Discrete particle modeling of carbon capture using semipermeable elastic microcapsules

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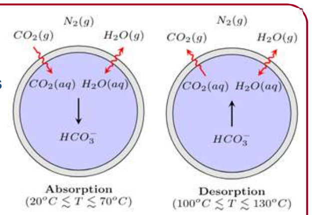
Introduction

Motivation

- New MECS technology[1] **combines benefits** of solvent and sorbent based capture.
- Carbonates are **benign, abundant, and cheap**! Good potential for temperature swing absorption (TSA) cycle.
- CFD can **explore process designs** and identify pitfalls.



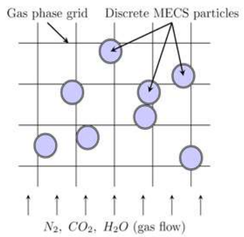
CCSI[2] Goal: *Enable device-scale predictive capability for CO_2 capture using MECS technology to accelerate development and deployment by industry.*

MECS considerations:

- Elastic, deformable shell
- Size/density changes
- Precipitation inside capsule
- Water loss/uptake
- Equilibrium reactions in solution

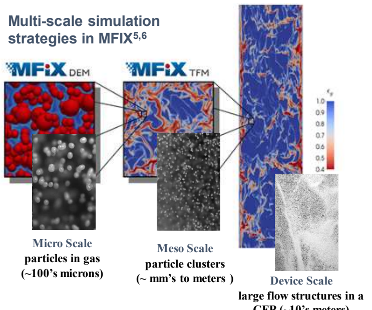
Approach

- Interphase coupling handled by **NETL's MFIX-DEM (CFD)**.
- Capsules are treated as discrete entities having particle-particle collisions.
- Develop physically-based heat, mass, momentum transfer models for MECS.
- Integrate basic data as CFD sub-models.



MECS represented as discrete particles in reactive gas flow.

Multi-scale simulation strategies in MFIX[5,6]



Chemically enhanced mass transfer:

$CO_2(g) \Leftrightarrow CO_2(aq)$

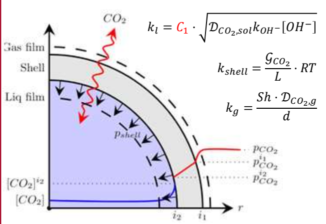
$$\dot{n}_{CO_2} = \frac{a}{RT} \cdot k_{ov,CO_2}(p_{CO_2} - H_{CO_2}[CO_2] - p_{shell})$$

$$k_{ov,CO_2} = \frac{1}{\frac{1}{k_{g,CO_2}} + \frac{1}{k_{shell,CO_2}} + \frac{1}{k_{l,CO_2}}\frac{H_{CO_2}}{RT}}$$

$$k_l = C_1 \cdot \sqrt{\mathcal{D}_{CO_2,sol} k_{OH^-}[OH^-]}$$

$$k_{shell} = \frac{\mathcal{G}_{CO_2}}{L} \cdot RT$$

$$k_g = \frac{Sh \cdot \mathcal{D}_{CO_2,g}}{d}$$



Model for CO_2 transfer (1/4 capsule shown)

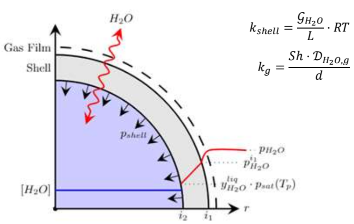
$H_2O(g) \Leftrightarrow H_2O(l)$

$$\dot{n}_{H_2O} = \frac{a}{RT} \cdot k_{ov,H_2O}(p_{H_2O} - y^{liq}_{H_2O} \cdot p_{sat}(T) - p_{shell})$$

$$k_{ov,H_2O} = \frac{1}{\frac{1}{k_{g,H_2O}} + \frac{1}{k_{shell,H_2O}}}$$

$$k_{shell} = \frac{\mathcal{G}_{H_2O}}{L} \cdot RT$$

$$k_g = \frac{Sh \cdot \mathcal{D}_{H_2O,g}}{d}$$



Model for H_2O transfer (1/4 capsule shown)

Chemistry of loaded carbonate solutions

NEW in-house solver for precipitating solvent equilibrium chemistry coupled to MFIX-DEM

