Advanced Manufacturing to Enable Enhanced Processess and New Solvents for Carbon Capture

primary project goals

Lawrence Livermore National Laboratory (LLNL), Harvard University, and Carnegie Mellon University (CMU) teamed up to develop processes that enhance and enable the use of new solvents to capture carbon dioxide (CO_2). Primarily, the project aimed to develop and evaluate the concept of Micro-Encapsulated CO_2 Sorbents (MECS) and to develop new concepts for absorber packings for solvent-based CO_2 capture (advanced packings). The technology uses advanced manufacturing techniques to reduce the cost of carbon capture for coal-fired power plants and supports the U.S. Department of Energy's (DOE) Carbon Capture Program's goal of advancing the technical, economic, and environmental performance of second-generation and transformational systems and technologies for future deployment.

technical goals

- Develop processes to enhance and enable the use of thermodynamically favorable solvents to capture CO_2 using advanced manufacturing techniques to encapsulate the solvents in a permeable membrane.
- Identify and assess improvements to the design of industrial CO_2 absorbers made possible by advanced manufacturing.
- Identify the best process configuration for encapsulated solvents.
- Measure the properties of potential solvents using LLNL's microfluidic technique for rapid characterization of solvent properties.

technical content

LLNL, Harvard University, and CMU formed a team to develop processes that enhance and enable the use of advanced solvents to capture CO_2 from coal-fired power plants using advanced manufacturing techniques. New solvents for the capture of CO_2 pose challenges for conventional equipment due to slow kinetics, high viscosity, phase changes, corrosivity, or other issues. The team formed to develop processes to enhance and enable the use of these otherwise thermodynamically favorable solvents to capture CO_2 using advanced manufacturing techniques to encapsulate the solvents in a permeable membrane to overcome these challenges.

One of the key goals of the project was to take the micro-encapsulation concept, which had previously been demonstrated with sodium and potassium carbonate, and apply it to new solvents, especially water-lean solvents. Compatibility among the solvent, shell material, and production methods turned out to be a critical

technology maturity:

Laboratory-Scale

project focus:

Encapsulation of Solvents in Permeable Membrane for CO_2 Capture

participant:

Lawrence Livermore National Laboratory

project number:

FWP-FEW0194

predecessor projects:

N/A

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partners:

Harvard University,
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start date:

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percent complete:

100%

challenge, and extensive efforts to solve this challenge ran the course of the project.

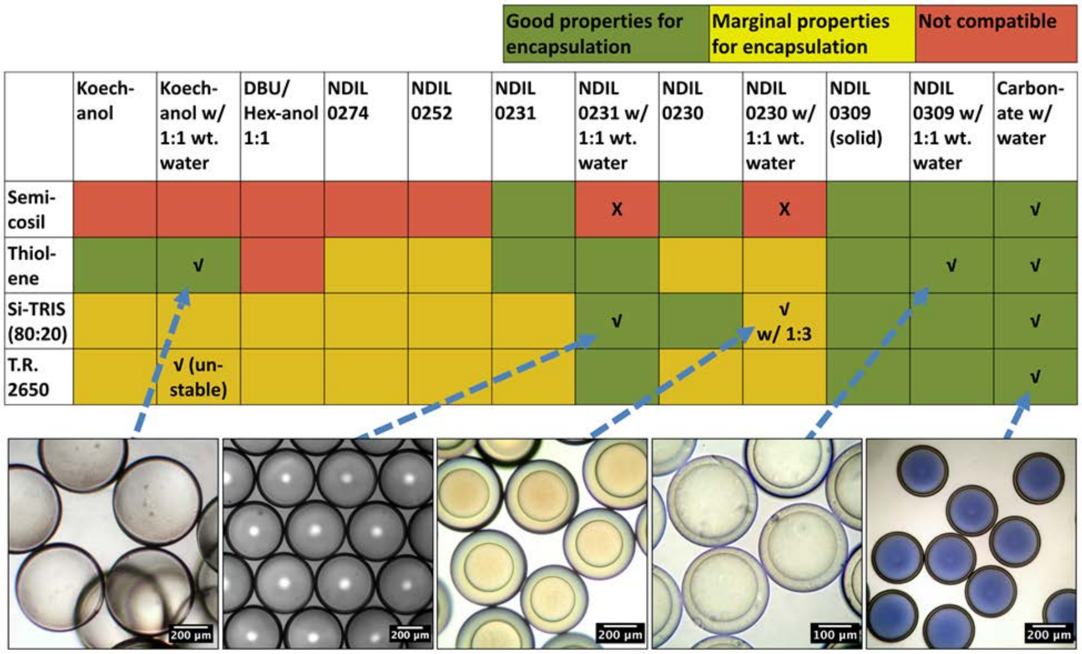
The primary selection criterion for a MECS shell material is high permeability to CO_2. Further criteria include heat stability at the regeneration temperature of the solvent (typically 80 to 120°C), mechanical robustness in the chosen process conditions (e.g., fluidized bed), and chemical compatibility with the solvents (CO_2-binding organic liquid [CO_2BOL], nanoparticle-organic hybrid material [NOHM], ionic liquid [IL], carbonates). For microfluidic production, ultraviolet (UV)-curable polymers with precursors that are liquid at room temperature are particularly suitable. Silicones have among the highest CO_2 permeabilities of common polymer classes, with typical values on the order of 3,000 barrer. After extensive screening and through past and concurrent work on encapsulation, two commercial silicones were identified as promising shell materials (Semicosil 949 and Tego-Rad 2650). Two new, in-house polymer classes, identified as Thiolene and SiTRIS, were developed for capsule screening. During the project, variations of Thiolene have been formulated by slightly changing the compositions for more robust capsule production and better suitability with scale-up production.

