Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO_2) Capture

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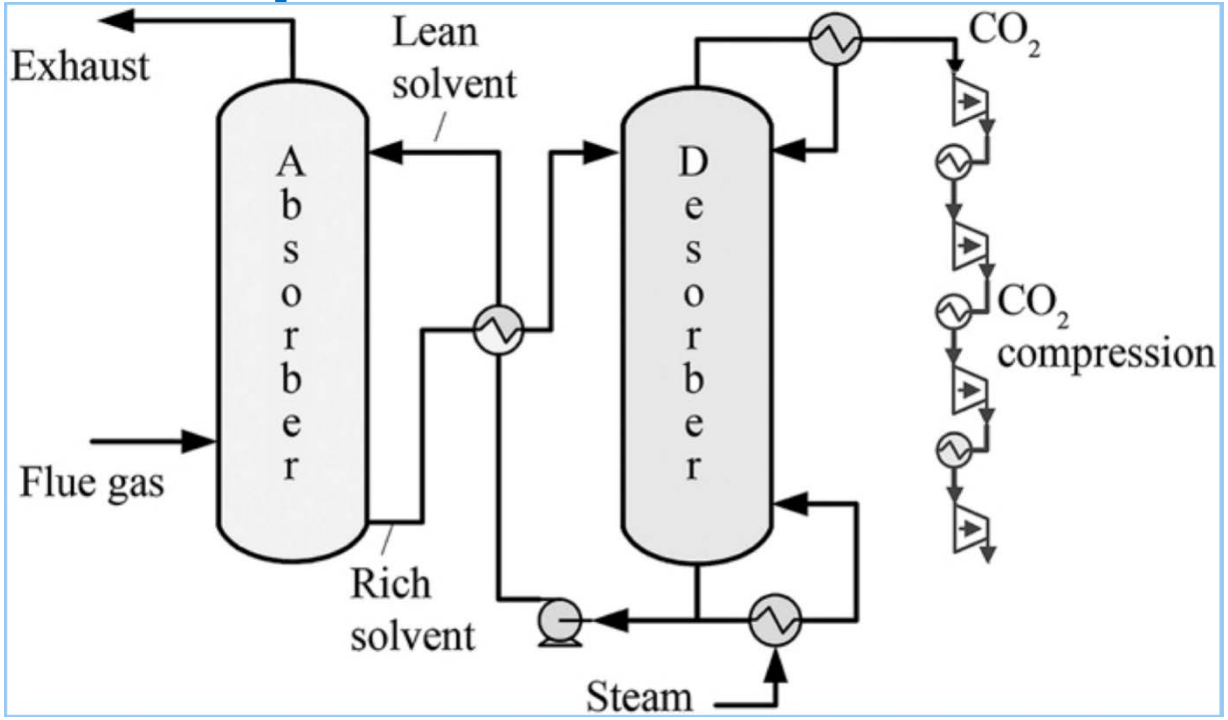
Conceptual Process Overview



- Effectiveness of a full scale CO2 separation/ purification from flue gas process will have the challenges:

  - Overall flow of the absorbing material
    - Need a “high capacity” absorbent,
    - ideally: good ratio: mass of CO2/mass of absorbent

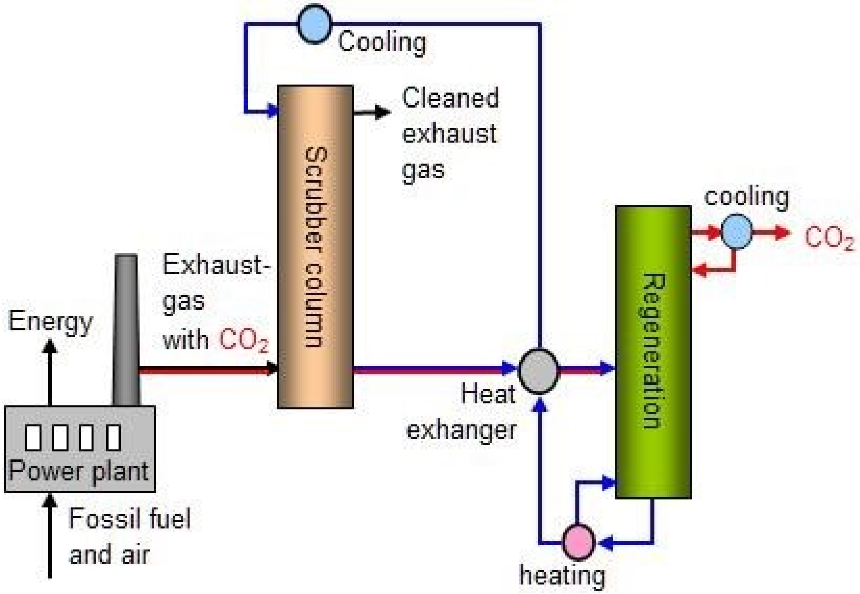
  - Energy/heat required to reverse reaction and release the CO2
    - Higher reaction enthalpy→ higher capacity… but more energy to reverse

  - Adiabatic heat rise in absorber
    - More “energetic” the absorption process, the more heat to be dissipated, but the higher capacity.
    - Either extensive internal heat removal or the absorbent must be flowing

Ionic Liquids for CO_2 capture

ILs are nonvolatile salts with low melting points, wide liquid phase operating ranges, and very wide range of reaction tunability.

