Development of a precipitating carbonate technology for post-combustion CO_2 capture.

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Overview

- Minimum energy consumption for solvent-based post-combustion CO_2 capture.
- Introduction Shell precipitating carbonate technology
- Pilot plant operation precipitating carbonate process
- Conclusions and outlook technology development

Fig 1. Precipitating carbonate pilot plant at STCA.

Minimum water vaporization at the top of the stripper (Habs = 30 kj/mol)

- For a post-combustion CO_2 capture process, the minimum ratio of H_2O to CO_2 at the top of the stripper can be determined:
  - P_{CO2}, P_{H2O} and temperature of the loaded solvent at the bottom of the absorber are known.
  - The T-P behavior of water is known (steam table)
  - The T-P behavior for CO_2 can be determined as a function of reaction heat of CO_2:

Eq 1. (Gibbs-Helmholtz) $$\ln(pCO_{2,T2}) = \ln pCO_{2,T1} - \frac{H_{abs,CO_2}}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

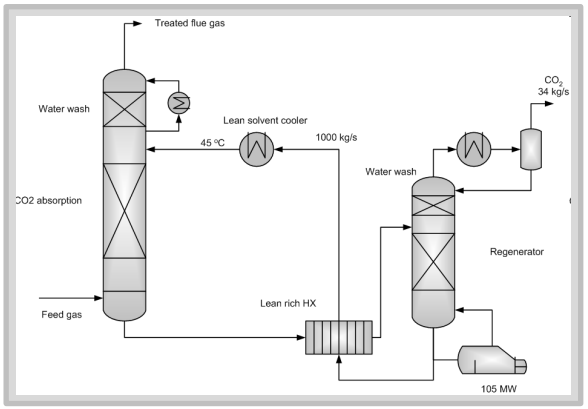
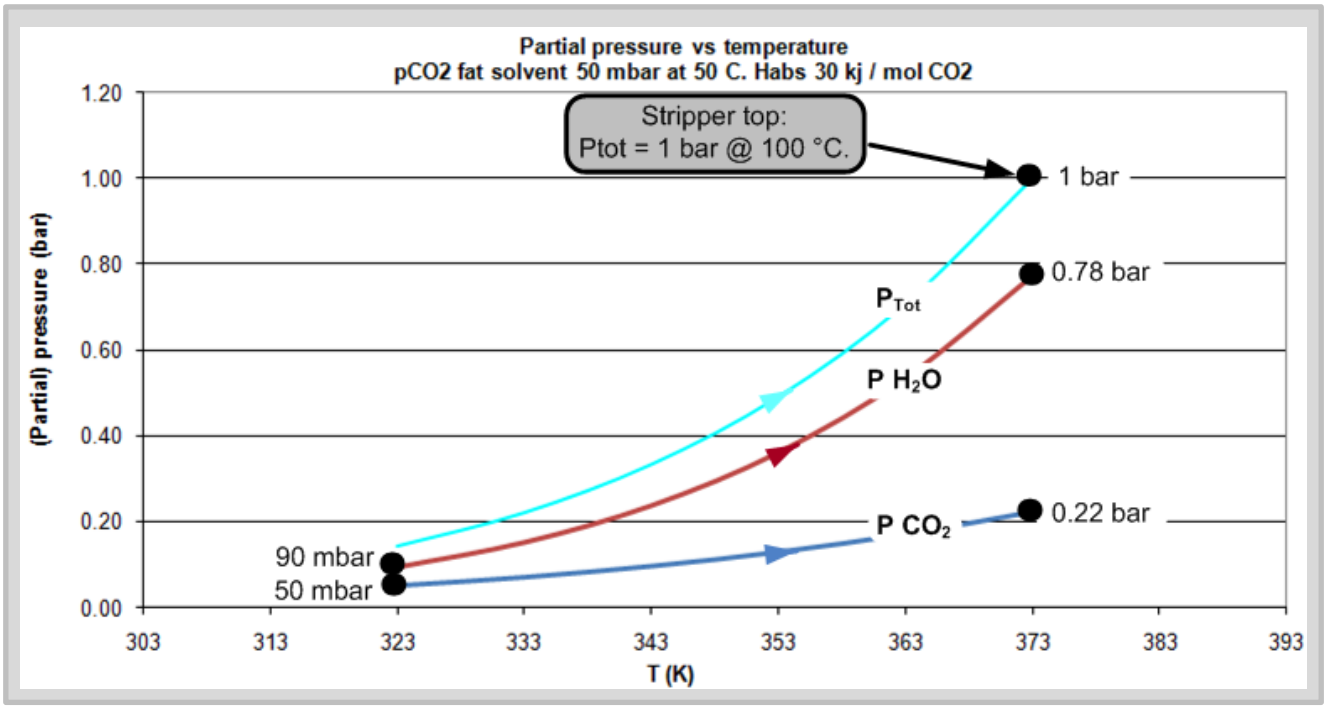


Fig 2. Default line-up post-combustion CO_2 capture.



