Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide Capture

primary project goals

The University of Notre Dame, in collaboration with Lawrence Livermore National Laboratory (LLNL) and colleagues at the University of Texas, has been developing technology for hybrid encapsulated ionic liquid (IL) and phase-change ionic liquid (PCIL) materials for post-combustion carbon dioxide (CO_2) capture. Although ILs have many favorable properties as CO_2-absorbing solvents, their typically high viscosities directly correlate with poor mass transfer rates and prohibit their practicable application in large-scale commercial operation when configured in conventional absorption/regeneration systems. Researchers' work in identifying ILs and PCILs with high capacity and low regeneration energy that, when combined with their technology for microencapsulation of the ILs or PCILs in polymer shells, may enable synthesis of high surface area IL- and PCIL-based materials well-suited for CO_2 capture from post-combustion flue gas. The goal of the project is successful synthesis of the microencapsulated ILs and/or PCILs and validated CO_2 removal from simulated flue gas in a laboratory-scale unit, with demonstration of dramatically improved mass transfer rates.

technical goals

- Encapsulated ILs/PCILs structural integrity: microcapsules in fluidized beds able to contain the ILs without leaking.
- Uptake of CO_2 by encapsulated ILs/PCILs: greater than 50% CO_2 absorption from a humid nitrogen (N_2)-CO_2 gas mixture in laboratory-scale testing.
- Durability/recyclability of the encapsulated ILs/PCILs: less than 20% decline in absorption capacity of CO_2 after five cycles in humid N_2-CO_2 gas mixture.
- Solvent regeneration: at least 80% of the absorbed CO_2 removed by hot vapor (steam) without significant damage to the particles.
- Substantial technology progress towards a capture system enabling 90% CO_2 capture with 95% CO_2 purity at a cost of electricity 30% less than baseline aqueous amine technologies.

technical content

Conventional solvent-based carbon capture methods typically employ amines such as monoethanolamine (MEA) as the capture solvent. However, amines are corrosive, degrade over time, and have relatively high vapor pressures, making their leakage into the environment more likely. ILs are a class of ionic salts tending to have large nitrogen or phosphorous-bearing cations with alkyl chain substituents. ILs are anhydrous, liquid at ambient temperatures, have low vapor pressures, are thermally stable and relatively non-corrosive, and certain ILs have a considerable affinity for absorption of CO_2 and selectivity towards CO_2 in gas mixtures. For example, the hexafluorophosphate (PF_{6-}) and tetrafluoroborate (BF_{4-}) anions have been shown to be amenable to CO_2 capture.

ILs might be used in a similar process to amine gas treating to effect carbon capture from flue gas, where the flue gas is contacted with the solvent in an absorption column, and the rich solvent is regenerated in a stripper column at

technology maturity:
Laboratory-Scale, Simulated Flue Gas (3.3 liters per minute)

project focus:
Microencapsulated CO_2 Capture Materials

participant:
University of Notre Dame

project number:
FE0026465

predecessor projects:
DE-FC26-07NT43091
DE-AR0000094

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start date:
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percent complete:
100%

higher temperature through use of steam heating. ILs consistently show CO_2 absorption behavior of decreasing solubility with increasing temperature, enabling conventional temperature swing absorption cycling. Because they have increasing CO_2 solubility with increasing pressure, ILs could also be stripped using pressure swing or swept with inert gases, possibly reducing the process energy requirement.

A current issue with ILs for carbon capture is that they have a lower working capacity than amines. Another pressing concern with their use is their high viscosity compared with that of commercial solvents. ILs that employ chemisorption depend on a chemical reaction between solute and solvent for CO_2 separation. The rate of this reaction is dependent on the diffusivity of CO_2 in the solvent and is thus inversely proportional to viscosity. The self-diffusivity of CO_2 in ILs is generally on the order of 10^{-10} m^2/s, approximately an order of magnitude less than similarly performing commercial solvents used for CO_2 capture. This represents a problematic mass transfer barrier for ILs and overcoming it would constitute a significant advance in IL-based carbon capture technology.

However, encapsulating ILs/PCILs in small spherical shells and suspending these in a low-viscosity medium would create a high-surface area IL/PCIL-based material into which CO_2 could much more easily diffuse and react, potentially overcoming the mass transfer barriers caused by the inherently high viscosities of the stand-alone ILs/PCILs. Therefore, the technologic development approach being explored here involves combining IL and PCIL materials having high CO_2 absorption capacity and low regeneration energy, and microencapsulation of these in polymer shells, with significant potential for resulting in high surface area materials to be very well-suited for CO_2 capture from post-combustion flue gas.

