NETL Project

Hybrid Encapsulated Ionic Liquids for Post Combustion CO_2 Capture

DOE Agreement No. DE-FE0026465

Project Kick-off Meeting

NETL, Pittsburgh, PA

Monday, November 30, 2015

Outline

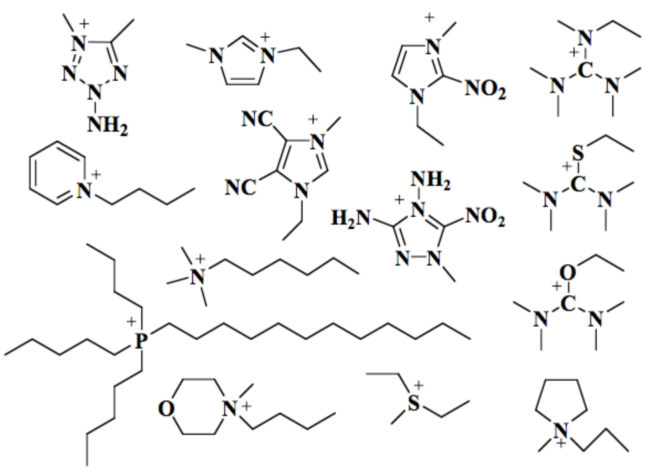
- **Background on the proposed technology and the scientific/technical merit**
- Project team/project organization
- Project objectives
- **Technical approach/project scope**
- Project budget
- Project schedule and associated milestones
- Decision points and success criteria
- Project risks/risk management

Background on the proposed technology and the scientific/technical merit

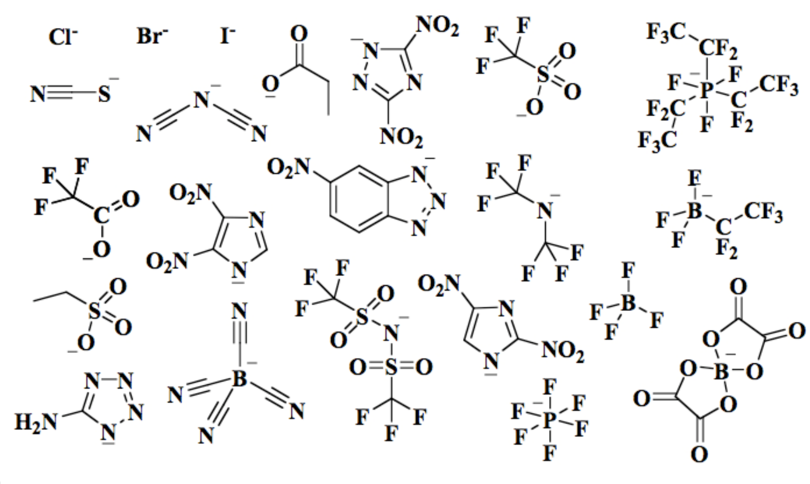
Ionic Liquids

- Pure salts that are liquid around ambient temperature
  - Not simple salts like alkali salts
- Many favorable properties
  - **Nonvolatile**
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity

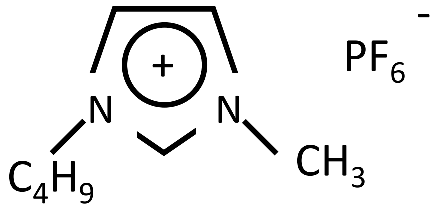
Examples of cations



Examples of anions



First Gas Solubility in IL



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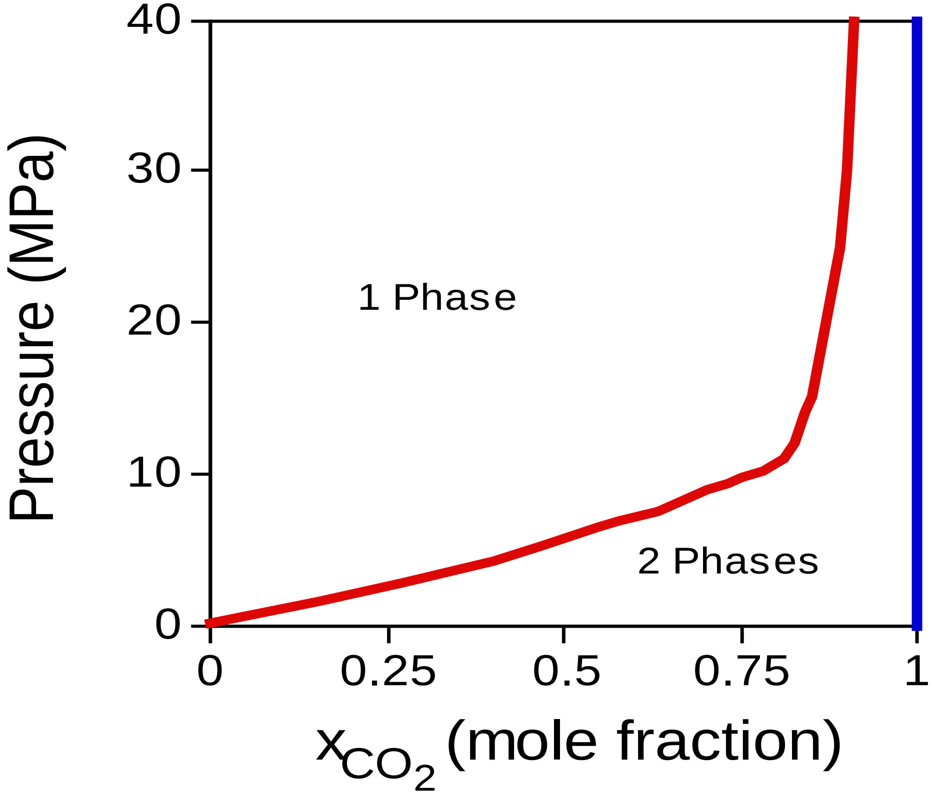


- no detectable IL in CO_2 phase at 40C and 13.8 MPa
- significant solubility of CO_2 in IL
- 1.3-7.2 mole % IL mixtures immiscible at 40 MPa