Stripper top: Min H_2O:CO_2 ratio:

Habs CO_2	= 30 kj/mol
T (@P_{tot}1 bar)	= 100 °C
P water	= 780 mbar
P CO_2	= 220 mbar
Ratio CO_2:H_2O	**= 0.28**

Conclusion:

Low reaction heat, but for every mole of CO_2 you will need to condense 3.5 moles of water.

Fig 3. Vapour pressure CO_2 and H_2O vs T

Minimum water vaporization at the top of the stripper (Habs = 80 kj/mol)

- The same analysis can be done for a solvent with a heat of absorption of 80 kj/mol, such as MEA.

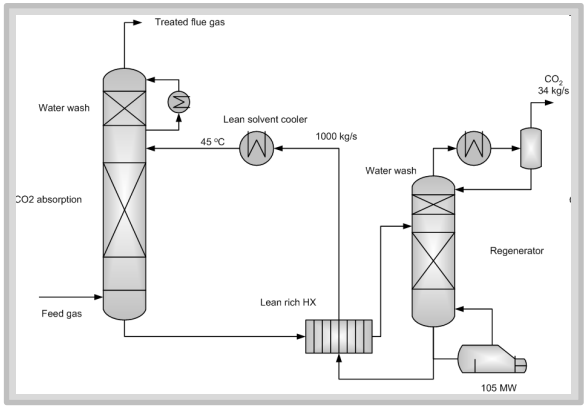


Fig 4. Default line-up post-combustion CO_2 capture.