Selection of Suitable ILs and PCILs

Strongly performing ILs and PCILs would have several favorable properties/characteristics, such as:

- Chemical complexation strong enough to increase capacity and to decrease required IL circulation rates.
- Chemical complexation weak enough to keep regeneration energies (and temperatures) down.
- High equimolar absorption capacity: value of 1 mol CO_2/mol IL at absorption conditions is favorable.
- No viscosity increases of the IL upon reaction with CO_2. Such increases occur because of the formation of hydrogen bonding networks.

It has been observed that ILs containing aprotic heterocyclic anions are favorable on these points. They enable relatively high absorption capacity. It is possible to tailor/tune heat of reaction of these ILs, guided by experience and previous density functional theory, in order to enable an optimal chemical complexation strength (this happens to be between about -45 and -60 kJ/mole enthalpy of reaction with CO_2). Also, they retain amine in the ring structure, and further reduction of free hydrogens to reduce hydrogen bonding is possible, avoiding the viscosity increase problem. Figure 1 depicts some types of these aprotic heterocyclic anions.

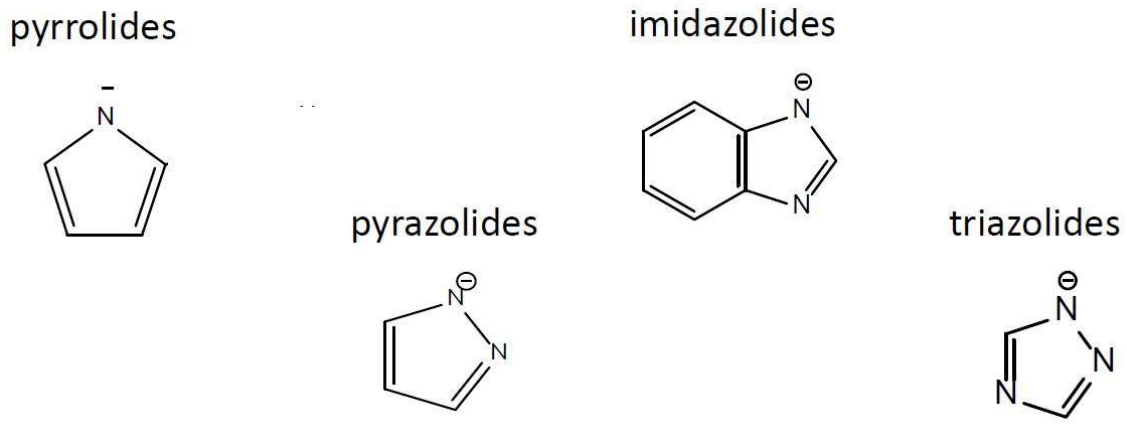

Figure 1: Several types of aprotic heterocyclic anions.

The researchers have evaluated a number of possibilities for ILs and PCILs prepared by LLNL, and settled on one IL and one PCIL for continued development in this technology. The IL (NDIL0230) is triethyl(octyl)phosphonium 2-cyanopyrrolide ($[P_{2228}][2CNPyr]$), and the PCIL (NDIL0309) is tetraethylphosphonium benzimidazolide ($[P_{2222}][BnIm]$), which was developed in an Advanced Research Projects Agency-Energy (ARPA-E) project. The PCIL will undergo a phase change to and from liquid and solid at the varying temperatures it experiences during regeneration and absorption. This is expected to confer certain energy efficiency advantages as discussed below in process implementation.

Microencapsulation

The central innovation of this developmental technology involves encapsulating ILs and PCILs in thin CO_2-permeable polymeric shells to produce particles of approximately 100 to 600 µm in diameter. It is thought that this approach will create a high volumetric surface area material that can put ILs within easy diffusion range of CO_2-containing flue gas in a fluidized-bed or moving-bed absorber in a post-combustion CO_2 capture cycle. This idea is depicted in Figure 2. The typical tower packing in amine absorption columns is either structured packing or random packing fill, which in either case establishes a surface area for liquid-gas contacting in the range of hundreds of m^2 surface per m^3 of column volume. However, note the microcapsules would generally establish surface areas near or above 10,000 m^2 per m^3.

