Advanced Manufacturing To Enable New Solvents and Processes For Carbon Capture

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NETL CO₂ Capture Technology Meeting
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New fabrication techniques can enable new materials and processes to achieve low-cost carbon capture.

- Precipitating carbonates
- Ionic Liquids (Ils)
- CO₂-binding organic liquids (CO₂BOLs)
- Nanoparticle Organic Hybrid materials (NOHMs)
- Micro-encapsulation
- Additive Manufacturing
- New Materials
- Process Design

Advanced Manufacturing

Process Innovations

Transformational Carbon Capture
FEW0194: Advanced Manufacturing To Enable Enhanced Processes And New Solvents For Carbon Capture
$4.15M over 3 years (April 15, 2015 – April 14, 2018)

Encapsulation of Advanced Solvents $475k/yr

Process design and scaleup with microcapsules $475k/yr

CO₂ absorber design with advanced manufacturing $250k/yr

Rapid determination of solvent properties via microfluidic reactors $133k/yr
Objective: enable solvent-based transformational carbon capture using advanced manufacturing techniques.

- Demonstrate encapsulation of new solvents with desirable properties for transformational carbon capture.
- Identify improvements to absorbers enabled by advanced manufacturing.
- Identify and refine a suitable process configuration for Microencapsulated CO$_2$ sorbents (MECS).
- Determine properties of candidate solvents via microfluidic techniques.
Project Team


Collaborators

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Advanced solvents have some common advantages:

- Lower energy of regeneration
- Low volatility
- Tunability for innovative processes

...and common problems:

- High viscosity
- Water intolerance
- Phase changes
- Slow heat transfer or mass transfer
- High solvent cost
Some solvents with potential for 30—50% energy savings and specific challenges:

1. **Sodium carbonate** solution: slow CO$_2$ absorption, precipitates solids.

2. **Ionic Liquids**: water intolerance, precipitate solids (PCIL’s).

3. **NOHM**s: high viscosity, slow CO$_2$ absorption.

4. **CO$_2$BOLs**: poor heat transfer rates (high viscosity).
→How can advanced manufacturing help?
Advanced Manufacturing:

a suite of fabrication techniques characterized by:

• additively assembled parts
• micro- or nano-scale control over structures (micro-architecture)
• micro- or nano-scale assembly of multiple components
• computational or analytical design directly input to the fabrication technique
Some additive manufacturing techniques under development at LLNL

**Projection Microstereolithography (PµSL)**
A photochemical and optical technique

**Direct Ink Writing (DIW)**
Utilizes unique flow and gelling properties

**Electrophoretic Deposition (EPD)**
Electric fields transport nanoparticles
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Microencapsulation: double emulsions are produced in a microfluidic device...

- Control of capsule diameter and shell thickness.
- Encapsulates ~100% of inner fluid
- Core fluid can also have solids
- Production rate: 1-100 Hz

...and then cured with UV light.
Micro-encapsulated Carbon Sorbents (MECS):
Liquid solvents or slurries encased in thin, permeable polymer shells

- Multiple solvents, shell materials, and sizes produced
Microencapsulation enhances kinetics.

$\text{CO}_2$ absorbs through shell

Surface area formed by capsule, not a tower

Embedded catalyst further enhances kinetics

“Zn-Cyclen”
Microencapsulation enhances kinetics.

CO₂ absorbs through shell

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Microencapsulation enables mixed phases and viscous solvents.

30 wt% Na₂CO₃ capsules exposed to CO₂ precipitating Nacholite

Encapsulating slurry of glass bubbles
Microencapsulation enables mixed phases and viscous solvents.

30 wt% Na$_2$CO$_3$ capsules exposed to CO$_2$ precipitating Nacholite ➞

Encapsulating slurry of glass bubbles↓
Encapsulation increases capture rate of carbonates by 10x compared to same volume of liquid.
Process options same as for solids:
• Fluidized bed
• Moving Bed
• Fixed bed

Thermally regenerable for many cycles (80 tested).
Challenges and planned work
Challenge: Capsule Production Scale-up

- Bulk emulsion methods exist, but yield a distribution of capsule properties.
- Two microfluidic production methods being pursued.

Etched glass chips from Dolomite Microfluidics

Tandem-Step chips developed at Harvard
Some success with 1st-generation multichannel chips
Two 4-channel chips producing capsules in parallel.
Scale-up alternative: Tandem Step Emulsification
Tandem Step Emulsification (Oil in Water)
Challenge: capsule curing in the presence of amines

Current shell material: Semicosil 949UV, Wacker Chemie AG
- Proprietary silicone rubber blend (likely polydimethyl siloxane; PDMS)
- UV curable (likely UV-activated cross-linking through hydrosilation chemistry)

Hydrosilation:

\[ R\text{-}CH=CH_2 + H\text{-}SiR_3 \xrightarrow{\text{Pt catalyst}} R\text{-}CH\text{-}CH\text{-}SiR_3 \]

Proposed alternatives

*Thiol-ene Click Chemistry*

\[ R\text{-}CH=CH_2 + H\text{-}SR \xrightarrow{\text{UV light, irgacure}} R\text{-}CH\text{-}CH\text{-}SR \]

*Acrylate Chemistry*
Challenge: determine solvent properties from small sample volumes.

Microfluidic characterization of CO₂ absorption solvents

- Image analysis of gas bubble size vs channel distance provides uptake data
- Different solvents show different capture performance
Raman spectroscopy characterization of amino acid solvent CO$_2$ capture

- Raman spectroscopy can identify carbamate, bicarbonate, and carbonate species
- We see disappearance of reactants and formation of products

Potassium lysinate before and after CO$_2$ capture
Improving absorber packings

Challenge:
overcoming the film thickness
or
disrupting the boundary layer
Core-shell Direct Ink Write

Printed tubes filled with carbonate solvent
Permeable packing material

→ better surface area-to-volume and faster reaction in absorbers

functionalized with CO$_2$ catalysts
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Questions