- Potential advantages
  - Good thermal and oxidative stability
  - No evaporation into cleaned gas stream
  - One to one molar reactivity
- Potential disadvantages
  - High molar mass
  - Even our ”best[#]” ILs are more viscous that is ideal
- [#]AProtic Heterocyclic Anion (AHA) ILs offer solutions to these issues (Gurkan *et al*. 2010)



http://www.bellona.org/factsheets/1191913555.13

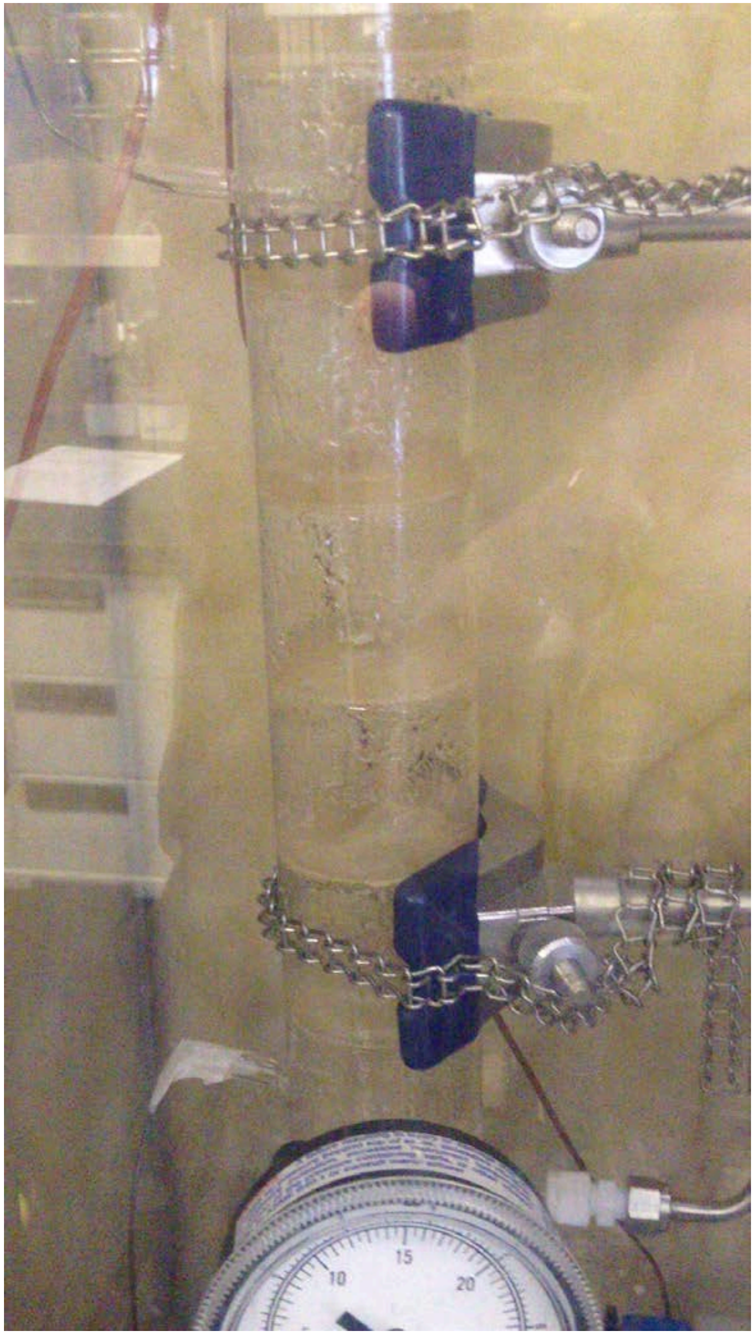
Previous effort from our group

”Molten” PCIL (phase change ionic liquid) flowing in a 10 cm tray column used for CO_2 absorption

For the process, the molten IL would have been a slurry.

In principle, this process could work but the “slurry” would be scary

There is a narrow temperature window for the viscosity of the liquid PCIL to, using a slurry would shrink this substantially.

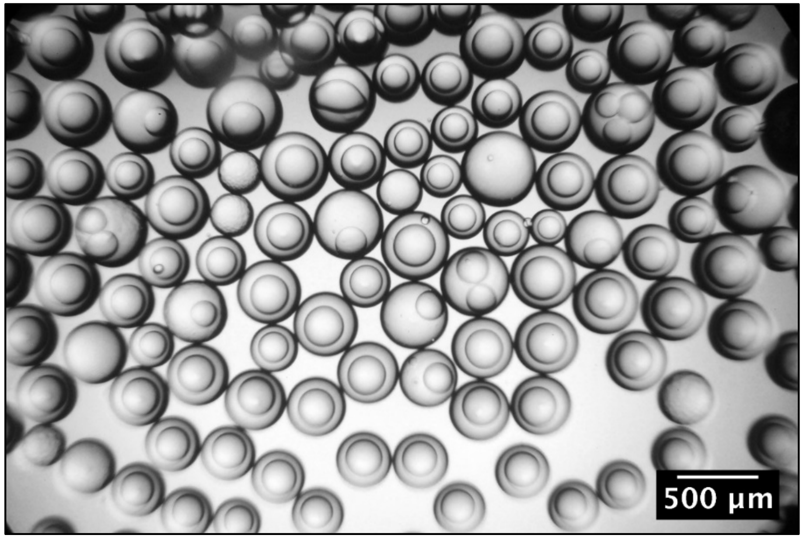


Challenge for any new process:

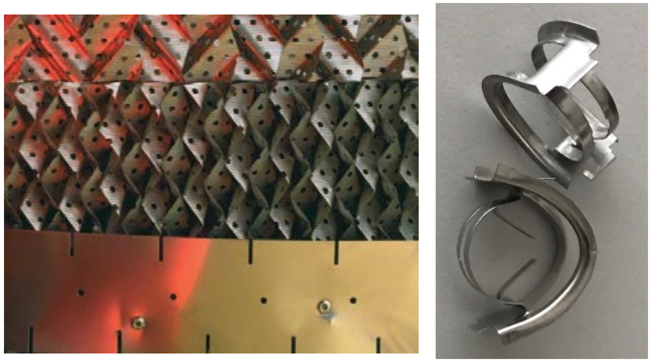
- In the CO_2 concentration range for flue gas, **aqueous amines** are the best commercial process
  - 10,000’s of sailors are kept alive on submarines
  - 1000’s of tons/hr of H_2 is produced using amine scrubbing.
- In terms of our process criteria:
  - Temperature is easily controlled even in a large absorber,
  - Continual improvements in capacity with clever chemistry, but still a ways to go.
  - Regeneration temperatures are high enough to allow heat integration with associated processes but the ΔH is large.

Microencapsulation

- Collaboration with Joshuah K. Stolaroff of LLNL:
- Encapsulate IL in a polymer coating
- Viscosity of IL is no longer directly a problem

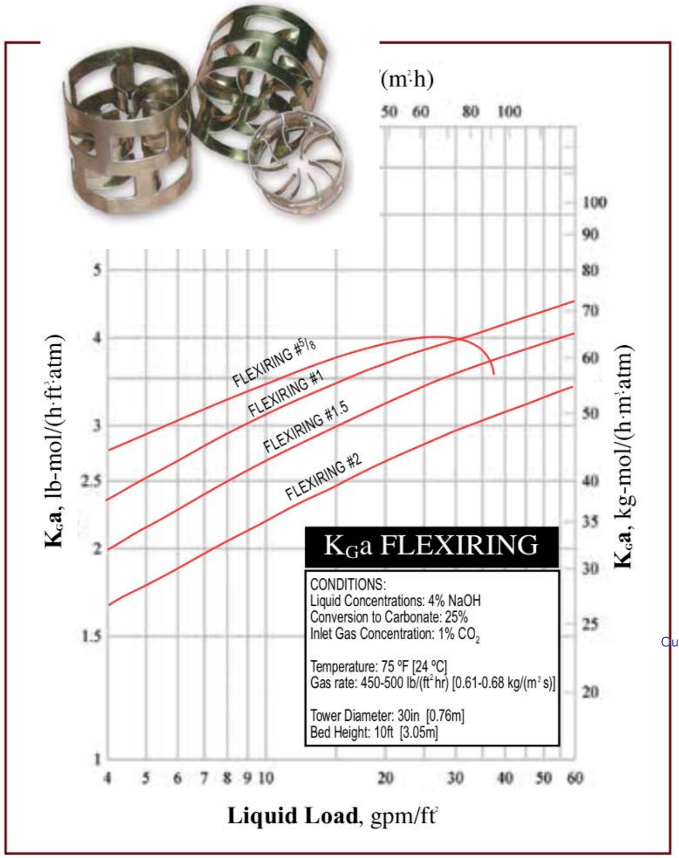


Operate absorber as fluidized bed



Random and structured packing

Absorber: Volumetric efficiency



CONDITIONS:
Liquid Concentrations: 4% NaOH
Conversion to Carbonate: 25%
Inlet Gas Concentration: 1% CO_2

Temperature: 75 °F [24 °C]
Gas rate: 450-500 lb/(ft²hr) [0.61-0.68 kg/(m² s)]

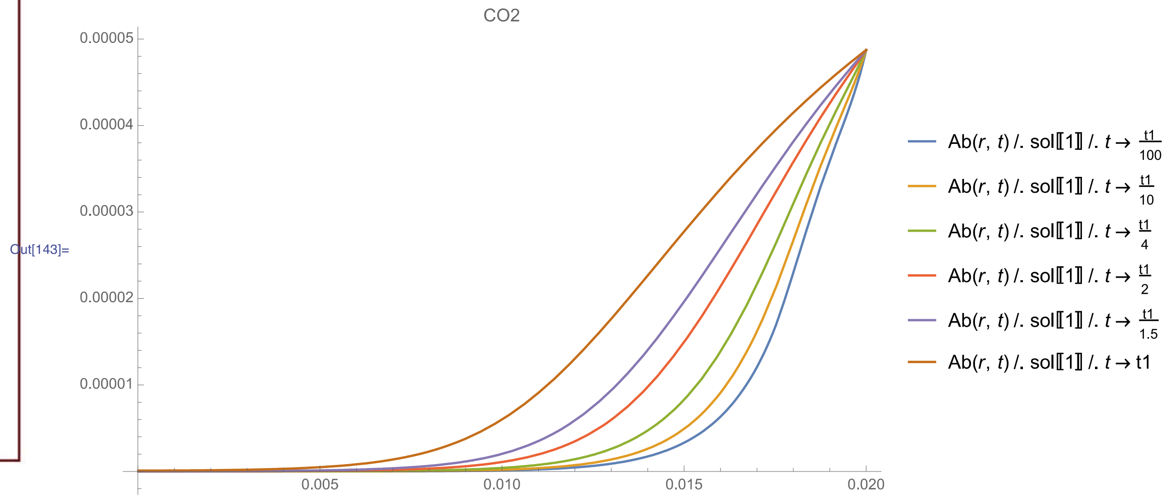
Tower Diameter: 30in [0.76m]
Bed Height: 10ft [3.05m]