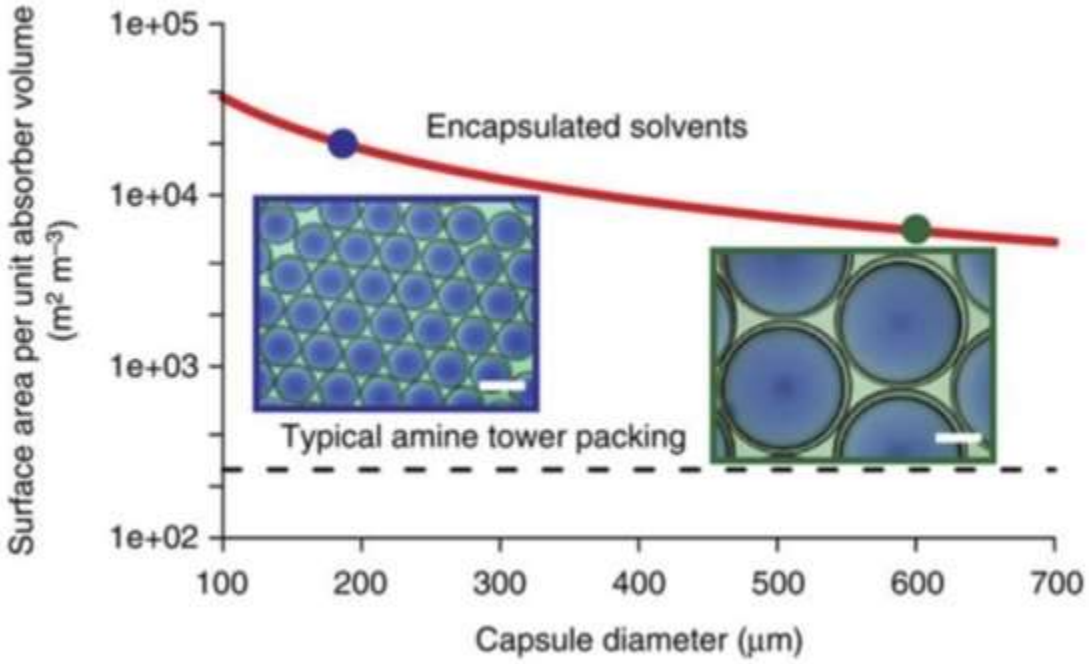

Figure 2: Surface area benefit of microencapsulation.

The technology for creating polymer-shell-encased IL microcapsules is now well established by LLNL. The microcapsules are produced in a microfluidic device where the solvent and uncured shell material are flowed together in a third, inert carrier fluid through a junction to create double emulsions – drops of solvent inside drops of shell material precursor, suspended in the carrier fluid. The apparatus is diagrammed in Figure 3. The shell material is subsequently cured by exposure to ultraviolet (UV) light. In project work, capsules are produced in single-junction devices assembled from glass capillaries, but the process can be parallelized for large-scale production.