The shell materials tested in this project are summarized in Table 1, showing some of their relevant properties.

TABLE 1: SUMMARY OF SHELL MATERIAL CANDIDATES WITH BASIC PROPERTIES

Name	Manufac-turer	Material	Permea-bility (barrer)	Amine Compati-bility	Mecha-nical Properties	Curing Time
Semicosil 949	Wacker	Silicone	3100	No	Elastic, strong, tacky	30 mins
Thiol-ene	LLNL	Silicone	2700	Yes	Elastic, strong, tacky	30 secs
SiTRIS (80:20)	LLNL	Acrylic	400	After curing	Stiff, strong, untacky	10 secs
Tego Rad 2650	Evonik	Silicone	3200	After curing	Elastic, friable, untacky	10 secs

Several core solvents (Koechanol, 1,8-diazabicyclo[5.4.0]-undec-7-ene [DBU]/hexanol, five ILs, and an NOHM) were tested for compatibility with shell material candidates. The screening process involved three main tasks: (1) a solubility test, to determine whether the solvent would dissolve solid shell material; (2) a test of interfacial stability, to determine if the solvent and shell material precursor maintain distinct liquid phases; and (3) a curing test to determine if the shell material cures by UV in the presence of the solvent. Results of the screening are summarized in Figure 1.



🟩 Good properties for encapsulation	🟨 Marginal properties for encapsulation	🟥 Not compatible

	Koech-anol	Koech-anol w/ 1:1 wt. water	DBU/ Hex-anol 1:1	NDIL 0274	NDIL 0252	NDIL 0231	NDIL 0231 w/ 1:1 wt. water	NDIL 0230	NDIL 0230 w/ 1:1 wt. water	NDIL 0309 (solid)	NDIL 0309 w/ 1:1 wt. water	Carbon-ate w/ water
Semi-cosil	🟥	🟥	🟥	🟥	🟥	🟩	🟥 X	🟩	🟥 X	🟩	🟩	🟩 √
Thiol-ene	🟩	🟩 √	🟥	🟨	🟨	🟩	🟩	🟨	🟨	🟩	🟩 √	🟩 √
Si-TRIS (80:20)	🟨	🟨	🟨	🟨	🟨	🟨	🟩 √	🟩	🟨 √ w/ 1:3	🟩	🟩	🟩 √
T.R. 2650	🟨	🟨 √ (un-stable)	🟨	🟨	🟨	🟨	🟩	🟨	🟨	🟩	🟩	🟩 √

Figure 1: Summary of IL/shell material compatibility screening tests. "X"s mark unsuccessful capsule production; checks mark successful capsule production.