Blanchard , Hancu, Beckman and Brennecke., Nature, May 6, 1999

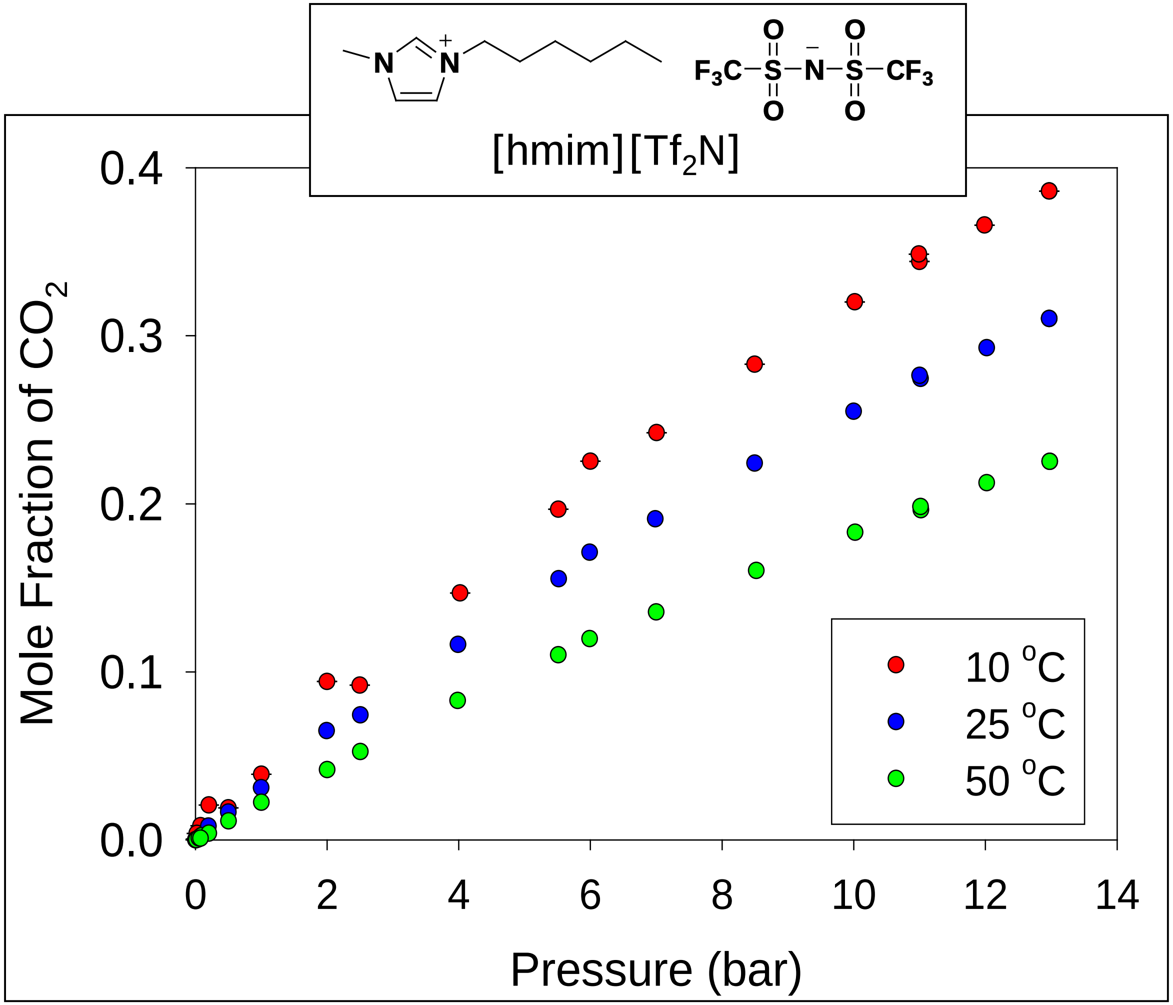
Physical Dissolution of CO_2

- Gas solubility

solubility pressure

solubility temperature

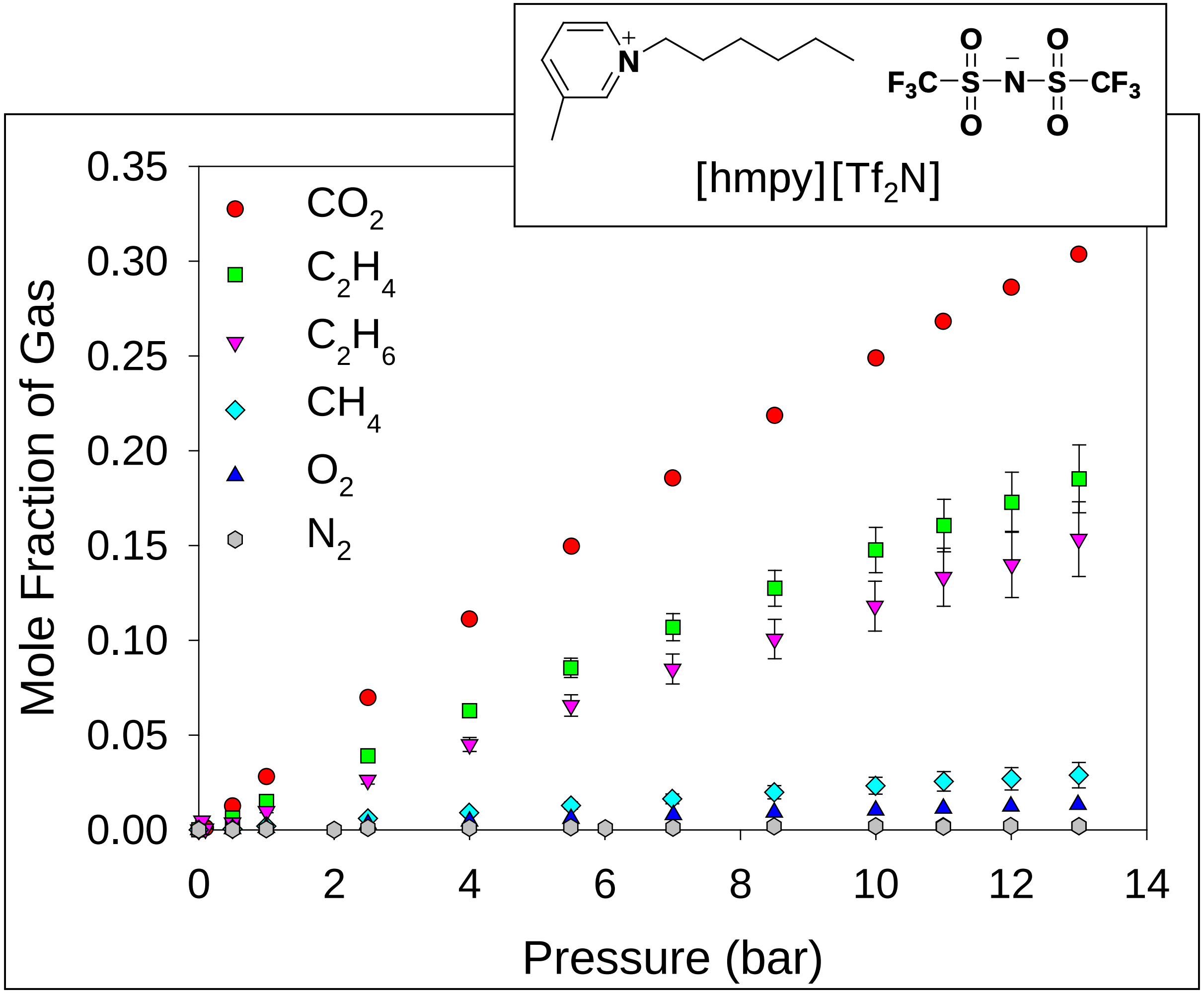
- Important for reusability of ILs
  - Absorb at low T
  - Remove at high T
- Trend seen for CO_2 solubility in all ILs measured