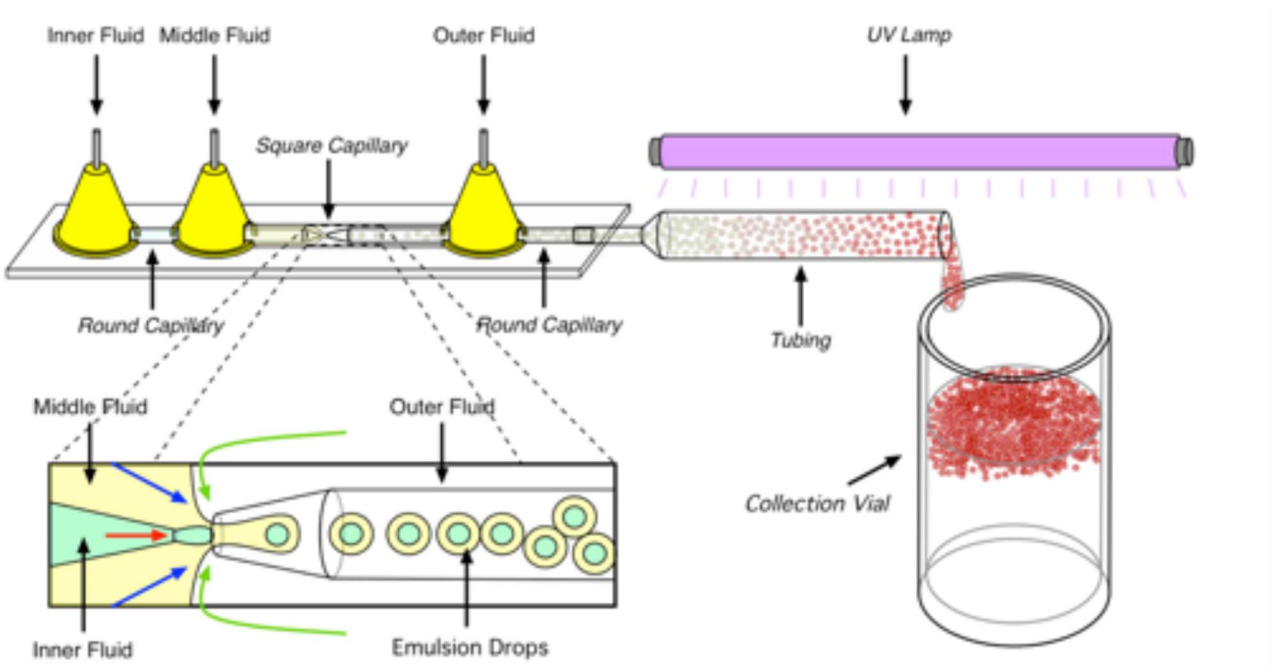

Figure 3: Diagram of the capsule production apparatus (Inner Fluid is the IL; Middle Fluid is the shell material precursor; and Outer Fluid is an aqueous, inert, carrier solution).

The polymer shell of the microcapsules must satisfy several conditions, including ability to reliably contain the IL contents and maintain general physical stability, provide negligible diffusion resistance to CO_2, and to not adversely affect the IL absorption reaction. Initially, issues were experienced with incompatibility of the ILs with the polymer material forming the polymer shell, but these have since been overcome. LLNL settled on their in-house developed and refined Thiolene-Q shell material formulation for NDIL0309, given its chemical compatibility and for which an alternative crosslinker for improved microcapsule production and in-air production was found. Figure 4 depicts this formulation. For NDIL0230, a different polymer SiTRIS was found to be compatible; Figure 5 is a magnified image of the microcapsules that have been successfully fabricated using these combinations.

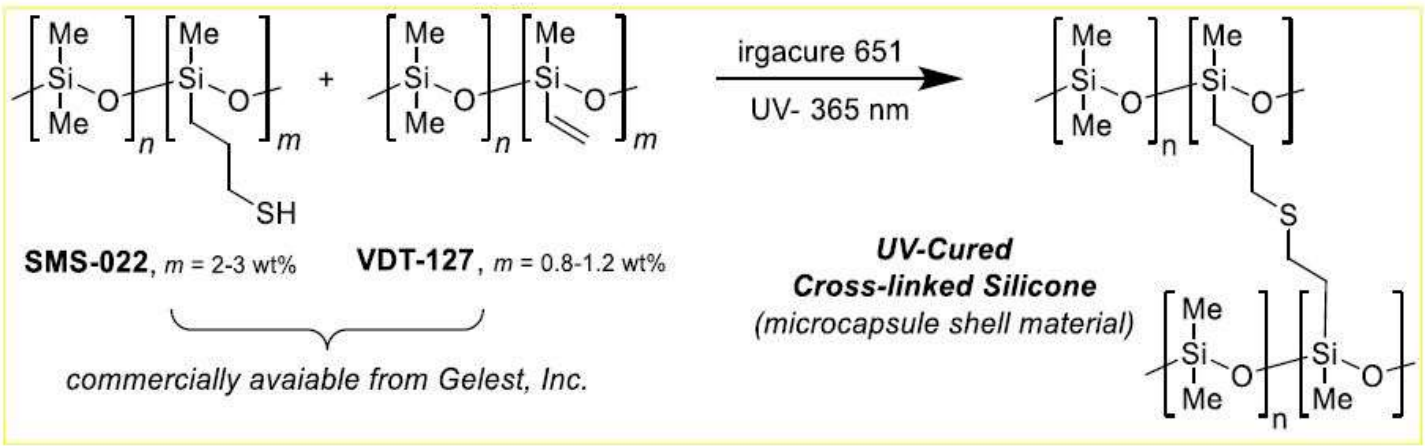

Figure 4: Thiolene-Q shell material.