Diffusion and reaction in capsule

$$\frac{\partial \mathrm{Ab}(r,t)}{\partial t} = \frac{\alpha_1 \frac{\partial}{\partial r}\left(r^2 \frac{\partial \mathrm{Ab}(r,t)}{\partial r}\right)}{r^2} - k_{\mathrm{on}}\,\mathrm{Ab}(r,t)\,\mathrm{Ag}(r,t) + k_{\mathrm{off}}\,B(r,t),$$

$$\frac{\partial \mathrm{Ag}(r,t)}{\partial t} = \frac{\alpha_2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial \mathrm{Ag}(r,t)}{\partial r}\right)}{r^2} - k_{\mathrm{on}}\,\mathrm{Ab}(r,t)\,\mathrm{Ag}(r,t) + k_{\mathrm{off}}\,B(r,t),$$

$$\frac{\partial B(r,t)}{\partial t} = k_{\mathrm{on}}\,\mathrm{Ab}(r,t)\,\mathrm{Ag}(r,t) - k_{\mathrm{off}}\,B(r,t)$$



Amine absorber: ~1 gmole/(m³ s)

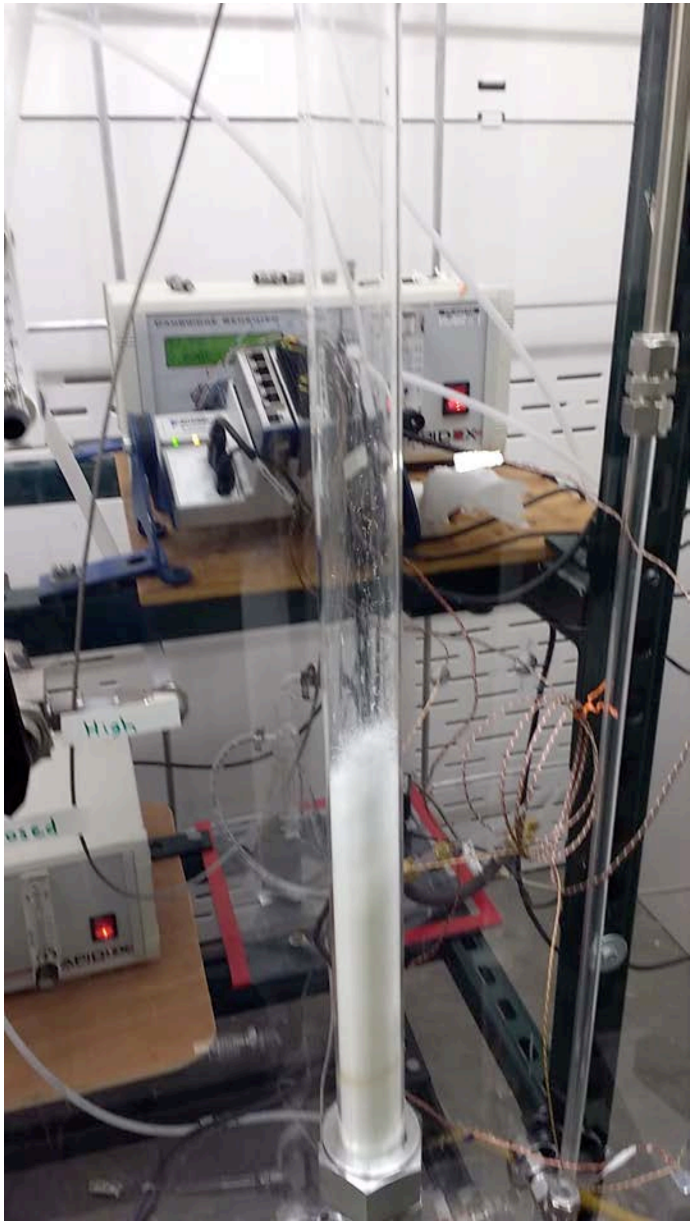
For 200 μm capsules: ~1 gmole/(m³ s)

Results from past 2 years

- Several refinements in the polymer to prevent chemical reaction with different ionic liquids
- Static, batch uptake of capsules is reversible and matches what is expected for neat IL
- Capsules can be fluidized in a laboratory scale (~2 and ~4 in diameter) columns
  - CO_2 absorption and recyclability of capsules commensurate with static, batch absorption-–desorption experiments.
- Modeling efforts can predict absorption rates
  - Internal mass transfer control

