27.8	74.4
Specific cooling water flow (m^3/t CO_2)	103	82.1
Lean loading (mol CO_2/mol solvent)	0.32	1.013
Rich loading (mol CO_2/mol solvent)	0.49	1.101

[a] Solvent.

Source: Oexmann J., Hensel C., Kather A., Post-combustion CO2-capture from coal-fired power plants: Preliminary evaluation of an integrated chemical absorption process with piperazine-promoted potassium carbonate, 2008.

Comparison to MEA process: Results

- Results for MEA and K_2CO_3/PZ CO_2-capture process comparison



	Abu-Zahra et al. MEA	This work K_2CO_3/PZ
CO_2 captured (kg/s)	112.5	110.4
Specific reboiler heat duty (GJ/t CO_2)	3.29	2.44
Specific power loss (kWh/kg CO_2)	0.342	0.288
Power loss for solvent regeneration	0.230	0.170
Power demand capture	0.033	0.047
Power demand compression	0.079	0.071
Power plant net efficiency (% LHV)	34.6	36.4
Efficiency decrease (%pts.)	11.3	9.5
Number of absorbers	2	3
Absorber height (m)	29[a]	12.0
Absorber diameter (m)	11[a]	12.7
Number of desorbers	1	2
Desorber height (m)	15[a]	6.9
Desorber diameter (m)	10[a]	11.3
Column investment costs (M€ 2007)	10.9	8.84
Specific column investment costs (€/(t CO_2/h))	352	288.3

[a] Estimated.

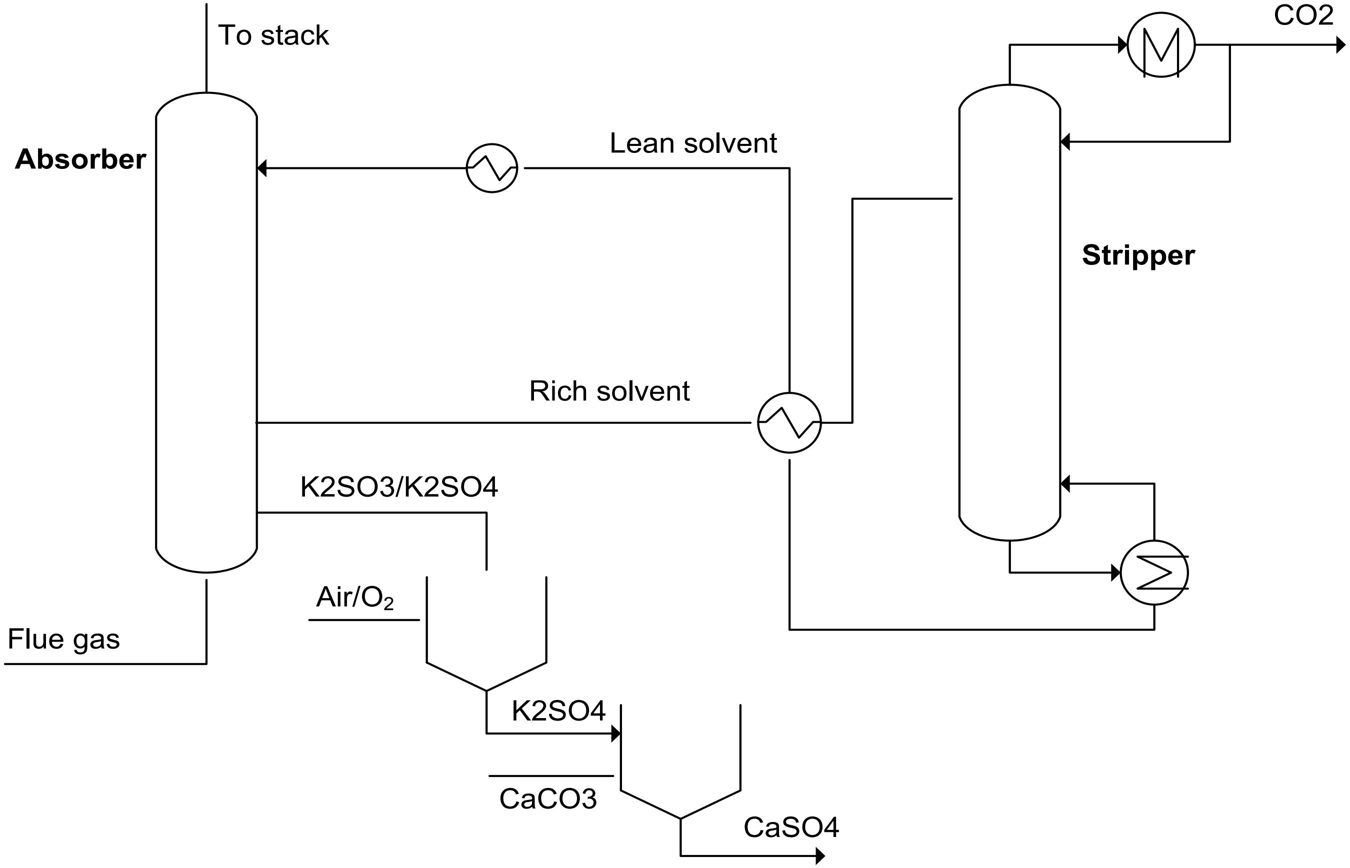
Source: Oexmann J., Hensel C., Kather A., Post-combustion CO2-capture from coal-fired power plants: Preliminary evaluation of an integrated chemical absorption process with piperazine-promoted potassium carbonate, 2008.