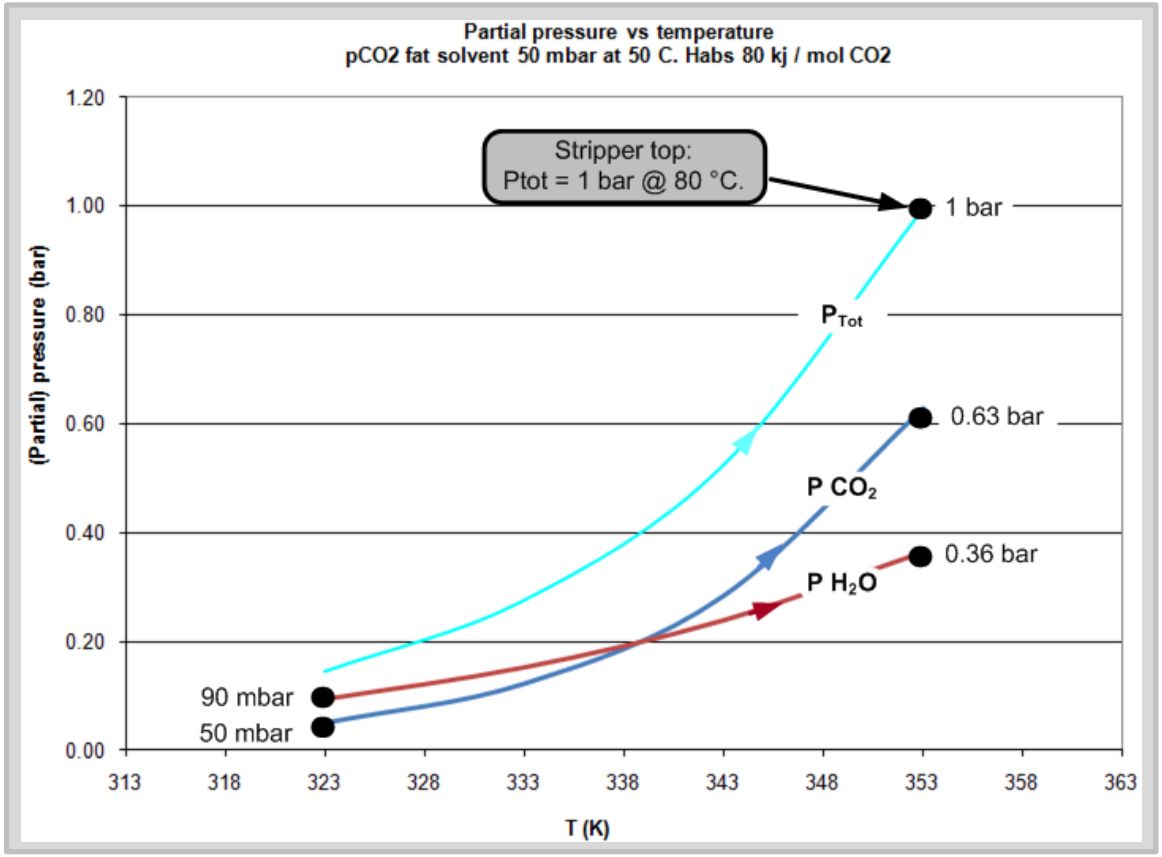


Fig 5. Vapour pressure CO_2 and H_2O vs T

Stripper top: Min H_2O:CO_2 ratio

Habs CO_2	= 80 kj/mol
T (@P_{tot}1 bar)	= 80 °C
P water	= 360 mbar
P CO_2	= 640 mbar
Ratio CO_2:H_2O	**= 1.7**

Conclusion:

High reaction heat, but for every mole of CO_2 you will need to condense minimum only 0.6 moles of water.

Minimum energy consumption for CO_2 capture

- Using this analysis, the minimum energy consumption for a post-combustion capture line-up can be determined.
  - Assumption of a cyclic loading of 8 wt% with a lean-rich heat-exchanger T-approach of 5 °C