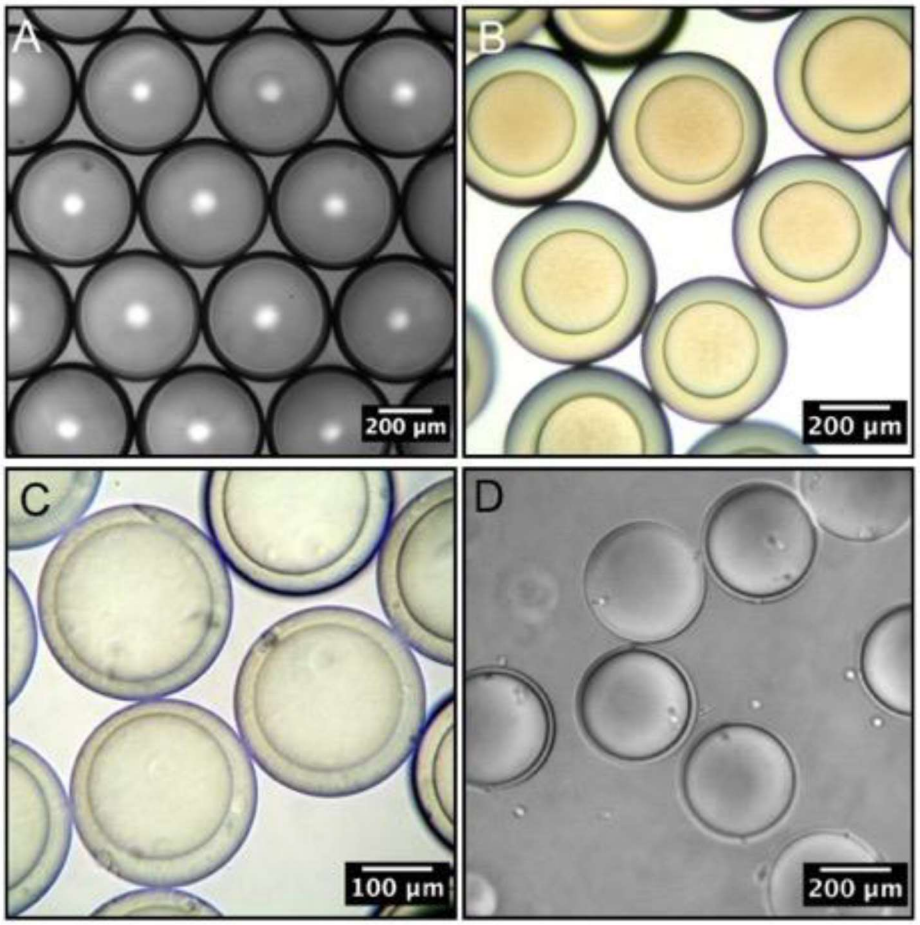

Figure 5: Successful microcapsules: A: NDIL0231/water-in-SiTRIS; B: NDIL0230/water-in-SiTRIS; C: NDIL0309/water-in-Thiolene-Silica; D: NDIL0309/water-in-Thiolene-Q.

Testing of the encapsulated ILs/PCILs in simulated flue gas showed the following:

- Effects of impurities: the IL and PCIL under consideration both react irreversibly with sulfur dioxide (SO_2) and nitrogen oxides (NO_X), whether free or encapsulated. Accordingly, CO_2 capture with these would need to follow the flue gas desulfurization (FGD) and NO_X reduction units in the flue gas cleanup system.
- Reaction of water with the IL or PCIL in the presence of CO_2 is completely reversible and recyclable. Therefore, water does not need to be excluded from the cores of the microcapsules. This is greatly advantageous given the inevitable presence of water vapor in flue gas.

PCIL Process Implementation

Process advantages result from the inherent characteristics of PCILs in temperature swing absorption cycles, as depicted in Figure 6. In the absorption column on the left, a PCIL slurry containing encapsulated PCILs at low temperature (at which the PCILs are in the solid phase) is contacted counter-currently with CO_2-containing flue gas passing up the column. The PCIL reacts exothermically with CO_2, creating heat that is absorbed by the PCIL particles, causing them to melt. The PCIL-CO_2 liquid leaving the column is sprayed into a dryer shown on the right, which serves as the regenerator in this process cycle. The PCIL is heated in the dryer, causing it to release CO_2 in relatively pure gaseous form, which is withdrawn and compressed for transport or storage. The heat duty of the stripper is reduced somewhat by the heat of fusion of the PCIL as it goes from liquid to solid phase. Also, the cooling duty of the PCILs on the absorption side is reduced by the phase change from solid to liquid phase.