- **Overall reaction**:
  $CO_2 + H_2O + CO_3^{--} \Leftrightarrow 2HCO_3^-$
- **Rate limiting step**:
  $CO_2 + OH^- \Leftrightarrow HCO_3^-$ with $r = k_{OH^-}[CO_2][OH^-]$
- Multiple equilibrium reactions in solution

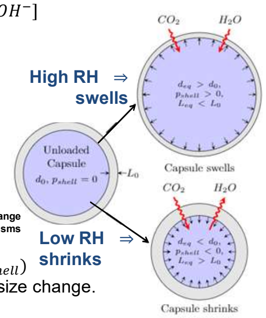
Capsule morphology

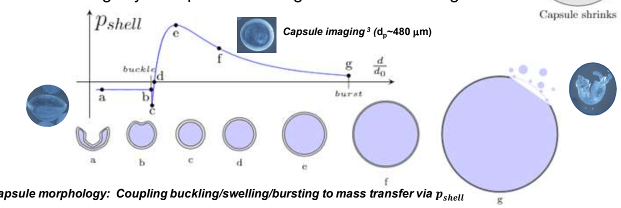
- Direction/rate of H_2O transfer can cause significant capsule size change.
- At equilibrium, shell pressure, p_{shell}, **balances partial pressure mass transfer gradient(s)**[2,6]

$$p_{out} = p_{in} + p_{shell} \quad \text{with}$$

$$p_{shell} = \begin{cases} \frac{8L_{shell}E_{shell}}{d_0} \cdot \frac{d_{eq}/d_0 - 1}{(d_{eq}/d_0)^4} & spherical \\ -7.25E_{shell} \cdot \left(\frac{L_0}{d_0}\right)^{2.5} & buckled \end{cases}$$

- Shell thickness (L_{shell}) and elastic modulus (E_{shell}) determine rigidity of capsule and magnitude of size change.

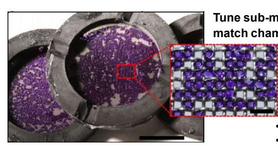




Capsule morphology: Coupling buckling/swelling/bursting to mass transfer via p_{shell}

Model calibration and validation

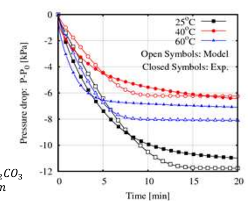
Vacuum chamber CO_2 absorption[1,4]



CO_2 absorption chamber[1]

Tune sub-models (k_{OH^-}, $\mathcal{D}_{CO_2,sol}$) to match chamber pressure drop.

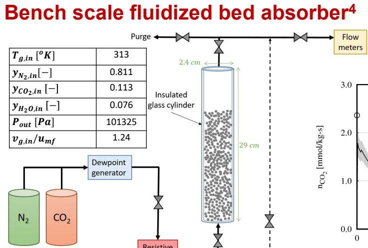
- 17 wt% encapsulated Na_2CO_3
- $d_p = 480\mu m$, $L_{shell} = 30\mu m$



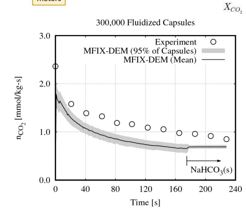
Measured / simulated chamber pressure during CO_2 absorption

Bench scale fluidized bed absorber[4]

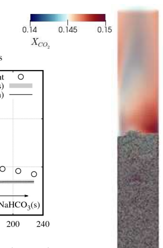
$T_{g,in}$ [^oK]	313
$y_{N_2,in}$[−]	0.811
$y_{CO_2,in}$ [−]	0.113
$y_{H_2O,in}$ [−]	0.076
P_{out} [Pa]	101325
$v_{g,in}/u_{mf}$	1.24



Experimental setup[4] (Hornbostel/LLNL)



Measured / simulated CO_2 capture rates



Simulated flow

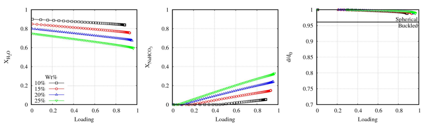
Results: Hypothetical TSA cycle

Deployment of sodium carbonate filled MECS in a TSA cycle is promising, in part, because a significant amount of H_2O can be removed from the capsules during absorption; As the capsules uptake CO_2 and precipitate $NaHCO_3$ they will simultaneously lose H_2O to the lower humidity flue gas. This lowers the energy penalty associated with regeneration. The model was used to investigate two practical issues associated with a hypothetical TSA cycle.