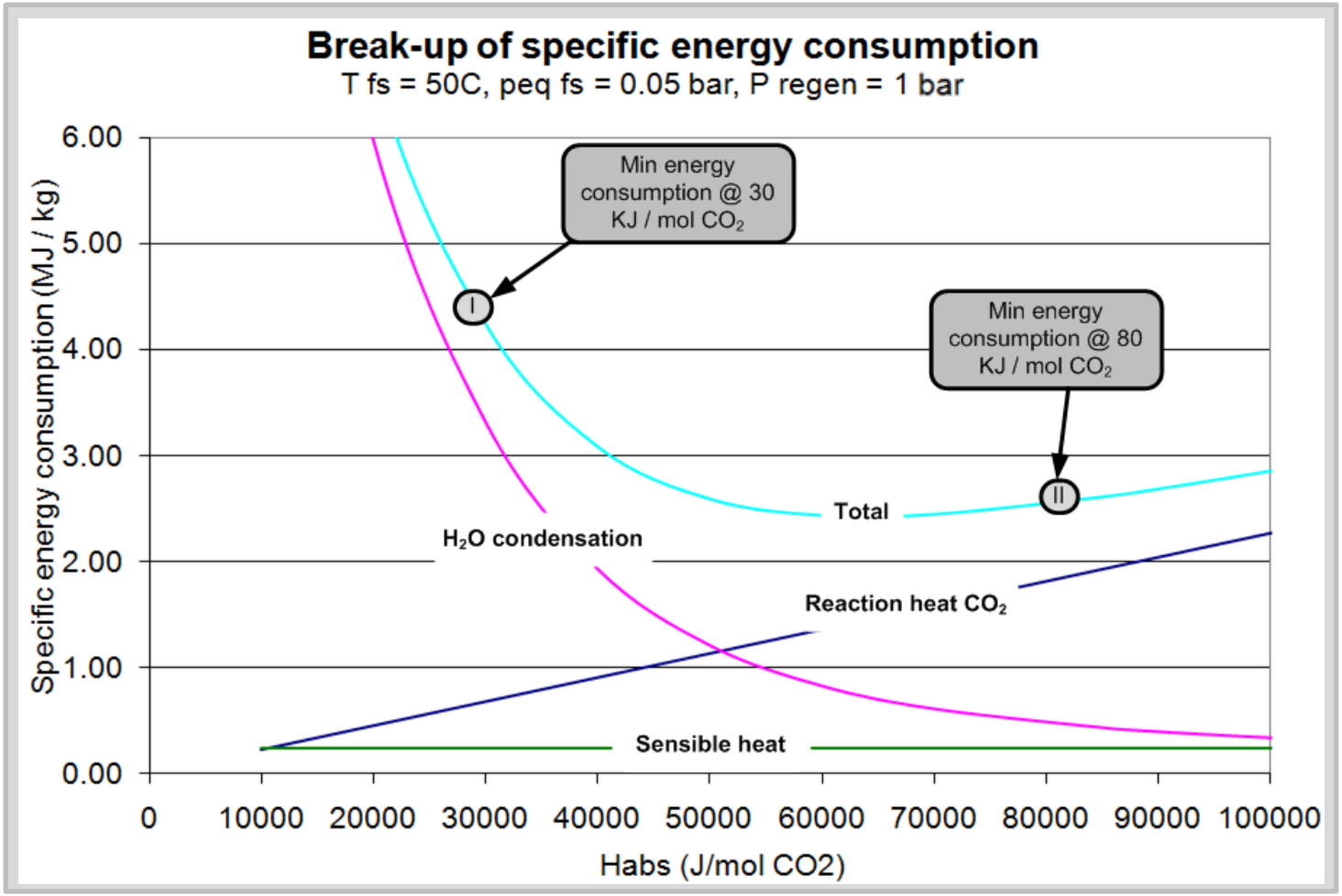


Fig 5. Minimum energy consumption stripper as a function of Habs

Minimum water vaporization at the top of the stripper (precipitating process, 30 kj/mol)

- For a process where a CO_2 species precipitates by cooling and consecutively is concentrated, the minimum ratio can also be described:
  - **Point A to B**: The fat solvent is cooled; a CO_2 species precipitates. The CO_2 loading of the formed slurry is increased by concentrating the slurry in a settler.
  - **Point B to C:** The concentrated slurry is heated. The solids dissolve and the loading of the liquid phase increases.
  - **Point C to D:** A clear liquid is heated further to the bubble point at 1 bar.