Multiple options to synthesize larger quantities (~1 kg) of encapsulated ILs were explored. Of those, the most successful was a new process developed specifically for the project. Figure 2 shows the In-Air Drop Encapsulation Apparatus (IDEA) built at LLNL. The system pumps fluids out of a coaxial nozzle to form a core-shell fluid jet in air. The jet of fluid is broken into drops with the use of an external device (a contact speaker in this case), which causes the nozzle to vibrate. When a sinusoidal wave with a certain frequency (related to fluid properties, flow rate, and nozzle size) is applied, monodisperse drops are formed. Capsules are produced when the drops are exposed to sufficient UV to crosslink the polymer shell. This method does not require a carrier fluid and potentially provides better control and reproducibility than the parallel microfluidic approach. IDEA was the leading option for scale-up of carbonate and IL capsules, with a maximum rate up to 400 g/hr per nozzle.

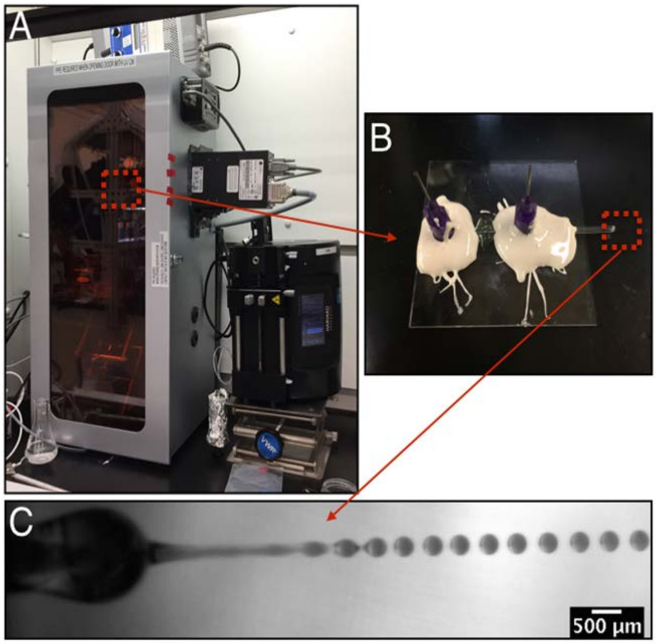


Figure 2: (A) Overview of in-air drop generator box; (B) a device example that was used to produce core-shell droplets; (C) production of carbonate SiTRIS droplets.

After developing formulations for the previously discussed solvents, six candidate MECS were selected for inter-comparison. The solvents were sodium carbonate (Na_2CO_3) solution, uncatalyzed and with two different promoters; two IL solvents; and one CO_2BOL. It was found that 17 wt% Na_2CO_3 capsules containing cyclen as a promoter outperformed Na_2CO_3 capsules with no promoter or with sarcosine as a promoter in terms of absorption rate. It was also discovered that the CO_2BOL liquid permeated or broke the capsule shell, and thus these MECS were not cycled. Both of the IL MECS outperformed the Na_2CO_3 capsules, having roughly twice the capacity and higher absorption rates. However, production of the IL MECS proved much more difficult to scaleup while maintaining multicycle performance.

One of the key innovations in this project is the development of printed composite sorbents, a variation of the capsule-based MECS that originated the research. The composites combine the same or similar silicone shell materials used for capsules with Na_2CO_3 or other solvents; however, rather than making core-shell spherical capsules, filaments or meshes of homogeneous material were produced.

The composite sorbents are similar to MECS in that the final material is composed of aqueous Na_2CO_3 solutions surrounded by CO_2 permeable silicone. Both materials use fine feature sizes (less than 500 μm) to enable high mass transfer rates into the carbonate solutions. However, the composite sorbents have the benefit of being 3D-printable, which enables geometric control of the material that can be optimized for parameters, such as pressure drop, though the system. The impact of geometry on CO_2 absorption rate was investigated. The smallest filament sizes were able to achieve slightly better rates than core-shell MECS.

These initial investigations of composites applied 3D printing. However, in follow-on projects, production was generalized to use either a simple extrusion of random mats or waffle patterns cast to make thin sheets. Thus, composites can achieve similar surface areas and mass transfer rates as spherical MECS and similar or better loading, but their production is more scalable. For this reason, composite MECS are the focus of several follow-on commercialization efforts.

