HiPerCap CO_2

HiPerCap

Absorption Technologies

Natural gas
Oil
Bio-fuel
Coal

Source

CO_2 capture

Transport

Storage

SINTEF NTNU TNO innovation for life PROCED Algae-Tech

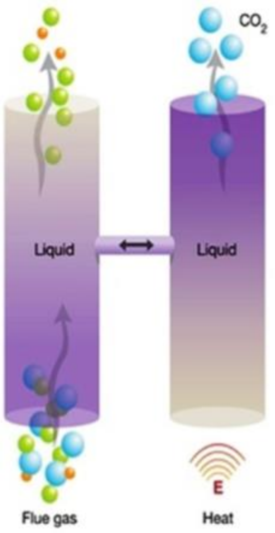
Earl Goetheer

Absorption Systems

- Enzyme based solvent system
- Bio-mimicking systems
- Combination with algae production

Inspired by nature

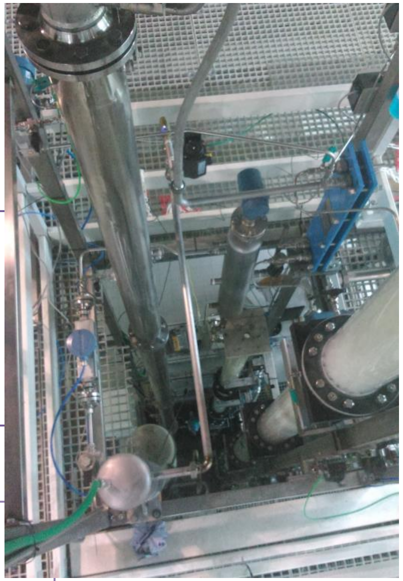
- Precipitating solvent system
- Strong bicarbonate solvent system



Enzyme catalysis of CO2 absorption (led by Procede)

Idea

- Enzymes in solvents can drastically accelerate the capture of It's an environmentally friendly promotor.



Work in the project

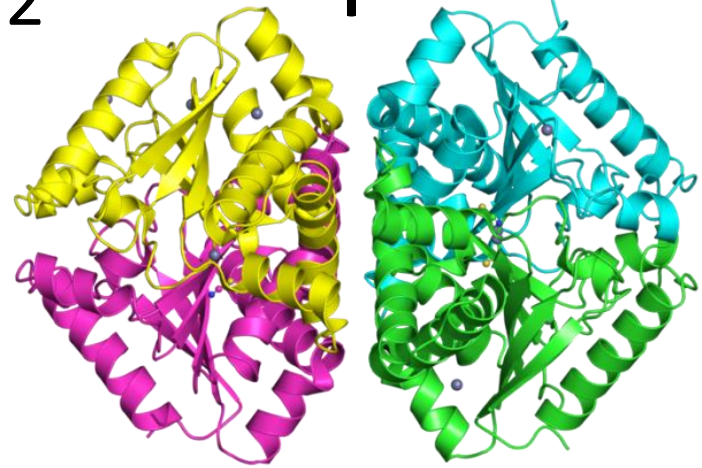
- Testing of carbonic anhydrase and develop and test an optimized process in a pilot plant

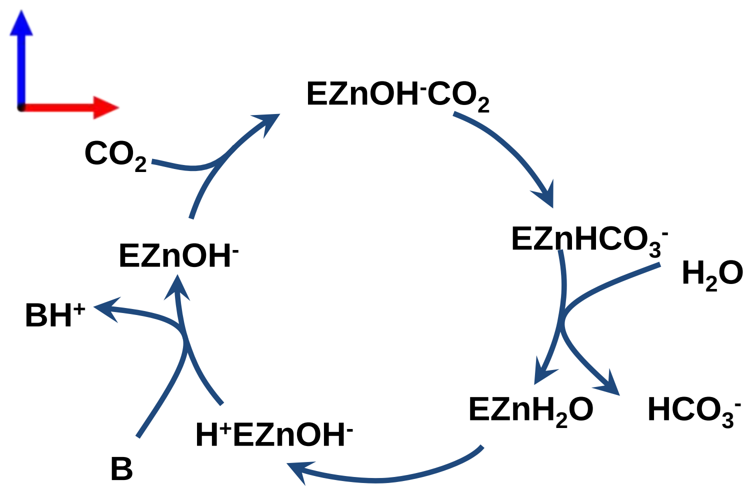
Challenges for this technology

- Enzyme stability throughout the process and separation of the enzymes prior to desorption due to the high temperature

Catalysis of CO_2 absorption

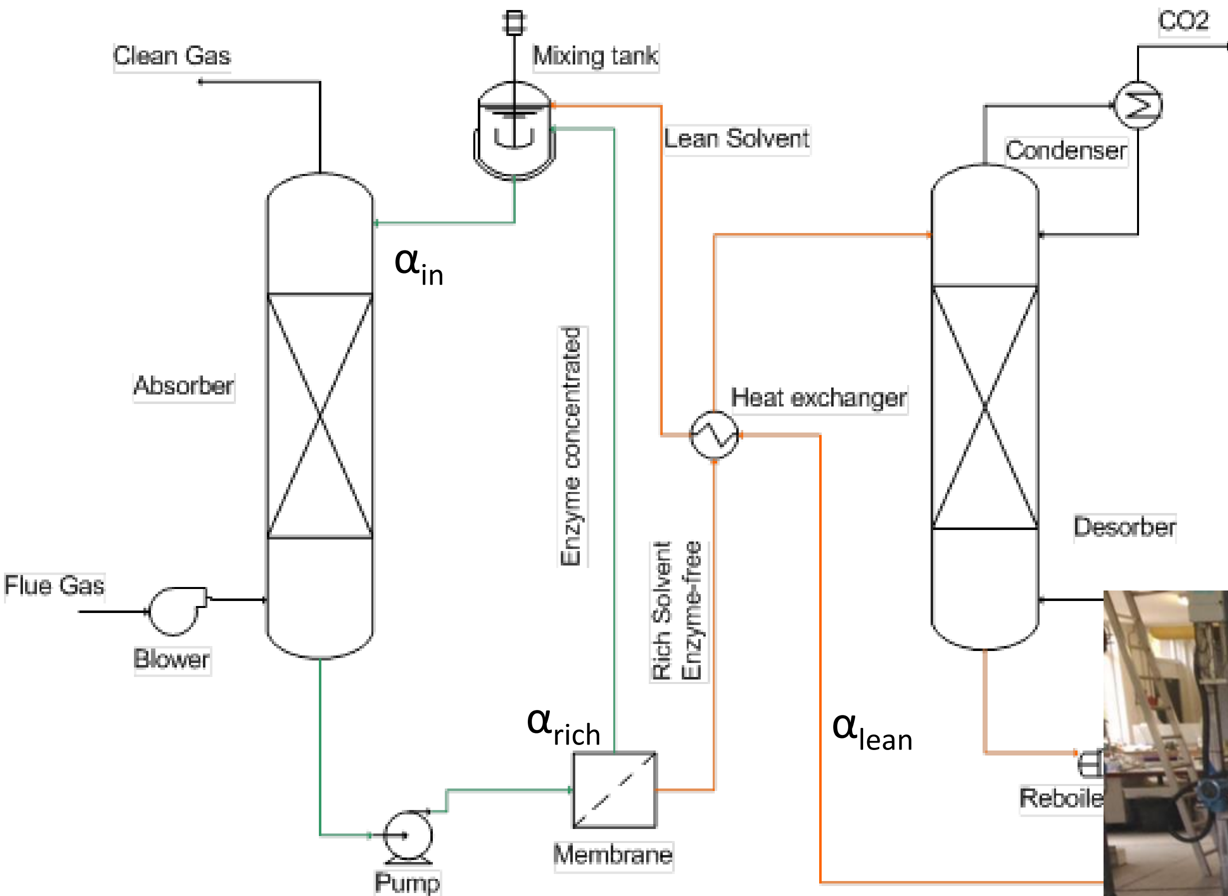
- Carbonate and tertiary amine solutions too slow for CO_2 capture → add catalyst
- Carbonic Anhydrase
  - Found in almost all living organisms, e.g. to facilitate CO_2 transport out of tissues
  - Directed evolution of β-class *Desulfovibrio vulgaris* to form tetrameric enzyme as developed by Codexis
  - However: low temperature resistance (< 60°C)
- Keep catalyst in absorber part of capture unit