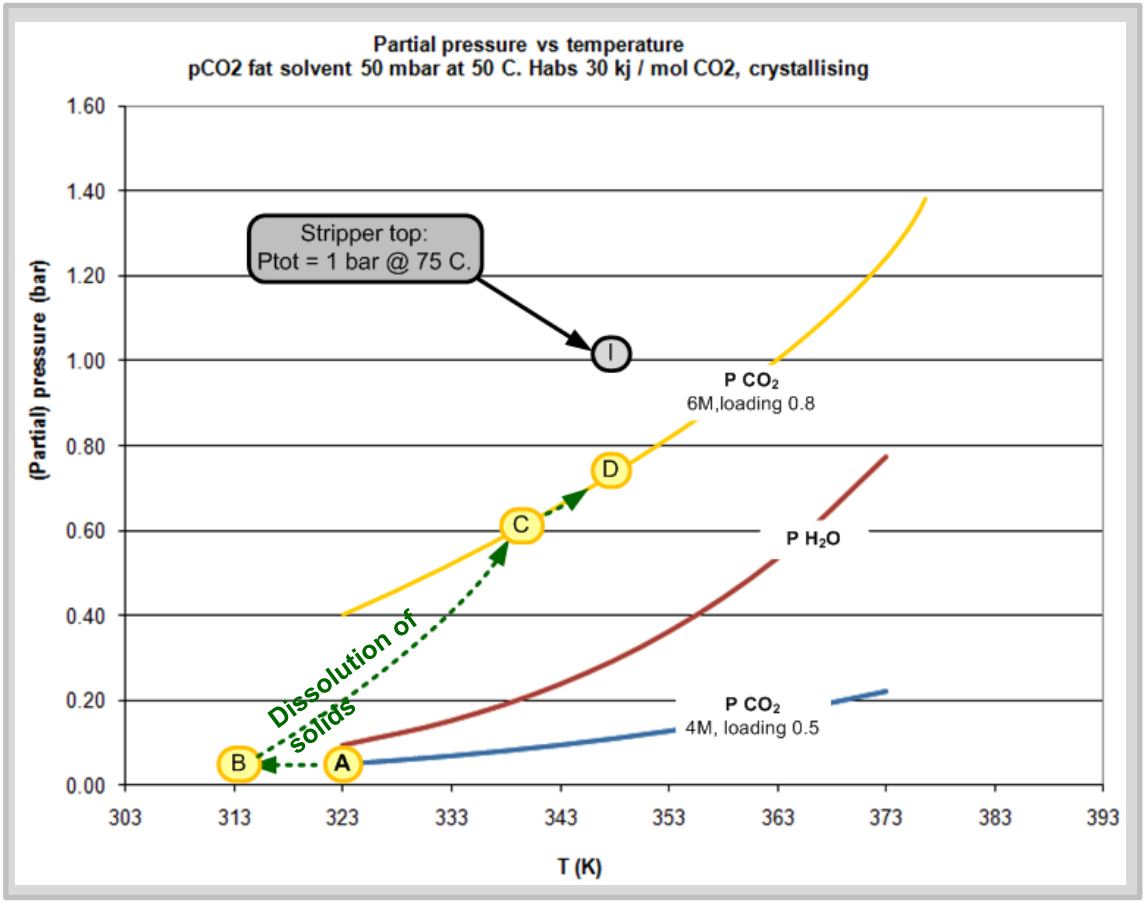


Fig 7. CO_2 to H_2O ratio in a line-up with precipitation and concentration of the solids.

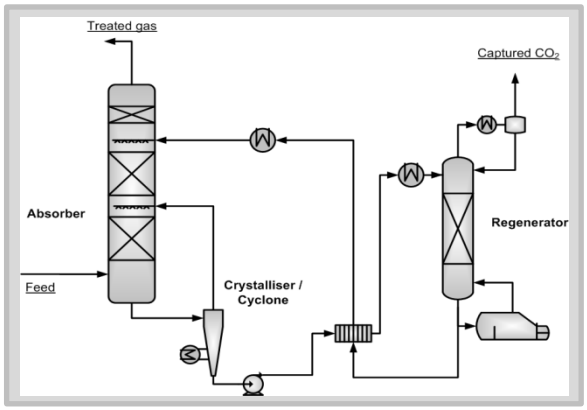


Fig 6. Line-up for a precipitating process with solids concentration.

Stripper top: Min H_2O:CO_2 ratio

Habs CO_2	= 30 kj/mol
T (@P_{tot}1 bar)	= 75 °C
P water	= 280 mbar
P CO2	= 730 mbar
Ratio CO_2: H_2O	**= 2.6**

Conclusion:

In a precipitating process, it may be feasible to have low water losses and a low heat of reaction.
The heat required to dissolve the solids is not included in this evaluation.