One of the key goals of the fourth project year was to develop an integrated, automated, bench-scale packed-bed apparatus for testing extended cycles of absorption-desorption and for testing realistic regeneration conditions with steam. This apparatus was built and successfully tested. It contains twin jacked reactor columns (see Figure 3), which can be operated simultaneously to cycle between absorption and regeneration. The design enables the use of steam to directly or indirectly heat up sorbents.

Figure 3: Detail of the automated sorbent testing system.

A process diagram is shown in Figure 4. A gas line can also be used to purge a column depending on cycling requirements.

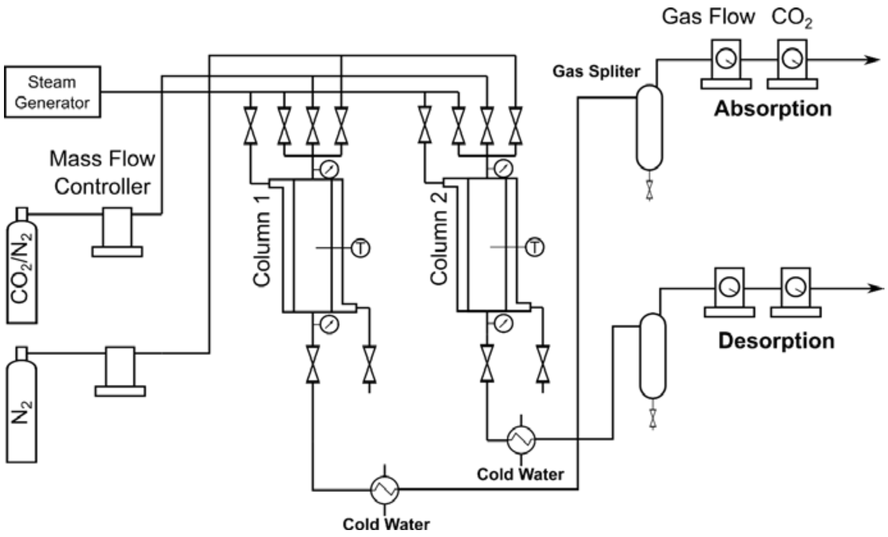


Figure 4: Process diagram of the automated sorbent testing system.

Steam, nitrogen (N_2), and/or a 10% N_2/CO_2 mixture can flow through the main columns. Steam can also flow through the jacketed portion of the column to indirectly heat the microcapsules. After passing through the column, the gas stream passes through a heat exchanger to condense any water and steam. The gas/condensed water mixture then passes through a gas splitter to separate the two phases. Lastly, the gas stream is passed through a flow meter and CO_2 meter.

After constructing the sorbent testing system, absorption-desorption tests on Na_2CO_3 MECS were conducted, focusing on direct steam regeneration. The gram-scale and smaller column experiments of prior test apparatuses could not be configured for these tests.

The CO_2 breakthrough curves for eight sequential cycles and the resulting integrated absorbed CO_2 amounts are shown in Figure 5. In the first cycle, just after loading the capsules into the column, breakthrough was nearly instantaneous, though there was a long tail to reach the final outlet concentration, suggesting slow absorption kinetics. In following cycles, breakthrough and equilibrium were both obtained more quickly. The result of this is that the amount of CO_2 that was able to be absorbed decreased over time.