Alvizo *et al.* *PNAS* **111 (46)** 2014, pp. 16436

Procede Pilot set-up



PROCEDE

Conclusions towards Objective

- ✓ Enzyme not degraded by stripper
  - Successful pilot demonstration of enzyme-enhanced CO_2 capture
  - Membrane unit successfully kept enzymes from stripper
    - No drop in enzyme activity during campaign
    - 2nd separation to prevent the permeated amounts (5-7%) to be denatured?
    - Enzymes inventory intrinsically depleted due to cake-layer formation (membrane unit) and adsorption to packing (absorber)
  - Economic evaluation should prove whether investment in 2nd membrane unit and reduction in absorber length (CAPEX) justify (prevented) loss of enzyme inventory (OPEX)

- ✓ 10% improvement in energy performance
  - 11% SRD reduction with solvent @ + enzyme compared to Reference

Study of bio-mimicking systems (Led by SINTEF)

Idea

- Perform a fundamental study of CO2 binding mechanism in nature an determine processed for the utilization industry.

Work in the project

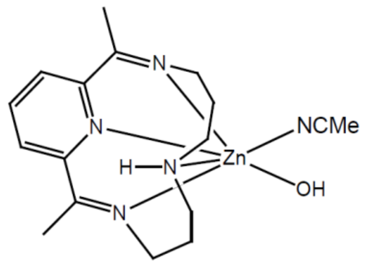
- Review and assessment of potential candidates. Perform screening experiments.

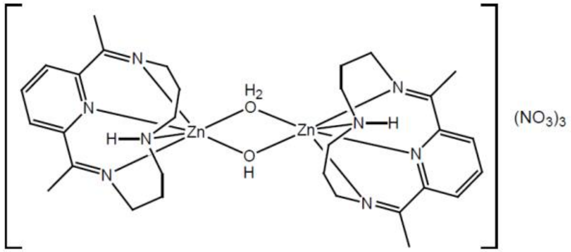
Goal

- Define possible systems.

Bio-mimicking systems

- Conversion of CO2 into bicarbonate is a slow reaction
- Carbonic anhydrase (CA) can significantly enhance the reaction.
- The use of CA is limited by its stability and activity abveo 50-60oC.





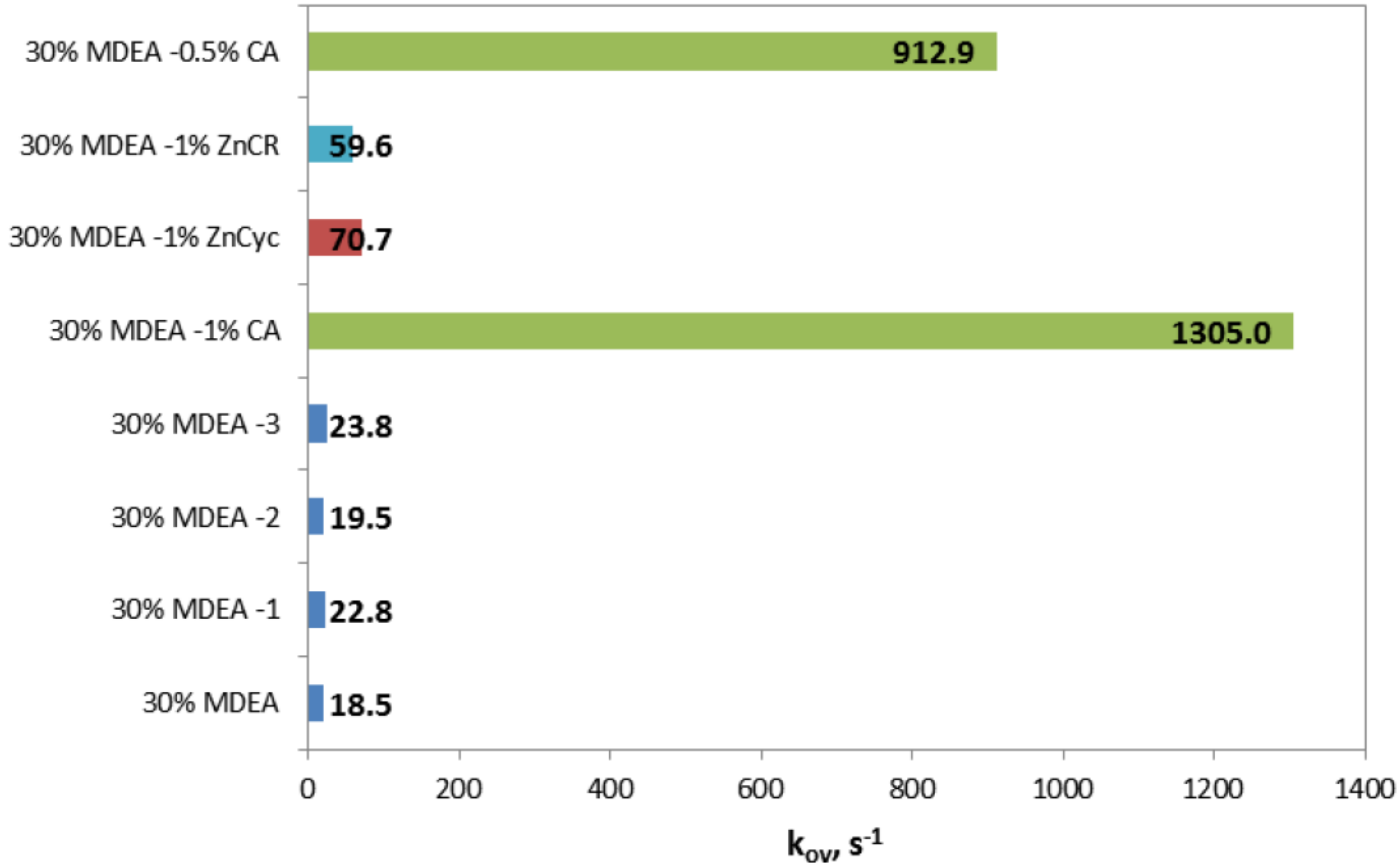
Options:

1) Development of thermostable CA enzymes
2) To mimic the enzymes → Bio-mimicking systems

Bio-mimicking systems

- Literature review showed that no data is available on the performance of bio-mimicking catalysts in the presence of amines.
- Two Zn-complexes chosen, synthetized and tested in a stirred cell.
  - Solutions: 30wt% MDEA+ 1wt% of biomimicking catalyst/CA at 25^{o}C

Results



30% MDEA -0.5% CA
912.9
30% MDEA -1% ZnCR
59.6
30% MDEA -1% ZnCyc
70.7
30% MDEA -1% CA
1305.0
30% MDEA -3
23.8
30% MDEA -2
19.5
30% MDEA -1
22.8
30% MDEA
18.5
0
200
400
600
800
1000
1200
1400
k_{ov}, s^{-1}

Integration of CO_2 absorption with utilization (by algae) (Led by TNO)

Idea

- Use algae to “eat” the CO_2 from the solvent loaded by the flue gas. Create biomass as a product.

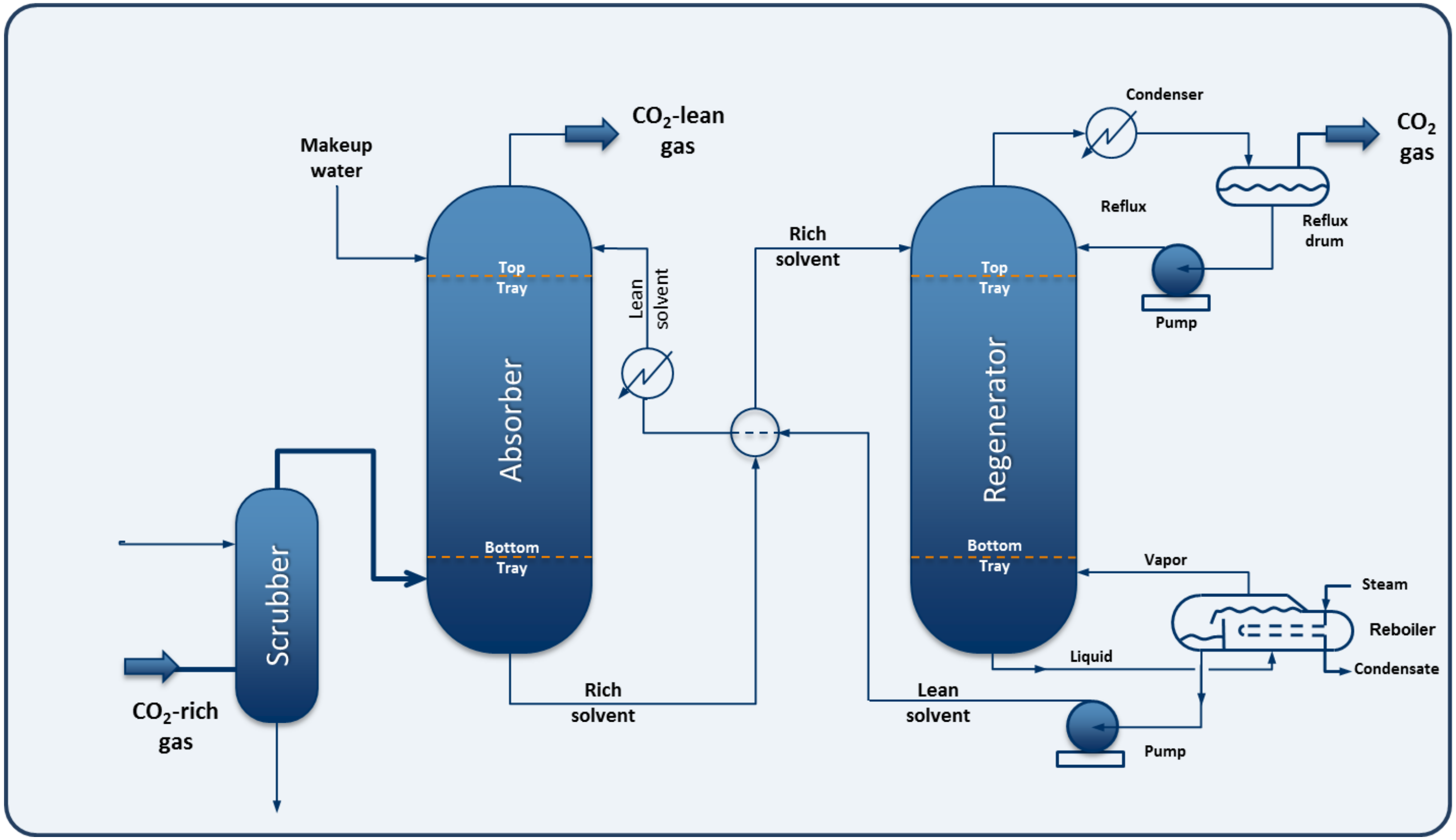
Work in the project

- Process development (algae strain, solvent, operation conditions). Test proof of concept with real flue gas.