Introduction Shell precipitating carbonate technology

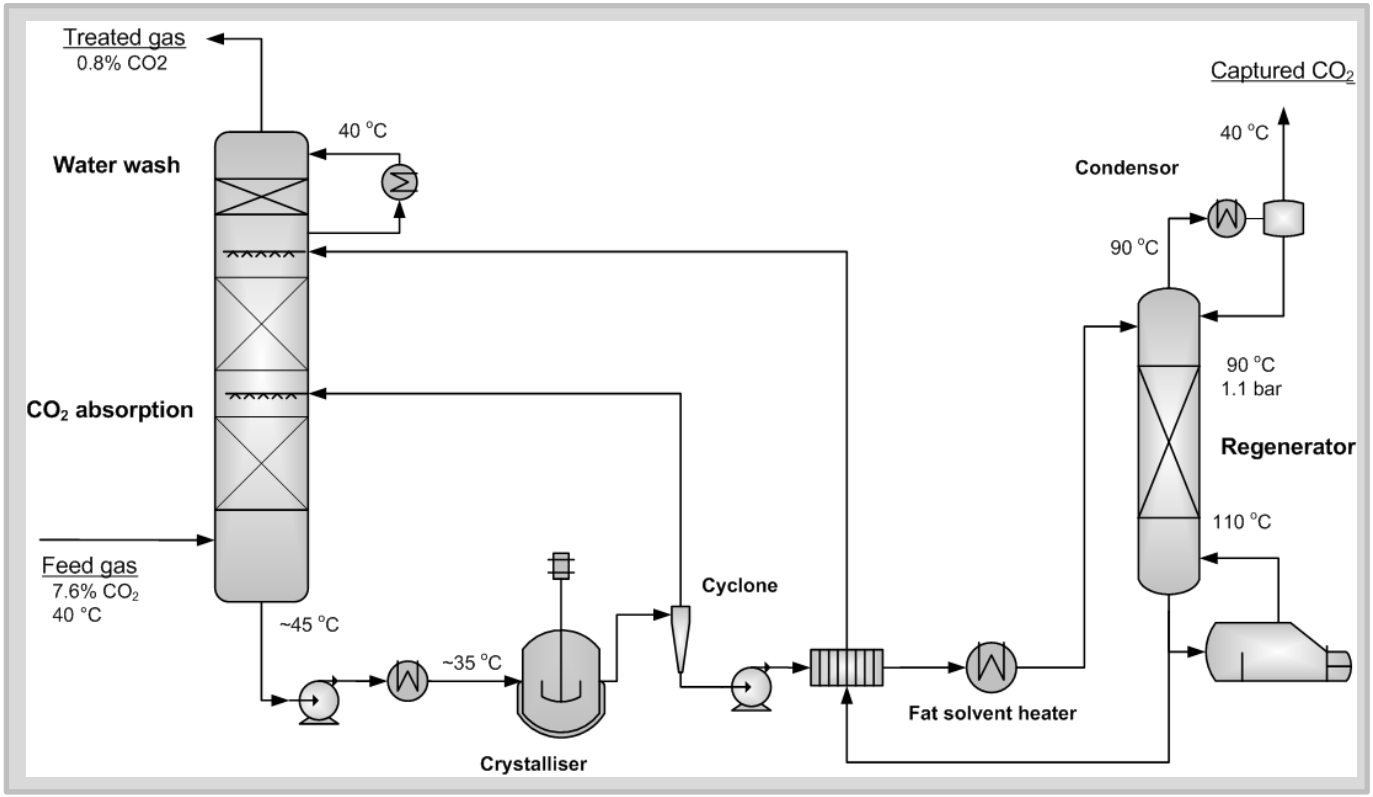


Fig 8. Conceptual PFS Shell precipitating carbonate technology.

Chemistry

1. CO_2 (aq) + H_2O + CO_3^{2-} → 2 HCO_3^-
2. K^+ + HCO_3^- → $KHCO_3$ (↓, S)

An accelerator is used to enhance mass transfer of CO_2 to liquid phase

Drivers technology development.

1. Potential for low energy consumption (Lower end of **2.5 – 4** MJ /kg range)
2. Options for heat integration to dissolve solids may bring down energy consumption further.
3. When a non-volatile accelerator is used, a water wash may not be required and there will be no amine emissions to air.

Development overview

- **Phase I. Determination of feasibility of process concept**
  - Concept development
  - Basic data measurement
  - Semi-batch absorption in bubble column
- **Phase II. Design and construction of pilot plant**
  - Crystallization studies
  - Detailed design and construction pilot plant.
  - Start-up pilot plant
- **Phase III. Operation pilot plant, other investigations**
  - Operation of pilot plant.
  - Laboratory screening of alternative accelerators
  - Development of electrolyte model (including precipitation) for target system
  - Laboratory screening of crystallisation behavior.
  - Techno-economic evaluation of full scale unit.

Fig 9. Product semi-batch crystallisation in a bubbled vessels.

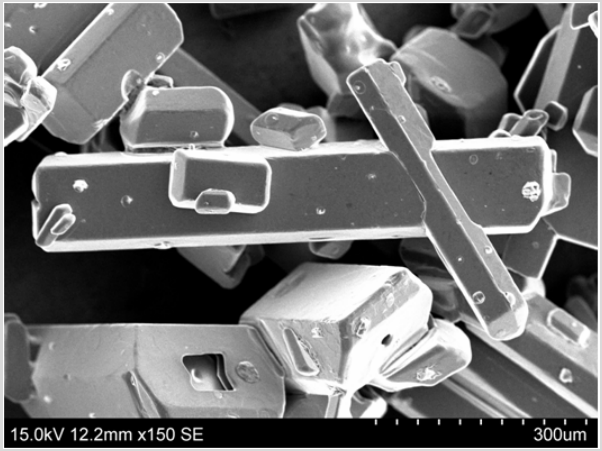


Fig 10. SEM photograph of crystals formed in a lab set-up.