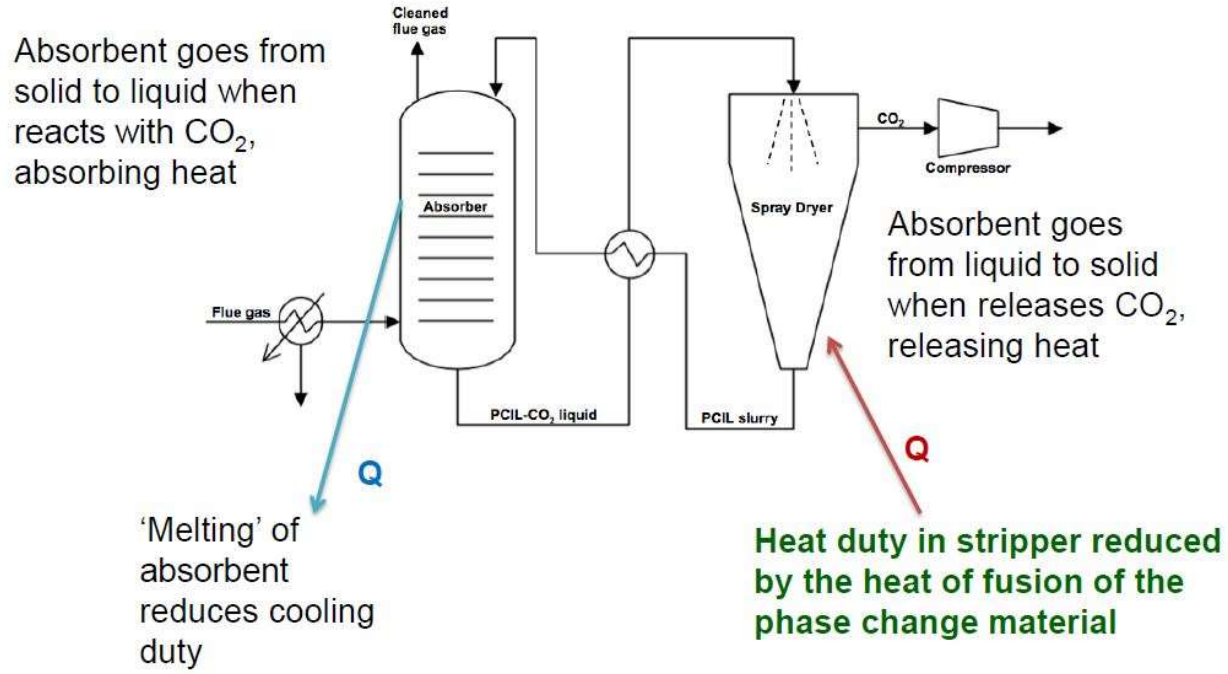

Figure 6: CO_2 capture cycling with phase-change material.

The result of this is that the overall heat duties on either side of the process cycle are moderated somewhat by the phase changes occurring. This is more clearly depicted in Figure 7, which accounts how the phase changes of the PCILs reduce the total molar heat duty on either side by 20 kJ/mol. Instead of needing to supply the entire 50 kJ/mol by external heating of the dryer/regenerator, only the net amount of 30 kJ/mol needs to be supplied; the other 20 kJ/mol being contributed by the PCIL phase-changes. This should lessen the parasitic energy demand for operating the process relative to a non-phase-change scenario.