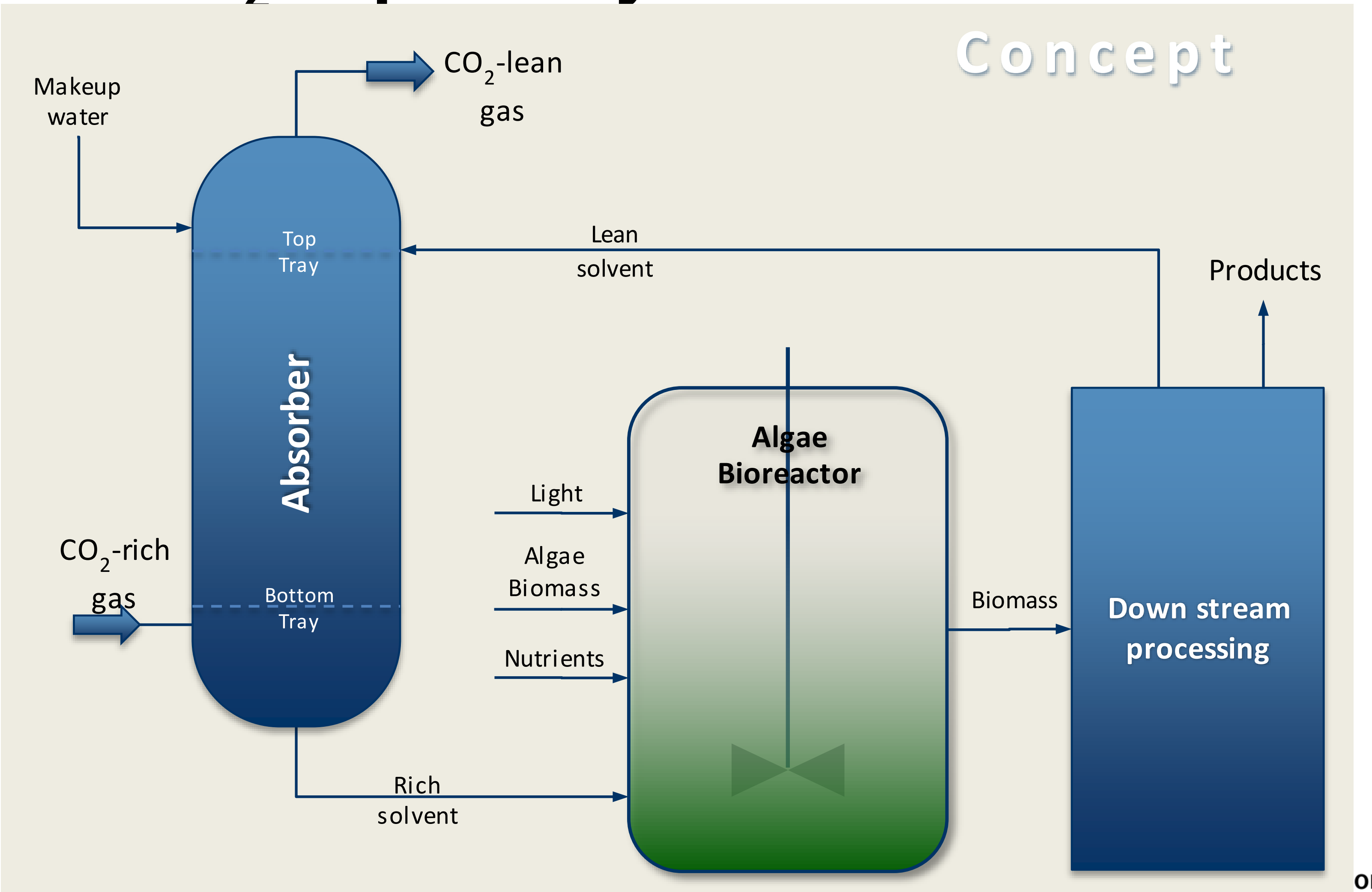
Challenges for this technology

- Solvent selection, optimize process conditions, resistance against impurities in flue gas.

Classic CO_2 capture system



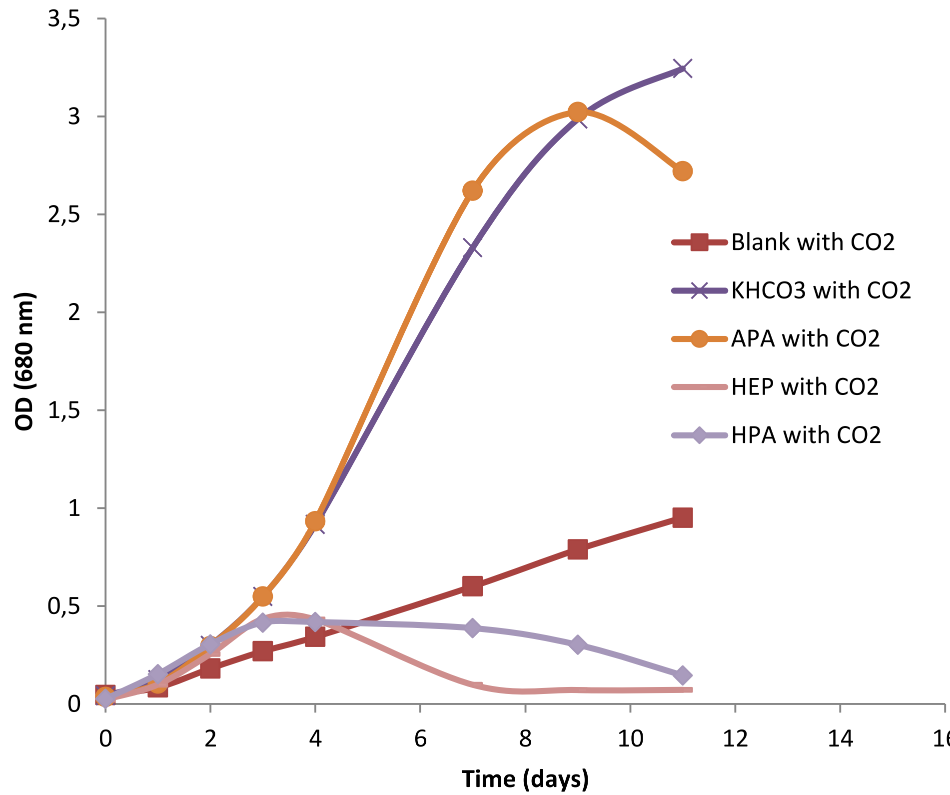
Novel CO_2 capture system



Which absorption solvent?

A selection of solvents was screened in batch experiments:

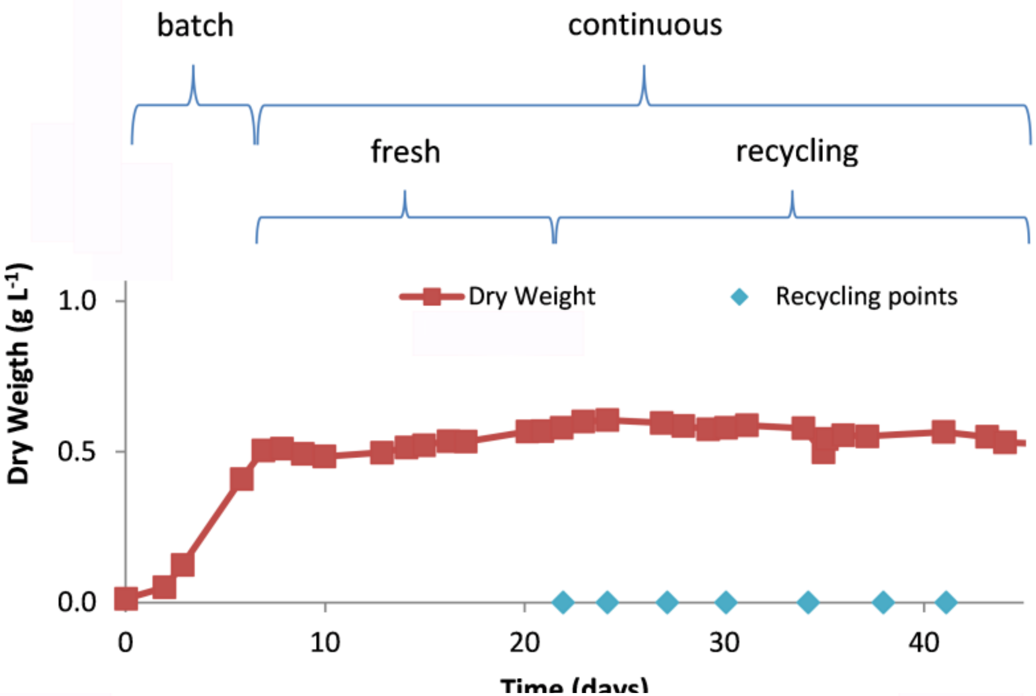
- APA and $KHCO_3$ performed best.
- $KHCO_3$ was selected (natural, cheap, high solubility)