Laboratory Scale Unit

- Video of capsules in 6 cm column, V = 12 cm/s



LSU – Mass Transfer Measurements

Total Flow Rate (liters/ min.)	Composition (vol % CO_2)	P_{Co2} (bar)	Temp (C)	Absorption Time (s)	Regen-eration Amount (L CO_2)	(mol CO_2)	Regen Temp (C)	mol ratio	k (cm/s)
3.3	45.67	0.547	71	1236	0.229	0.0096	114	0.65	1.5E-05
3.3	44.55	0.537	73	433	0.224	0.0094	106	0.64	2.2E-04
3.3	45.93	0.561	78	733	0.23	0.0096	109	0.66	3.1E-05
3.3	44.74	0.533	69	673.5	0.228	0.0095	108	0.65	8.8E-05
3.3	45.22	0.542	71	356	0.243	0.0101	114	0.69	1.0E-04

Recyclability (5 cycles) shows consistent CO_2 capacity of 0.66 +/- 0.02 moles CO_2/mol PCIL

Rate Based Model

- Comparison of measured vs. predicted mass transfer flux in a fluidized bed of microcapsules containing NDIL0309

Measured mass transfer flux (mol/(m^2·s))	Predicted mass transfer flux (mol/(m^2·s))
4.84×10^{-4}	3.33×10^{-4}

True prediction (no adjusted parameters)

Excellent agreement

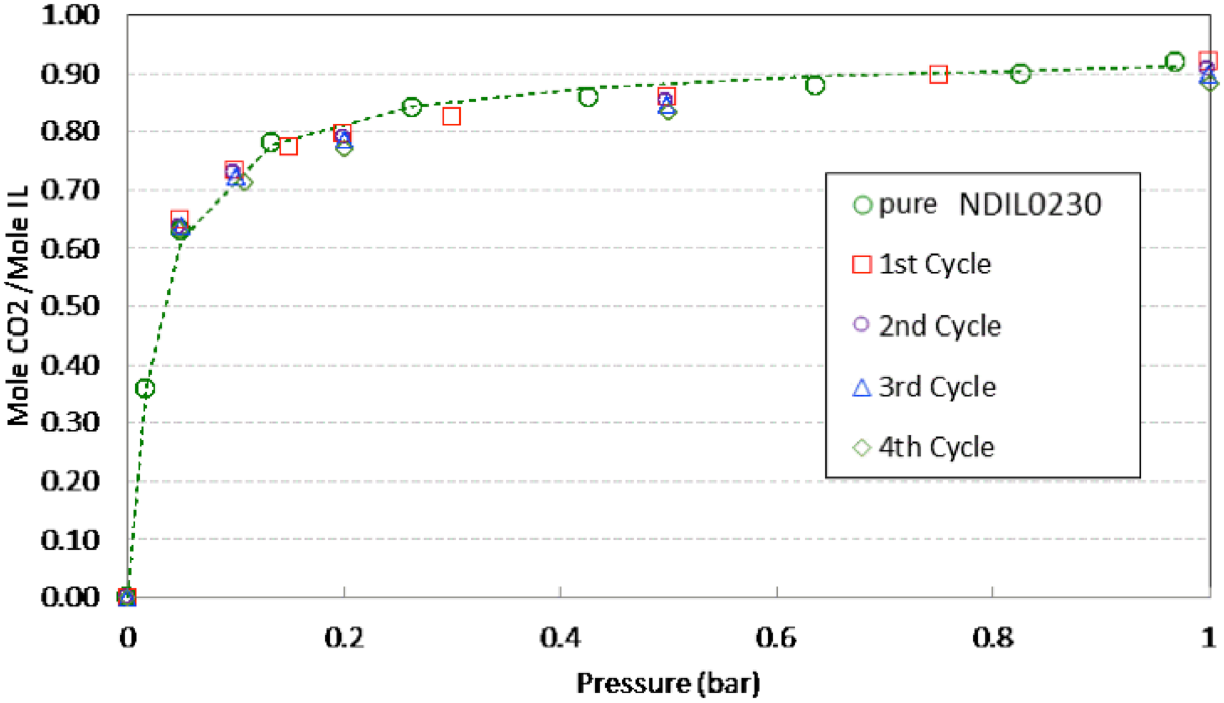
Confidence in model

- Absorption temperature = 70 °C; Capsule diameter = 560 μm; Exposure time = 100 s

New results

- Recyclability of capsules in the presence of water
- Additional modeling comparisons with mass transfer rates for fluidized capsules
- Preliminary results for effect of NO and SO_2 on CO_2 absorption
- Overall conclusion of optimal heat of absorption.