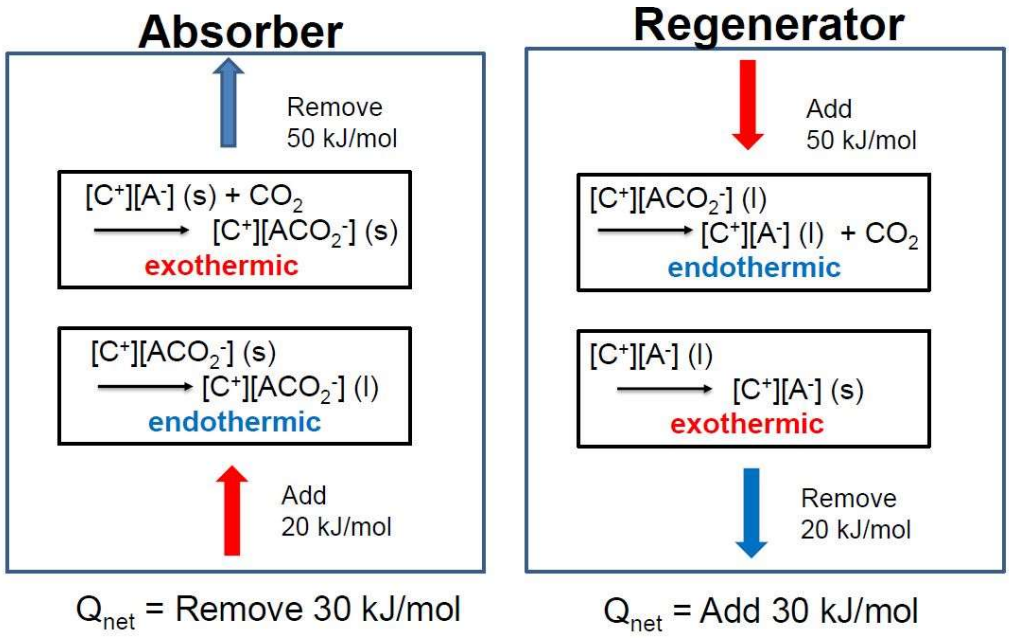

Figure 7: Heat duties for CO_2 capture with PCILs.

Project Summary Findings

Small quantities (~1 g) of microcapsules with good integrity of both the IL and the PCIL have been successfully produced. The CO_2 uptake by these capsules is the same as for the free IL and PCIL and the capacity of the capsules decreases

only slightly after five absorption and desorption cycles. Over five cycles of absorption and regeneration, the CO_2 capacity has been consistently measured at 0.64 to 0.68 moles CO_2/mol PCIL.

Large samples (~70 g and 100 g) of encapsulated PCIL were produced in a parallel microfluidic device and in an in-air device, respectively. These capsules have been tested in a laboratory-scale unit (LSU) at 3.3 liters per minute simulated flue gas flow rate to demonstrate uptake capacity in a fluidized bed. The LSU also allowed determination of recyclability and mass transfer coefficients. Equivalent experiments with the IL were not possible due to difficulties with producing large samples of the encapsulated IL. This IL encapsulation "scale-up" problem was not solved during the course of the project. Nonetheless, testing of the PCIL microcapsules verified that the mass transfer is internally controlled. In concert with a new rate-based model of a microcapsule fluidized-bed absorber, it was found that productivity is increased by a factor of 4.75 in the microcapsule fluidized-bed absorber compared to a conventional liquid-gas packed-bed absorber.

An initial techno-economic model (assuming a process design as depicted in Figure 8) shows that the capital cost for the microcapsule IL continuous fluidized-bed process is similar to that of an aqueous amine process (specifically, the Econamine FG Plus technology). However, the stripping heat requirements are about 35% less for the model IL microcapsule case compared to the MEA case. Thus, encapsulated ILs/PCILs in a continuous fluidized-bed absorber for post-combustion CO_2 capture are a significant improvement over the free IL/PCIL case and represent a major reduction in the parasitic energy requirements compared to an aqueous amine process.