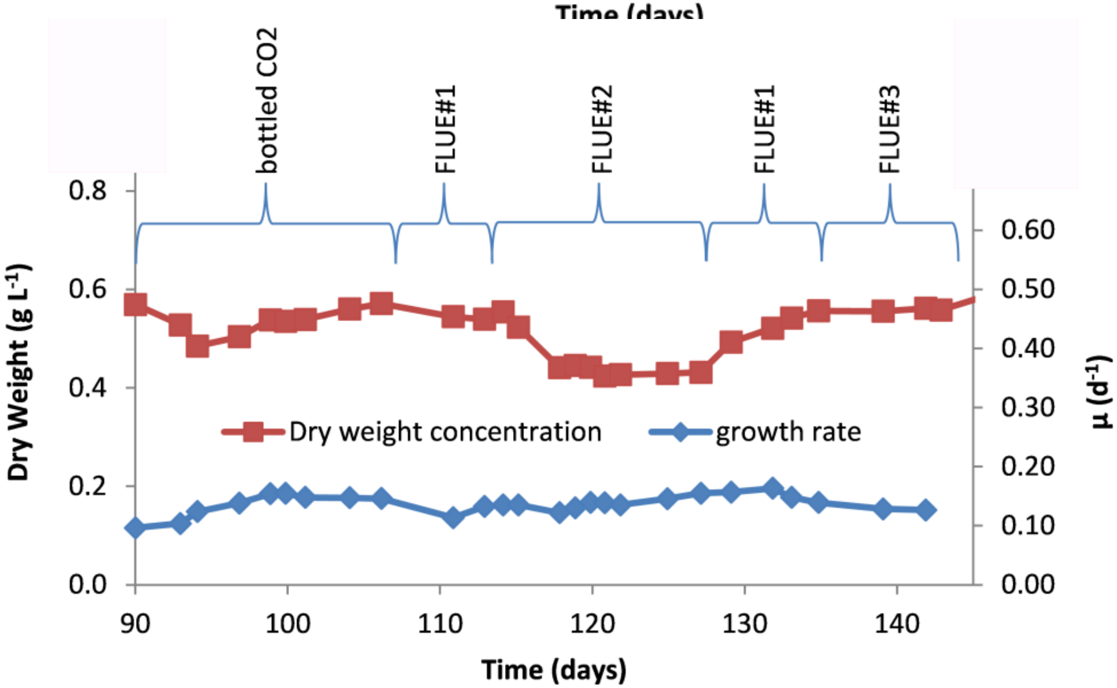
APA	N-(2-Amionoethyl)-1.3-propanediamine
HEP	1-(2-Hydroxyethyl)-Piperazine
HPA	bis(2-hydroxypropyl)amine (Diisopropanolamine)

Media and feeding

Harvesting



- Algae were successfully grown continuously.
- Solvent was recycled during 20 days without decline in productivity.



- Algae grew successfully on CO_2 from flue gas.

Multiple patents have been filed on the process technology

TNO is working on an Algae demo at refinery of Aruba)

Strong bicarbonate forming solvents (Led by NTNU)

Idea

- Bicarbonate forming solvents with high pKa will accelerate reaction kinetics and allow for lower regeneration temperature.

Work in the project

- Screening activity to find promising candidates for detailed studies.

Challenges for this technology

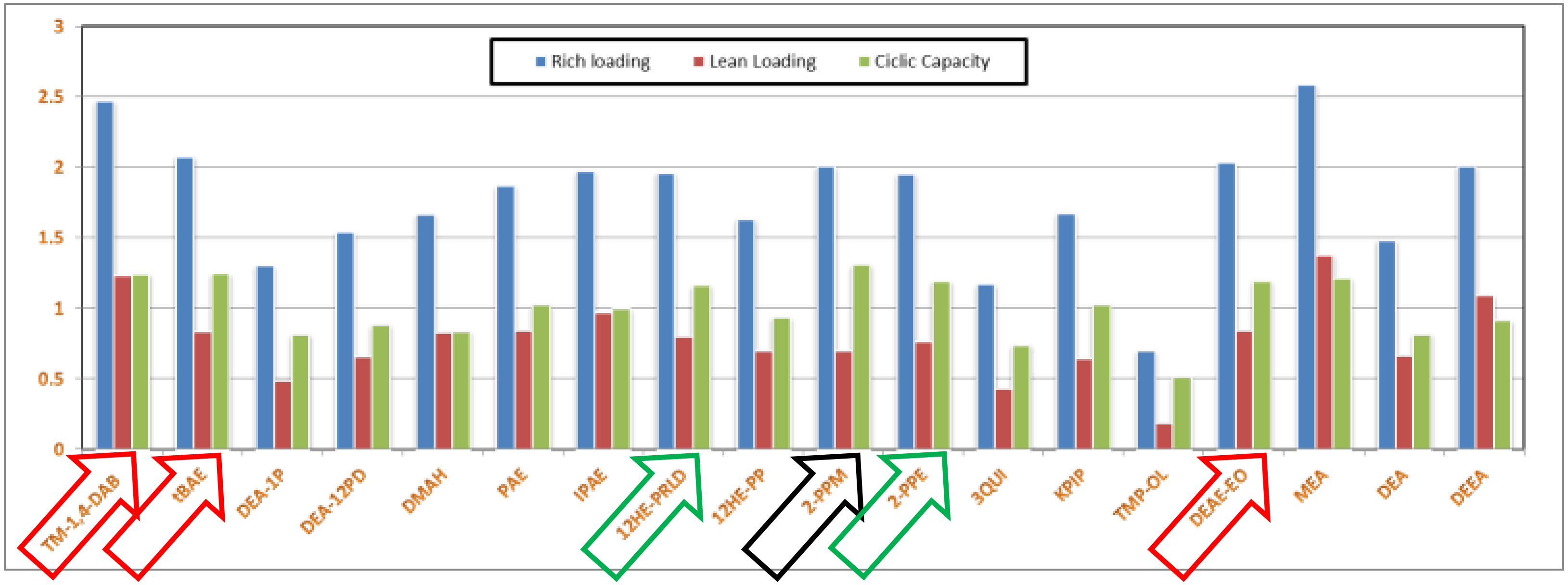
- There are many candidates. Low absorption rates might require a promotor (investigate connection with the enzyme task)

Solvent screening

- 15 strong bicarbonate forming solvent candidates tested for absorption and desorption capacity
  - Two solvents selected for further characterization

- 6 different promoters tested for selected bicarbonate forming solvents to increase the absorption rate.
  - Three different blends characterized.