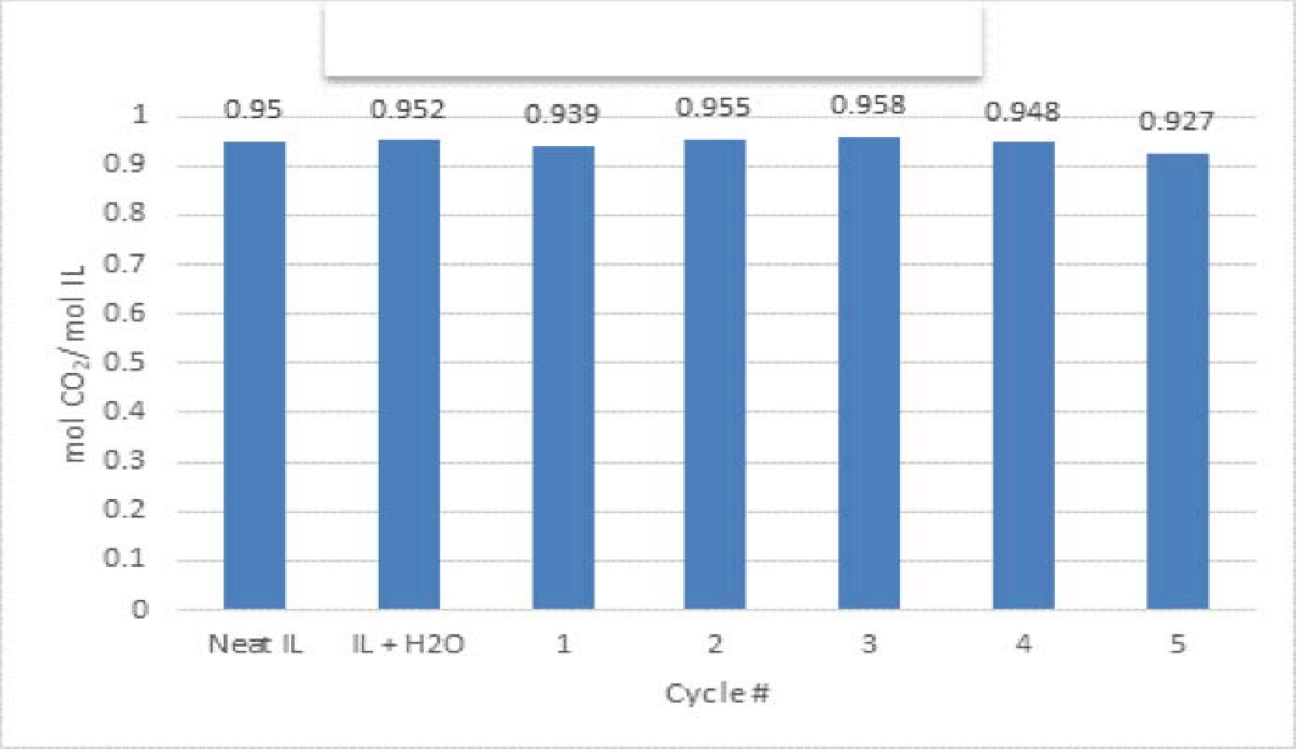
Task 21: Recyclability and uptake is excellent even with water present



Corrected for physical CO_2 uptake by shell material

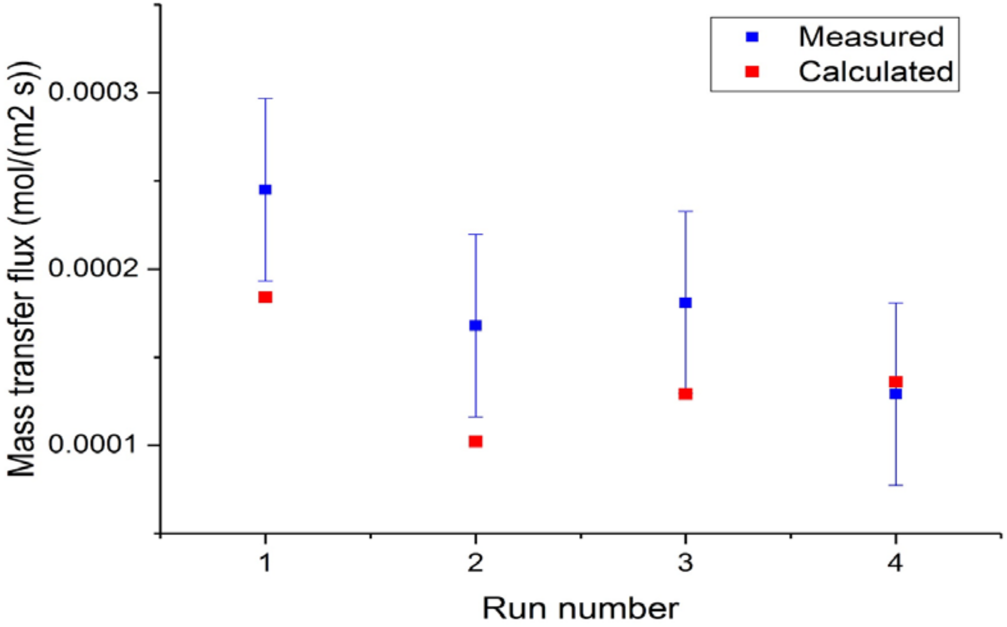
Meets CO_2 uptake criterion

CO_2 uptake recyclability of NDIL0230 capsules in the presence of water.