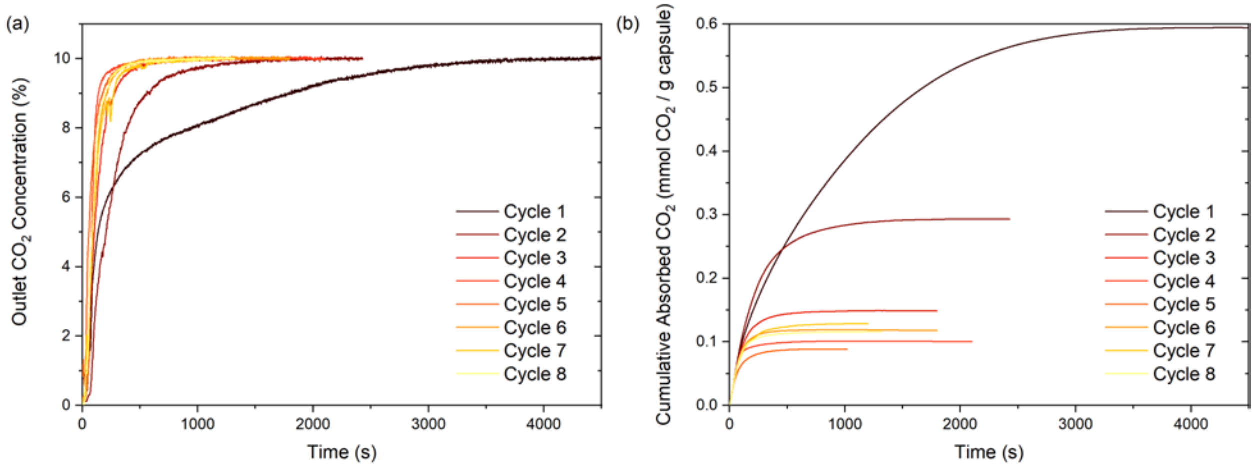


Figure 5: (a) CO_2 breakthrough curves for 10% CO_2/N_2 at ~500 sccm through the MECS column, followed by desorption in steam. (b) Cumulative absorbed CO_2 as a function of time.

Despite the initial setbacks with the material, the system can perform cyclic absorption and steam desorption. In future work, consistent performance should be demonstrated, such as that observed in the previously mentioned gram-scale experiments, using a different MECS formulation.

In the second half of the project, much of the focus for MECS was on process design and measurements to enable techno-economic analysis (TEA). From the beginning, fluidized-bed, fixed-bed, and moving-bed configurations had been considered. It remained difficult to down-select among these options. In an absorber sizing study and a separate process design and TEA, it was found that capsule MECS-based fixed beds or fluidized beds were generally larger than solvent towers with monoethanolamine (MEA) for carbon capture from a coal power plant. The TEA also found that the MECS system had higher overall costs than an MEA system. Because of this, and even allowing that better process configurations for MECS may be achievable, it is still unlikely that MECS will outperform second-generation solvents for carbon capture at power plants. Solids handling and heat integration with solids is a major challenge for MECS and for any sorbent system to outperform commercial solvents.

However, Na_2CO_3-based MECS have some special properties that may make them commercially attractive in niche applications. Chief among these is bio-compatibility (low toxicity). Also, as a sorbent, MECS downscale to small capture applications much better than solvents and, unlike most sorbents, are water-tolerant. MECS are also inexpensive compared to many other chemisorbents, like metal-organic frameworks (MOFs). Leveraging these advantages, MECS commercialization efforts are ongoing.

TABLE 2: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	980–1,050	—
Bulk Density	kg/m^3	~650	—
Average Particle Diameter	mm	0.5	0.3
Particle Void Fraction	m^3/m^3	0	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	100–1,000	5—10
Adsorption			
Pressure	bar	0.05–10	—
Temperature	°C	20–60	—
Equilibrium Loading	mol CO_2/kg	0.8–2	2–3
Heat of Adsorption	kJ/mol CO_2	~44–90	—
Desorption			
Pressure	bar	1	1–80
Temperature	°C	80–100	80–160
Equilibrium CO_2 Loading	g mol CO_2/kg	—	—
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	packed bed or fluidized bed	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 1--140	
Adsorber Pressure Drop	bar	<0.5	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemical.

Sorbent Contaminant Resistance –Water tolerant.

Sorbent Attrition and Thermal/Hydrothermal Stability – Lowered CO_2 capture capacity is seen with cyclic absorption and steam desorption in the bench-scale system. In future work, the team would most likely be able to demonstrate more consistent performance, such as that observed in the gram-scale experiments, using a different MECS formulation.

Process Design Concept – See above

technology advantages

- Microcapsules are high surface area, permeable microreactors that enable advanced solvents to achieve transformational carbon capture.
- MECS may overcome all or many of the characteristics inherent in some new CO_2 capture sorbents, which include slow kinetics, high viscosity, phase changes, corrosivity, or other issues.
- Overcomes mass transfer limitations of advanced solvents, reducing size and capital cost of absorber.

R&D challenges

- Selection of suitable shell materials.
- Testing packing methods.
- Developing capsule production scale-up.
- Capsule curing.
- Determining thermodynamic properties of micro-scale solvents.

status

This project has concluded.

available reports/technical papers/presentations

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