Screening of bicarbonate forming solvents

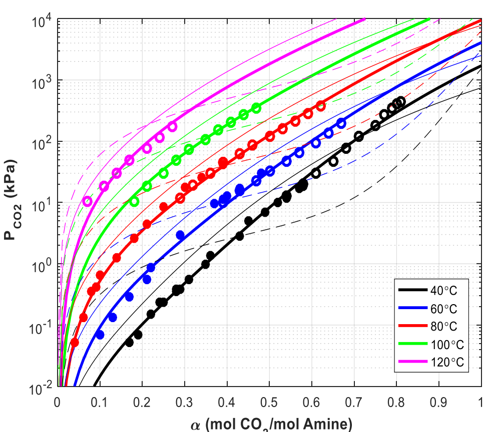


- 6 solvents were had cyclic capacity comparable to MEA 30 mass%
- 3 solvents have foaming tendency (Red arrows)
- 1 solvent has high a melting point (Black arrow)

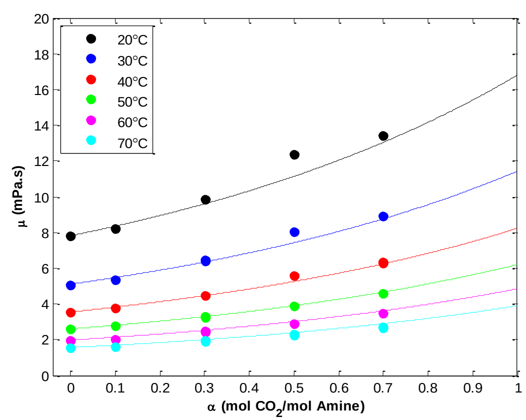
  → 12HE-PLRID and 2-PPE selected (green arrows)

Solvent characterization

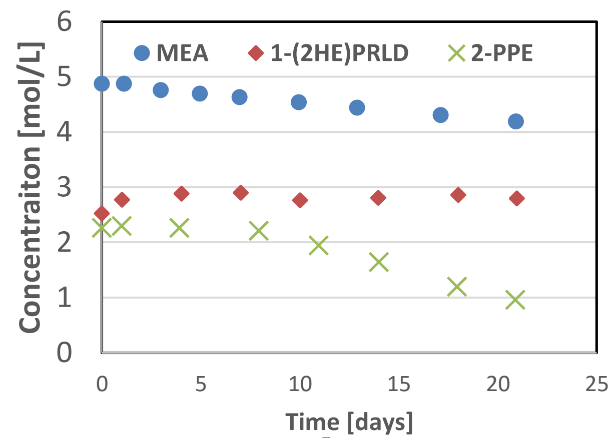
- Phase equilibrium (VLE) at 40-120 °C
- Heat of absorption
- Density and viscosity
- Oxidative and thermal degradation of amines
- Eco-toxicity and biodegradation of amines (selected systems)
- Kinetics (selected systems)
- Energy consumption estimated using CO2SIM



VLE



Viscosity

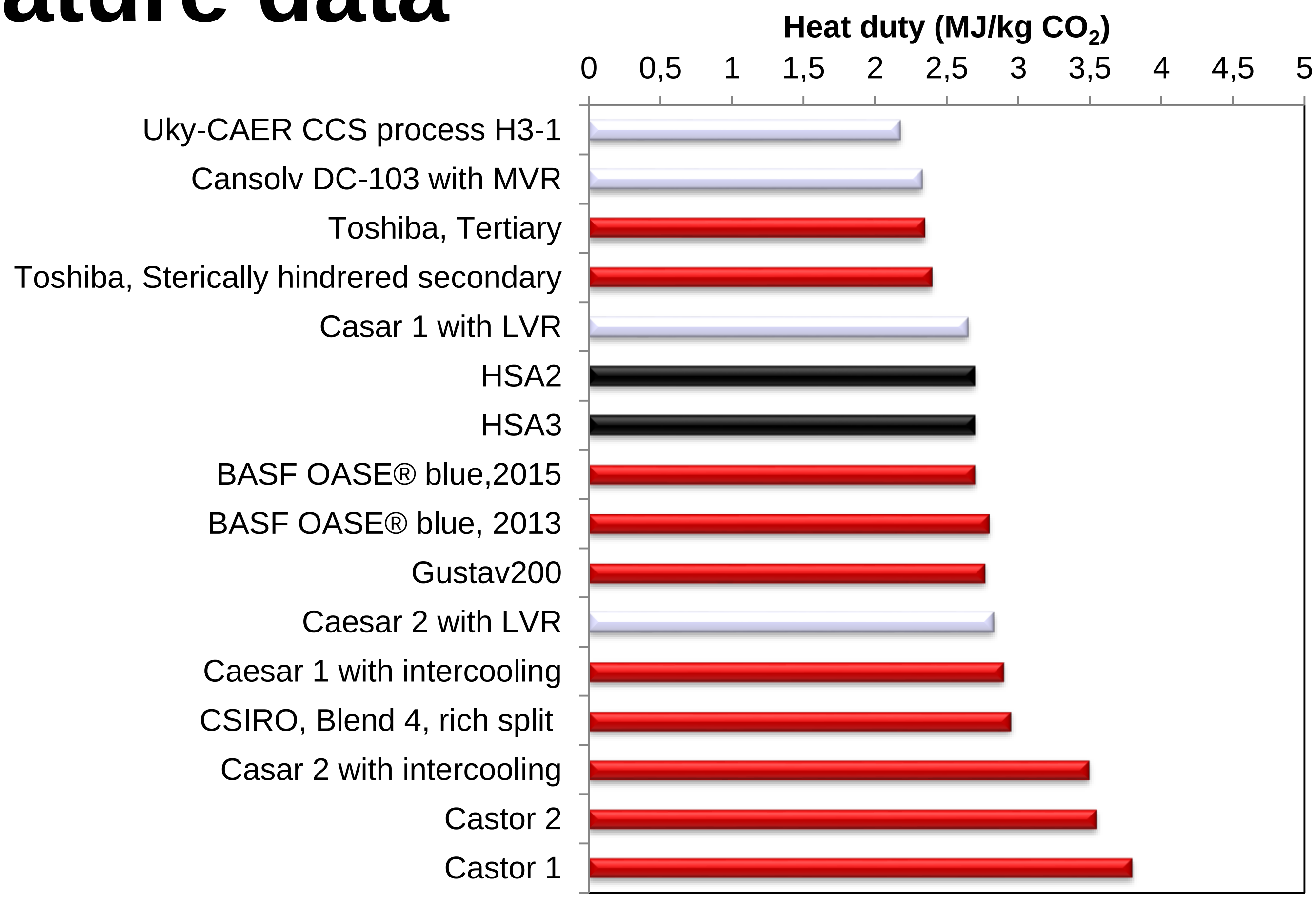


Degradation

Process simulations were performed to find the energy consumption

	Capture efficiency (%)	MJ/kg CO_2
30 wt% MEA	90	3.5
CESAR 1	90	3.0
HS1 (2-PPE)	90	2.8
HS2 (1-2(HE)PRLD)	75	2.7
HSA1	90	2.7
HSA2	90	2.9
HSA3	90	2.7

Developed solvents compared to literature data



Precipitation solvent systems (led by TNO)

Idea

- Regeneration of only the CO2 containing part of the solvent. Minimization of emission by the use of amino acids.