Shell pilot plant precipitating carbonate technology

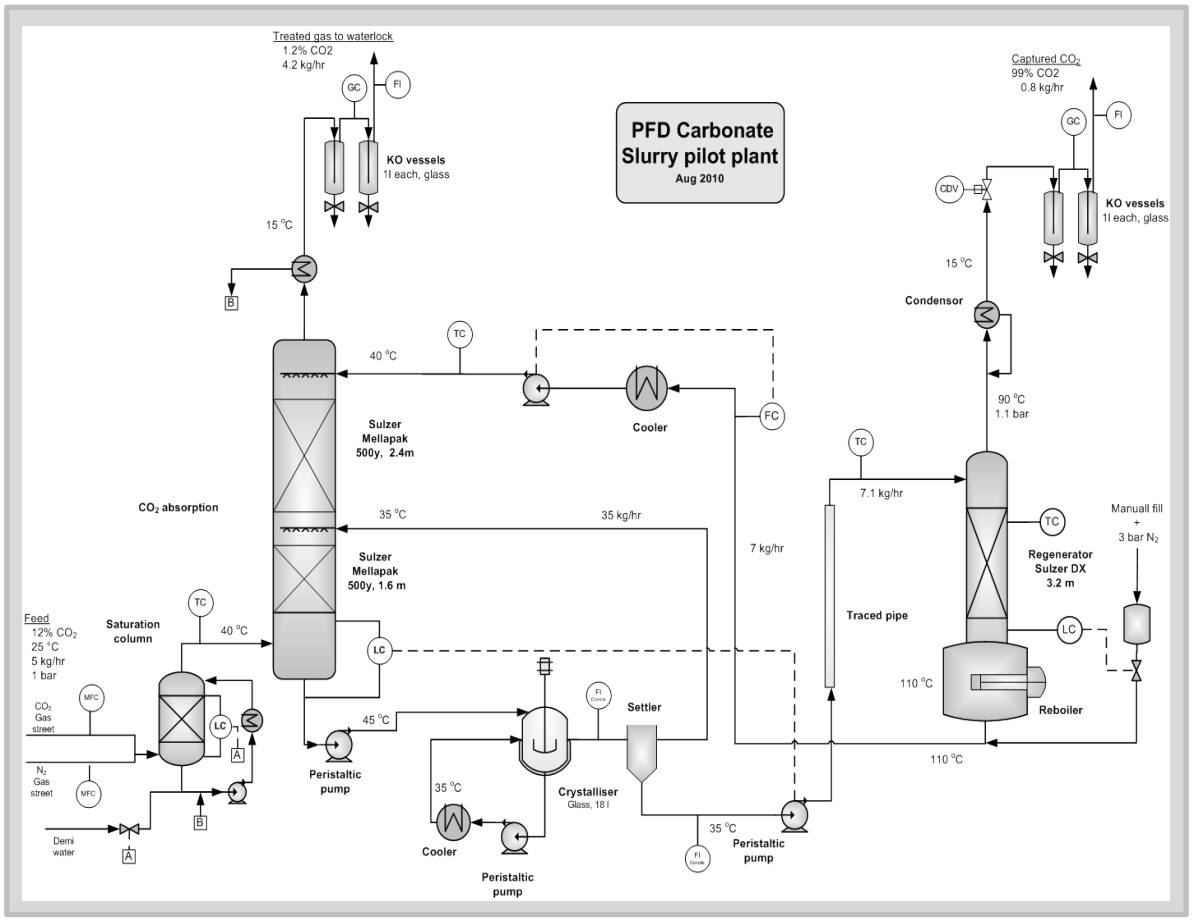


Fig 11. PFS of precipitating carbonate pilot plant at STCA

- Pilot plant operated at Shell Technology Center Amsterdam.
- Start-up Q4, 2010.
- Capacity of pilot plant max 25 kg/d CO_2.
- Dimensions 10m x 1.5m x 6m (H x L x W)
  - Absorber 5 cm diameter. Total 4m Sulzer Mellapak 500y packing.
  - Stripper 3 cm diameter. 3.2m Sulzer DX packing.
  - Crystalliser 20 l

Link to video of operation

Conclusions and outlook

Conclusions

- The continous operation of a precipitating carbonate process for post-combustion CO_2 capture, in the presence of an amine accellerator, has been demonstrated.
- Pilot plant operation and detailed modeling confirms energy consumption in the lower end of the 2.5 -4 MJ/kg range. The heat of dissolution of $KHCO_3$ (s) forms a significant part of the total energy consumption (~ 1 MJ / kg CO_2).
- Opportunities have been identified to bring down energy consumption further by applying heat integration to dissolve the $KHCO_3$ crystals.
- Due to the solids concentration step, the fat solvent loading and energy consumption for the process is hardly dependent on pCO_2 in the feed gas in the range 4 – 15% CO_2.
- Robust operation of a precipitating process with solids handling requires very close attention, both during design and during operation.

Outlook

- Operation of pilot plant using alternative accellerators.
- Detailed OPEX and CAPEX review based on pilot plant results, crystallisation studies and process modeling.
- Preparations for an industrial pilot plant.