Double looped process - Preliminary conclusions

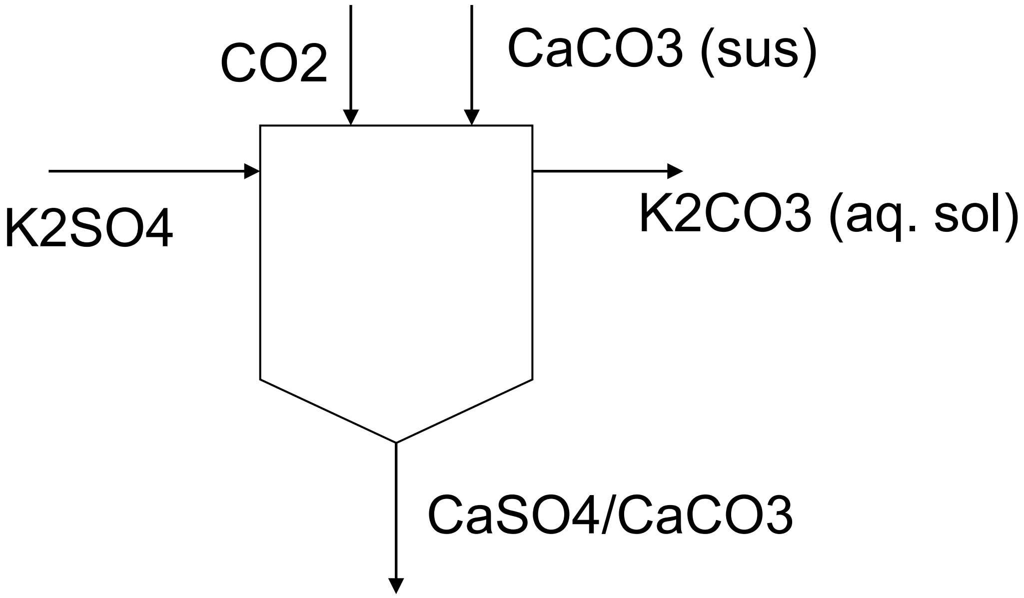
- Proof of Principle delivered
- Proof of concept in progress

<u>However, operational benefits can be debated</u>

Modified DECASOx Conceptual Process Design



Modified DECASOx



CO2

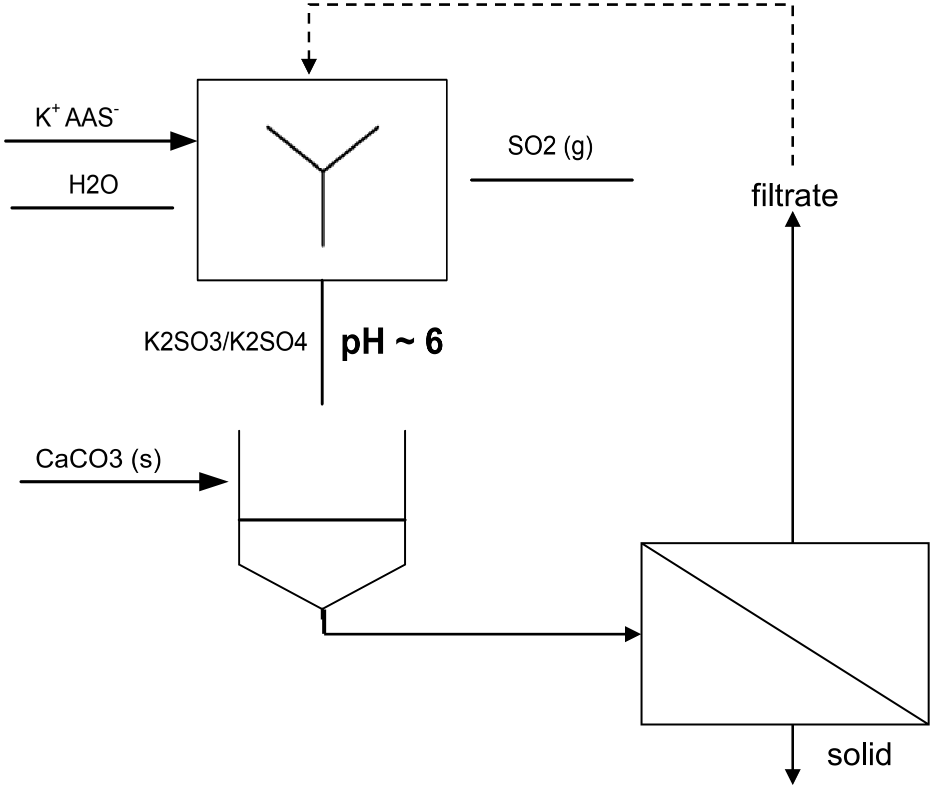
CaCO3 (sus)

K2SO4

K2CO3 (aq. sol)

CaSO4/CaCO3

Proof of Principle of Modified DECASOx concept



Yield sulfur 80%

First route scouting modified DECASOx shows promising results

Modified DECASOx - Preliminary conclusions

- Promising route, warrants further investigations
- Endproduct sulfur containing species (K2SO4 or CaSO4) dependent on the market needs
- Economics should be further investigated

Acknowledgement

iCO$_2$cap