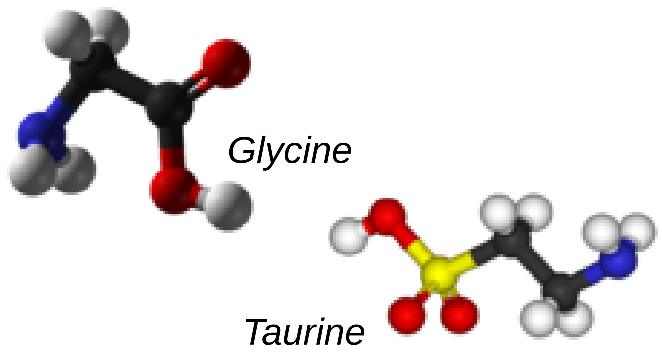
Work in the project

- Develop an process with the focus optimization of the absorber packing.

Challenges for this technology

- Process control with solids present and the handling of large scale slurries.

CO_2 absorption with amino acid salts



- ✓ Resistant to oxidative degradation
- ✓ Less waste generated products
- ✓ Zero emissions of active reactant
- ✓ Potential energy savings
- Limited solubility in water

Carbamate formation (primary and secondary amines)

$$CO_2 + 2\ {}^{-}OOC\text{-}R\text{-}NH_2 \leftrightarrow {}^{-}OOC\text{-}R\text{-}NH\text{-}COO^{-} + {}^{-}OOC\text{-}R\text{-}NH_3^{+} \quad (1)$$

amine — *carbamate* — *protonated amine*

Carbamate hydrolysis

$${}^{-}OOC\text{-}R\text{-}NH\text{-}COO^{-} + H_2O \leftrightarrow {}^{-}OOC\text{-}R\text{-}NH_2 + HCO_3^{-} \quad (2)$$

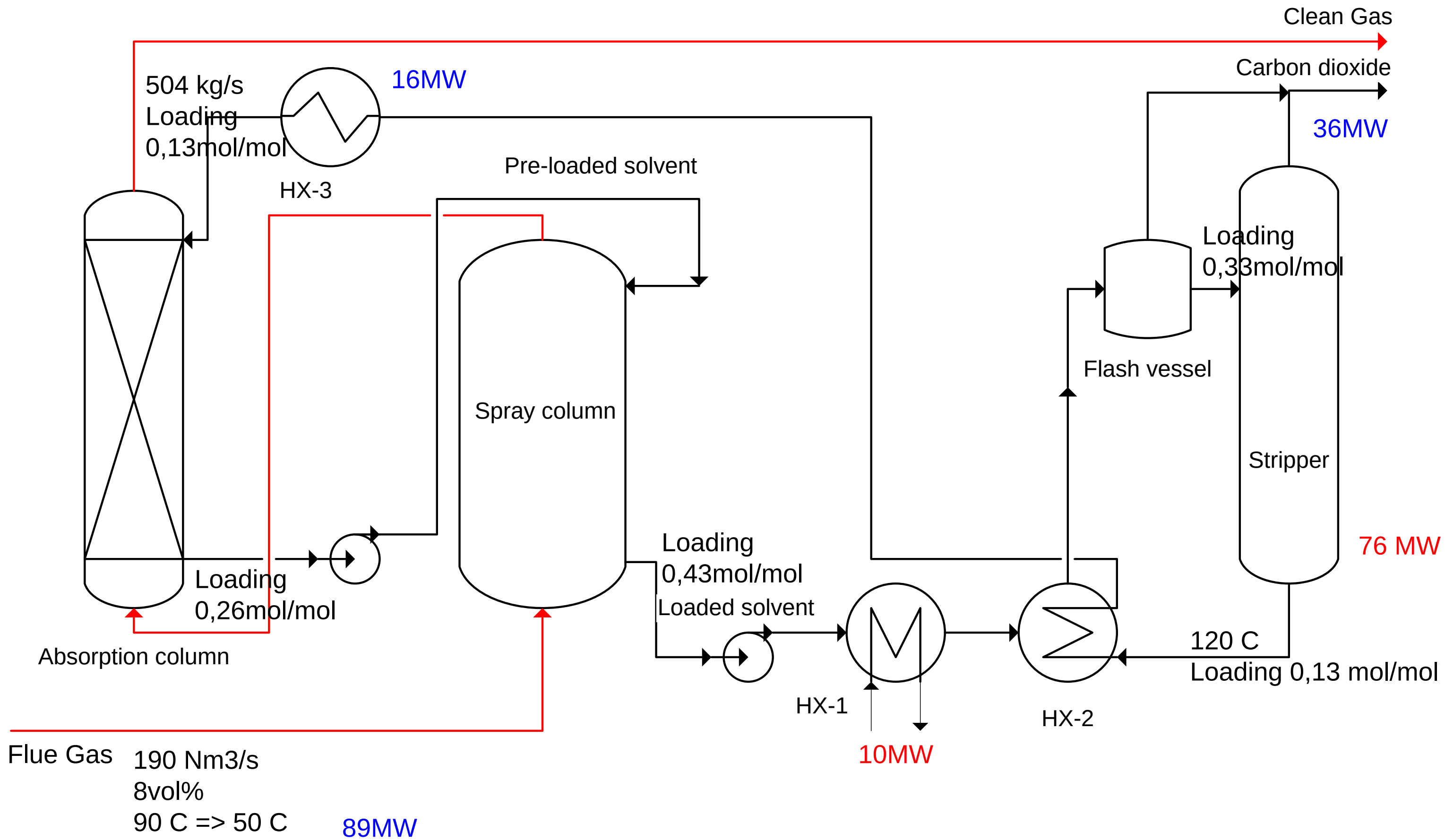
carbamate — *amine* — *bicarbonate*

Bicarbonate formation (tertiary amines, sterically hindered secondary amines)

$$CO_2 + {}^{-}OOC\text{-}R\text{-}NH_2 \leftrightarrow {}^{-}OOC\text{-}R\text{-}NH_3^{+} + HCO_3^{-} \quad (3)$$

amine — *protonated amine* — *bicarbonate*

DECAB Process
(Design & Modelling Results)