Tuning magnitude of H_2O loss

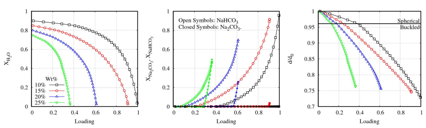
The *rate* of water loss during CO_2 absorption depends primarily on the strength of the encapsulated solvent and the flue gas relative humidity (RH). We explore the balance of CO_2 uptake and H_2O loss during exposure to flue gas (11% CO_2, 6% H_2O).

$d_0 = 480\mu m$, $L_0 = 30\mu m$, $Na_2CO_3 = 10 - 25\ wt\%$



40^oC, RH ≈ 80%

- High RH ⇒ only slight dehydration
- Capsules **shrink** slightly when loaded
- Most encapsulated H_2O sent to stripper



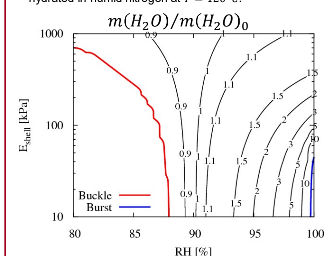
60^oC, RH ≈ 30%

- Low RH ⇒ rapid dehydration
- Buckling accelerates dehydration
- Very little encapsulated H_2O sent to stripper. Potentially good
- Dehydrate too fast ⇒ Precipitate unreacted Na_2CO_3. **Bad!**

Re-hydrating dry capsules

If the capsules are significantly dehydrated in the absorber, they will need to be re-hydrated before beginning the next cycle. We examine the sensitivity of capsule water content to ambient humidity and shell stiffness when the capsules are re-hydrated in humid nitrogen at $T = 120^oC$.

$d_0 = 480\mu m$, $L_0 = 30\mu m$, 17 $wt\%$ Na_2CO_3



Want cycle-to-cycle repeatability:

- Ideally, capsules start each absorption cycle in the same state:

$m(H_2O)/m(H_2O)_0 = 1$ and $d/d_0 = 1$

$RH_{eq} \approx 91\%$

Hydrated state sensitivity:

- Final water content very sensitive to RH at $T = 120^oC$
  2% deviation in RH ⟹ 10% swing in $m(H_2O)$!
- Buckled capsules for $RH \lesssim 88\%$ at $T = 120^oC$
- Bursting a concern in saturated gas for soft capsules ($E_{shell} \lesssim 50kPa$)

Conclusions and outlook

- ✓ MECS model developed in MFIX-DEM accounting for carbonate chemistry, CO_2 and H_2O mass transfer, capsule size changes.
- ✓ Validation of MECS model using CO_2 absorption data in pressure drop chamber and fluidized bed (LLNL)
- ✓ Explored practical issues surrounding water transfer for using carbonate filled MECS in TSA cycle.

Future goals

- Migrate to **solvent agnostic** implementation: "drop-in" modules for carbonates, ILs, NOHMs, etc.
- **Scale-up** model for MFIX-TFM / MFIX-PIC to enable device scale simulations.
- Develop **reduced order models** to accelerate adoption of MECS by industry.

More Information: Justin R. Finn, Janine E. Galvin, Modeling and simulation of CO2 capture using semipermeable elastic microcapsules, International Journal of Greenhouse Gas Control, Volume 74, Pg 191-205, 2018.

References: [1]Vericella et al., Nature Comms, v. 6, 2015; [2]Nabavi et al., Langmuir, v. 32, 2016; [3]Panday and Rogers, Private communication; [4]Hornbostel et al., submitted, 2018; [5]https://mfix.netl.doe.gov/experimentation/; [6]Shaffer, F., et al., NETL MFSW, 2010. Image: Streamers, clusters, particles in CFB; [6]Quilliet, The Eup. Phys. J. E, v 35, 2012.

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