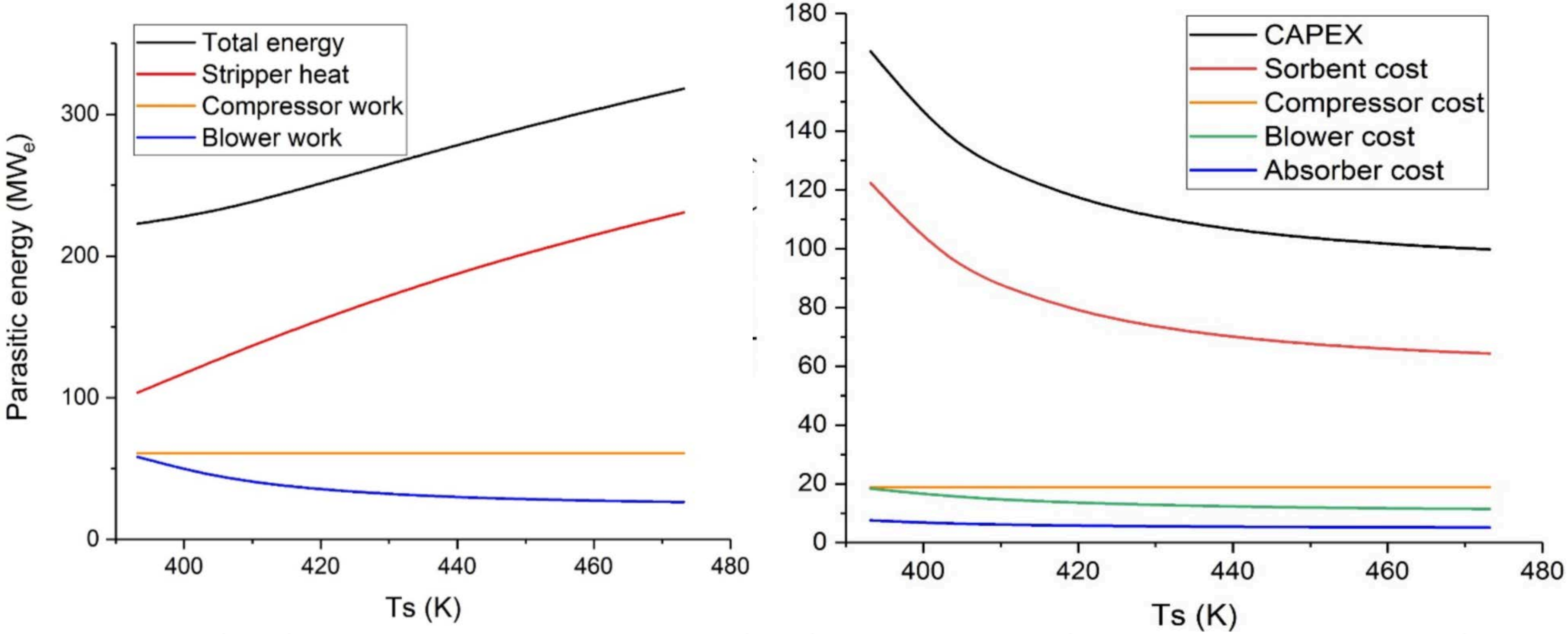
Task 22: Additional comparisons of experimentally measured and predicted CO_2 flux data for NDIL0309 microcapsules in laboratory-scale fluidized bed

- Particle size = 586 microns. Total surface area = 0.774 m^2. IL content = 65 wt% IL, assuming perfect drying.



	Run 1	Run 2	Run 3	Run 4
Temperature	74.5	77.6	72.7	71.7
Inlet Pressure (bar)	0.41	0.19	0.25	0.26
Inlet CO_2 (vol%)	13.44	13.49	13.33	13.70
Gas flow (L/min)	34.16	31.33	32.16	32.27