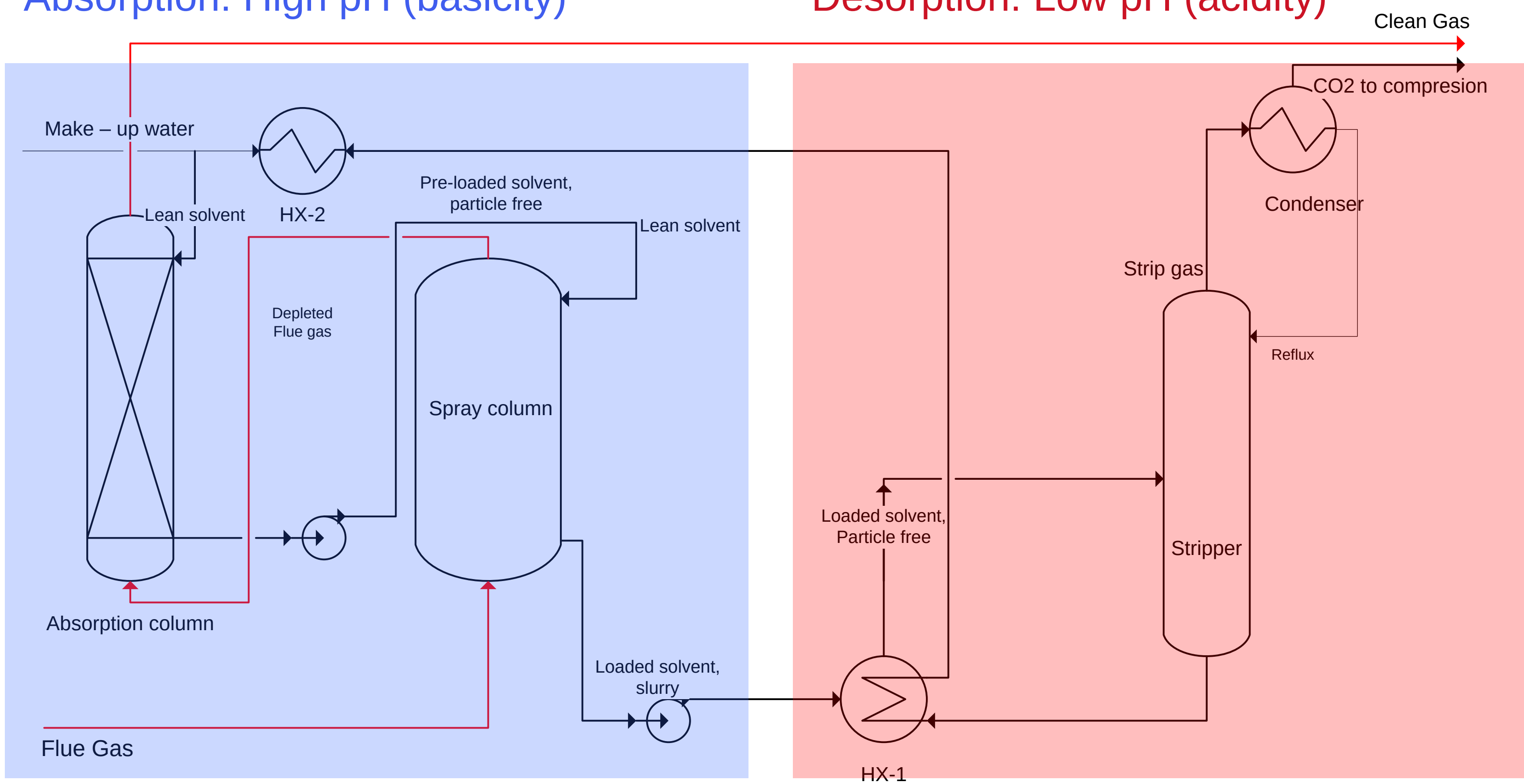


From DECAB to DECAB+

Conditions to enhance absorption and desorption

Absorption: High pH (basicity)

Desorption: Low pH (acidity)



The concept seems technical feasible

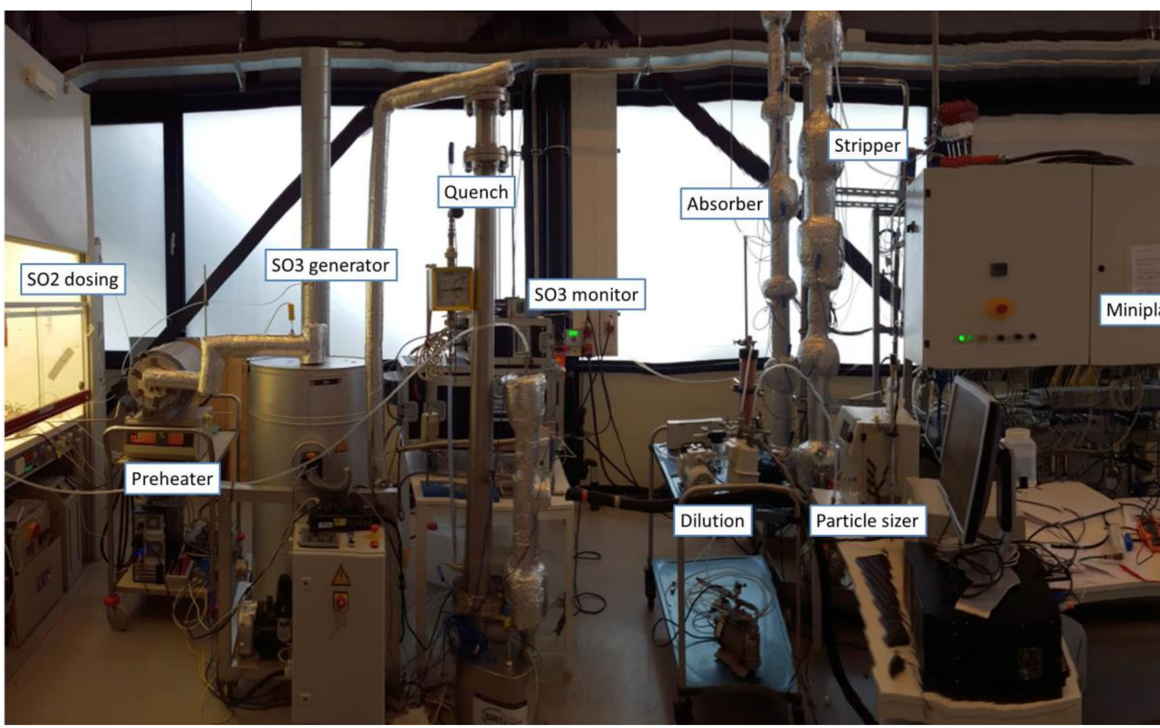
Absorber packing material selection can cope with precipitating materials

Thermodynamic model has been constructed based a.o. calorimetrical data

Preliminary flow sheet calculations of the absorption process, using a black-box approach for all process units, predict specific reboiler duties in the range of 2.4 to 2.5 GJ_{th}/ton CO_2 for CO_2 product pressures around 1 to 2 bar

Validation started

- 2 weeks continuous tests in an absorber-desorber configuration in a mobile mini-plant setup



Conclusions

- HiPerCap has advanced 5 different absorption technologies
- Fundamental knowledge on (catalysed) bicarbonate formation obtained
- Biomimicking strategy created valuable insights leading a.o. to demonstration plants in the Caribean
- Two candidates have shown based on energy numbers good potential:
  - Strong bicarbonate forming system HSA2
  - Precipitating solvent system

Acknowledgements