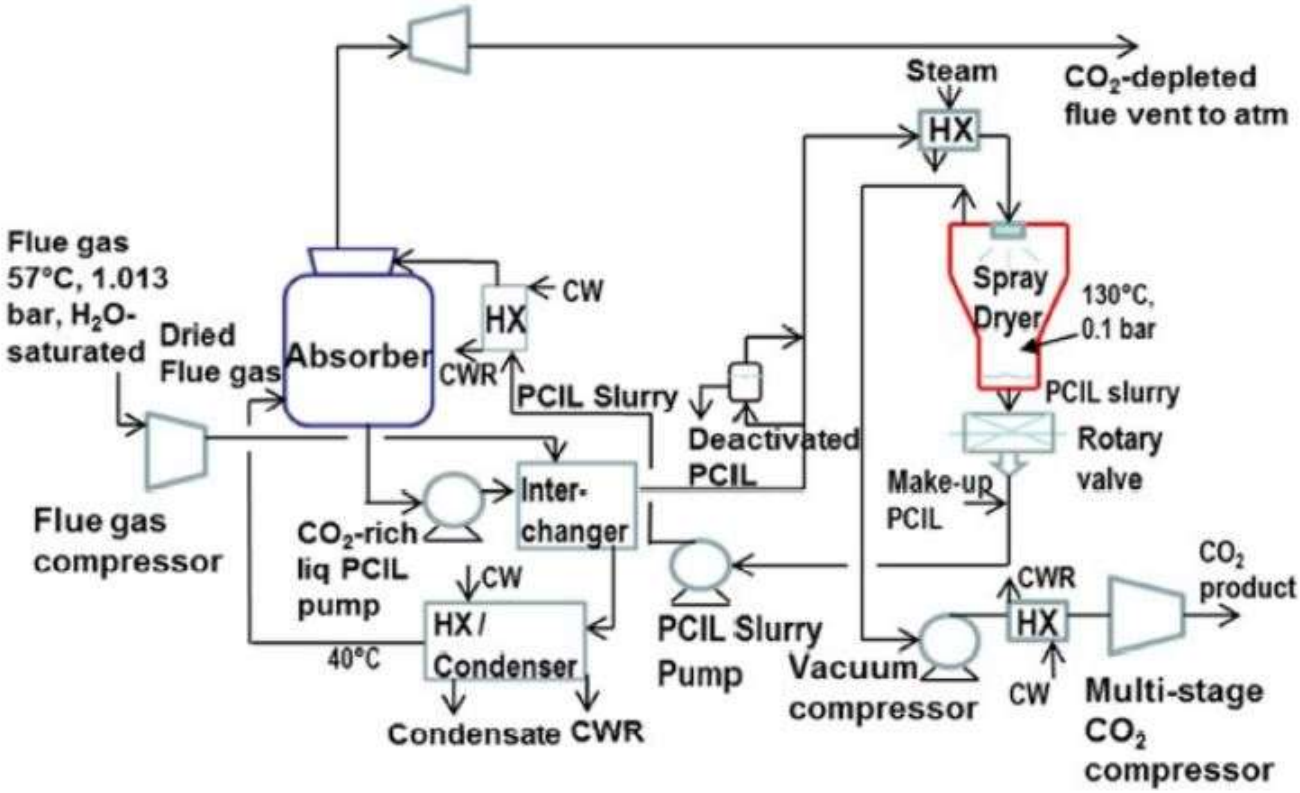

Figure 8: Process flow diagram for CO_2 capture in a full-scale plant using PCILs.

technology advantages

- The encapsulation of ILs and PCILs in micrometer-sized shells is projected to increase the mass transfer area by an order of magnitude or more.
- Significant reduction of the capital costs of the absorber and regenerator in CO_2 capture systems.
- Lowered energy demands to operate absorption/regeneration cycle with the encapsulated solvents.

R&D challenges

- IL absorption capacities decrease with lower partial pressures of CO_2, and CO_2 concentration in flue gas is low at only about 0.15 bar.
- Viscosities of ILs generally increase upon reaction with CO_2, occurring because of the formation of hydrogen bonding networks.
- ILs tend to degrade strongly in the presence of typical flue gas contaminants, such SO_2 and SO_X.
- Encapsulation of ILs in polymer shells: getting sufficiently high loadings of the IL/PCIL in the shells, possible compatibility issues or unfavorable effects of the IL and polymer material on each other, and viscosity and surface tension issues in microencapsulation.
- Solids handling issues that arise from encapsulating liquids in shells, essentially turning a liquid into a finely granular solid material, and the necessity of reliably circulating this material around a complicated absorption-regeneration cycle.
- The shells themselves must withstand damage and reliably contain the ILs; leakage of the IL/PCIL if shell polymeric cross-linking is insufficient.

status

The project has been completed.

available reports/technical papers/presentations

Final Scientific/Technical Report, "Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO_2) Capture," June 29, 2019.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide Capture*," presented by Mark McCready, University of Notre Dame, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August, 2018.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide Capture*," presented by Mark McCready, University of Notre Dame, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August, 2017.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO_2) Capture*," Topical Report, November 2016.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion CO_2 Capture*," presented by Joan Brennecke, University of Notre Dame, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Hybrid Encapsulated Ionic Liquids for Post Combustion CO_2 Capture*," Project kickoff meeting presentation, November 2015.