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 CO₂ 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.
For a post-combustion CO₂ capture process, the minimum ratio of H₂O to CO₂ 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 CO₂ can be determined as a function of reaction heat of CO₂:

\[
\ln(p_{CO₂,T₂}) = \ln(p_{CO₂,T₁}) - \frac{H_{abs,CO₂}}{R} \left( \frac{1}{T₁} - \frac{1}{T₂} \right)
\]

Eq 1. (Gibbs-Helmholtz)

Stripper top: Min H₂O:CO₂ ratio:

- Habs CO₂ = 30 kJ/mol
- T (@P_{tot} 1 bar) = 100 °C
- P water = 780 mbar
- P CO₂ = 220 mbar
- Ratio CO₂:H₂O = 0.28

Conclusion:
Low reaction heat, but for every mole of CO₂ you will need to condense 3.5 moles of water.

Fig 2. Default line-up post-combustion CO₂ capture.

Fig 3. Vapour pressure CO₂ and H₂O vs T
The same analysis can be done for a solvent with a heat of absorption of 80 kJ/mol, such as MEA.

**Stripper top: Min H₂O:CO₂ ratio**

- Habs CO₂ = 80 kJ/mol
- T (@P_{tot} 1 bar) = 80 °C
- P water = 360 mbar
- P CO₂ = 640 mbar
- Ratio CO₂:H₂O = 1.7

**Conclusion:**
High reaction heat, but for every mole of CO₂ you will need to condense minimum only 0.6 moles of water.
Minimum energy consumption for CO₂ 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 CO₂ 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 CO₂ species precipitates. The CO₂ 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 6. Line-up for a precipitating process with solids concentration.](image)

![Fig 7. CO₂ to H₂O ratio in a line-up with precipitation and concentration of the solids.](image)

Stripper top: Min H₂O:CO₂ ratio

- Habs CO₂ = 30 kj/mol
- T (@P_t 1 bar) = 75 °C
- P water = 280 mbar
- P CO₂ = 730 mbar
- Ratio CO₂: H₂O = 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

Chemistry
1. \( \text{CO}_2 \text{(aq)} + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow 2 \text{HCO}_3^- \)
2. \( \text{K}^+ + \text{HCO}_3^- \rightarrow \text{KHCO}_3 \) (↓, S)

An accelerator is used to enhance mass transfer of \( \text{CO}_2 \) 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

- Pilot plant operated at Shell Technology Center Amsterdam.
- Start-up Q4, 2010.
- Capacity of pilot plant max 25 kg/d CO₂.
- 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

Fig 11. PFS of precipitating carbonate pilot plant at STCA

Link to video of operation
Conclusions and outlook

Conclusions

- The continuous operation of a precipitating carbonate process for post-combustion CO₂ capture, in the presence of an amine accelerator, 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 KHCO₃ (s) forms a significant part of the total energy consumption (~ 1 MJ / kg CO₂).
- Opportunities have been identified to bring down energy consumption further by applying heat integration to dissolve the KHCO₃ crystals.
- Due to the solids concentration step, the fat solvent loading and energy consumption for the process is hardly dependent on pCO₂ in the feed gas in the range 4 – 15% CO₂.
- 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 accelerators.
- Detailed OPEX and CAPEX review based on pilot plant results, crystallization studies and process modeling.
- Preparations for an industrial pilot plant.