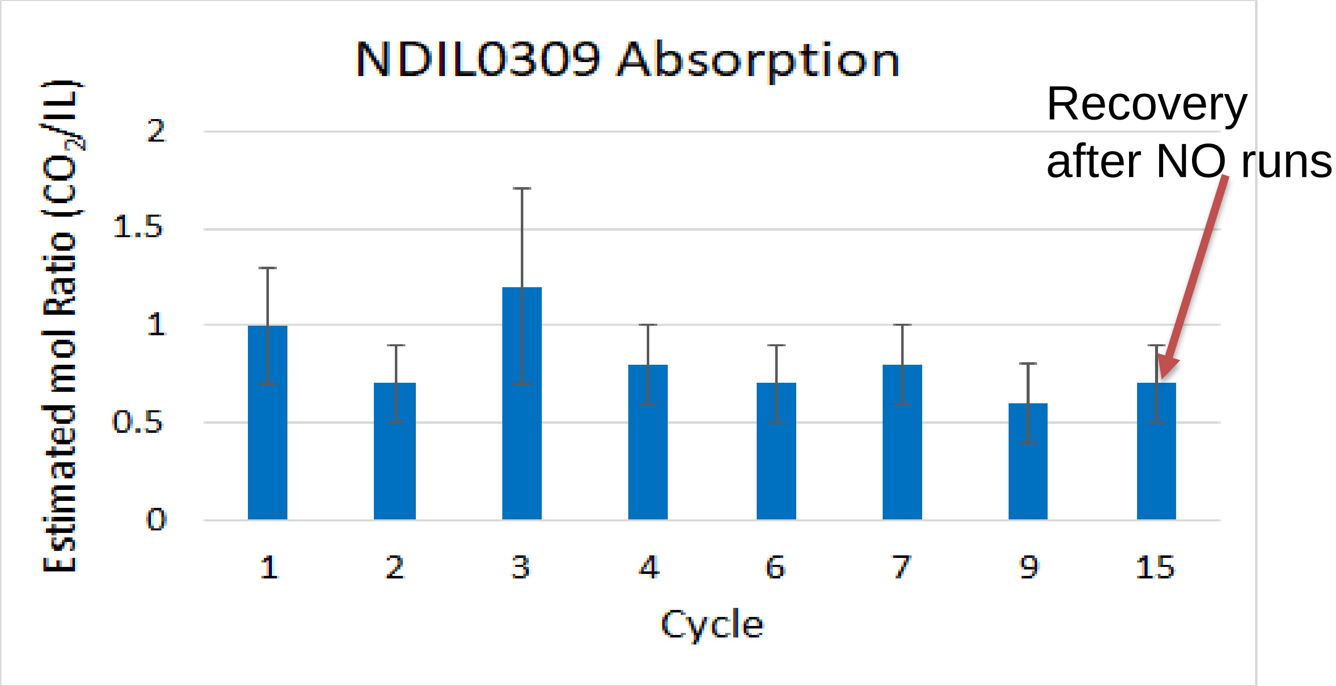
Task22:Operating/Capital Cost



absorber temperature = 293.15 K, absorber pressure = 1 bar, stripper pressure = 1 bar, heat of chemical absorption = −50 kJ/mol, entropy of chemical absorption = −130 J/(mol K), IL viscosity = 100 cP, weight fraction IL in capsule = 0.5, and microcapsule diameter = 200 micron. The IL cost was taken to be \$20/kg and the microcapsule shell material cost \$20/kg.

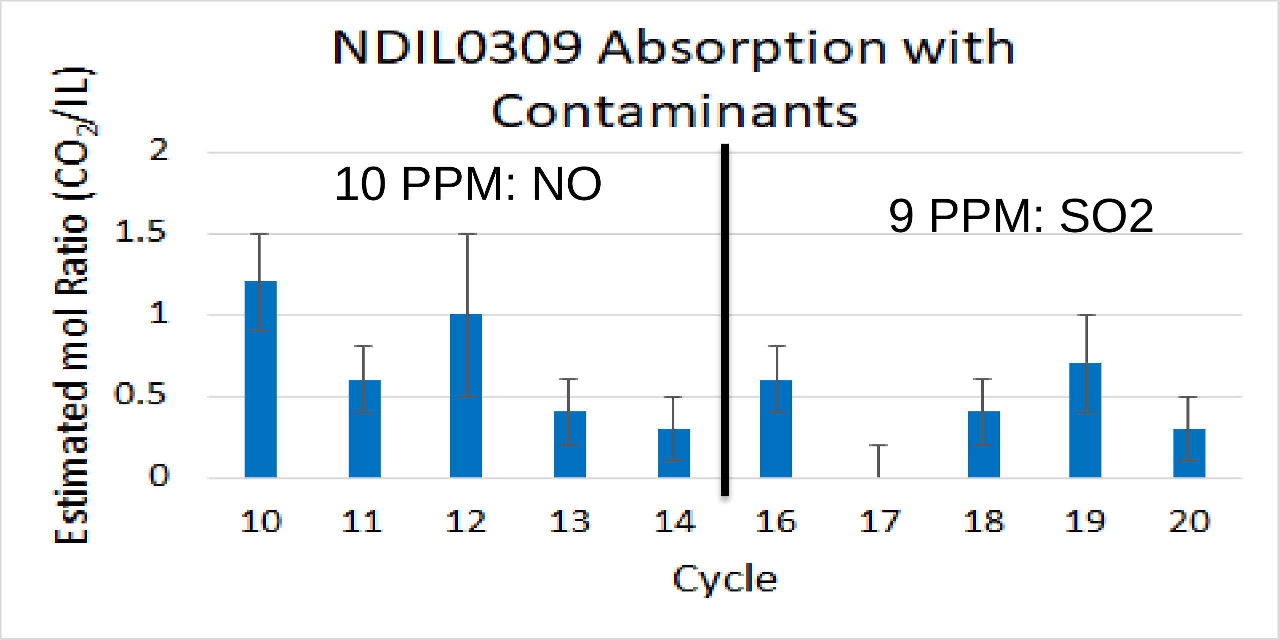
Task 19: Effect of Contaminants

- The fluidized absorber was used for multiple runs where the CO2-N2 mixture was spiked 10 PPM of NO or SO_2
- As would be expected from experiments with “neat” Ils, there was some degradation of absorption performance.



NDIL0309 Absorption

Recovery after NO runs



NDIL0309 Absorption with Contaminants

10 PPM: NO

9 PPM: SO2

Concluding remarks

- We have shown that polymer-encapsulated ionic liquids and phase change ionic liquids
  - Can be made chemically compatible in the presence of CO2 and water.
  - That these capsules can be fluidized and used to efficiently absorb CO2 in on a laboratory scale
  - That the mass transfer resistance is controlled by diffusion within the capsule (the polymers have a higher diffusivity than the Ils)
  - That we can model the absorption process and predict an optimal heat of reaction and an optimal stripper temperature
  - That this combination can be used successfully in the presence of water

- Experiments so far indicate that as with a neat IL, NO and SO2 compete for reaction sites, and hence reduce absorption performance.
  - Some of the degradation is reversible.

Acknowledgments

- David Lang
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