Muldoon, et al., JPC B, 2007, 111, 9001-9009

Physical Dissolution of Gases in ILs

- Selectivity of CO_2 over N_2, O_2, etc. is good even for physical dissolution of CO_2 in ILs



Anderson, et al., ACR, 40, 2007, 1208-1216

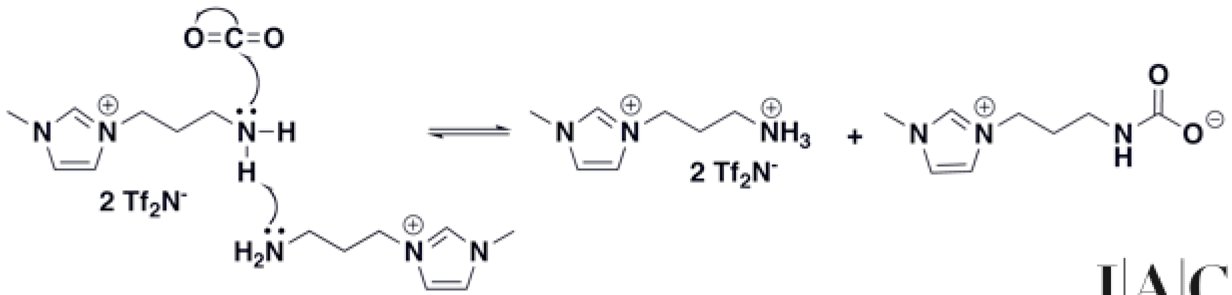
Need Chemical Complexation with CO_2

Low partial pressures for post-combustion

- **Physical solubility**
  - **Low heat of absorption**
  - **~ -12 kJ/mol by T dependence of isotherms and direct calorimetric measurements**
  - **Low regeneration energy**
  - **Large IL circulation rates**
  - **Desorption at low P increases compression costs**
  - **Would need ~10x increase in solubility to beat aqueous MEA**
- **Chemical complexation**
  - **Strong enough to increase capacity and decrease IL circulation rates**
  - **Weak enough to keep regeneration energies (and temperatures) down**

Build on Amine Chemistry

TSIL CO_2 reaction mechanism



J|A|C|S COMMUNICATIONS

Published on Web 01/19/2002

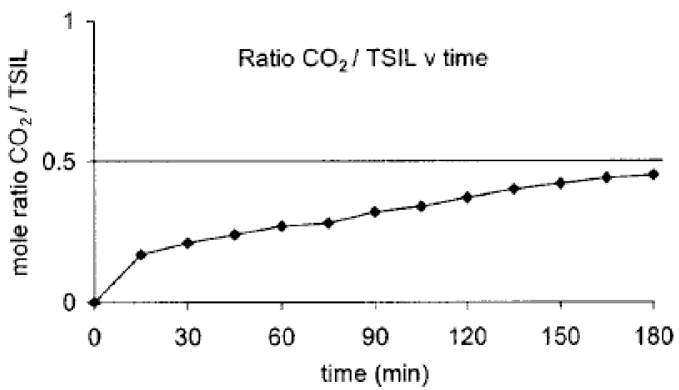
CO_2 Capture by a Task-Specific Ionic Liquid

Eleanor D. Bates, Rebecca D. Mayton, Ioanna Ntai, and James H. Davis, Jr.*

Department of Chemistry, University of South Alabama, Mobile, Alabama 36688

926 VOL. 124, NO. 6, 2002 ■ J. AM. CHEM. SOC.

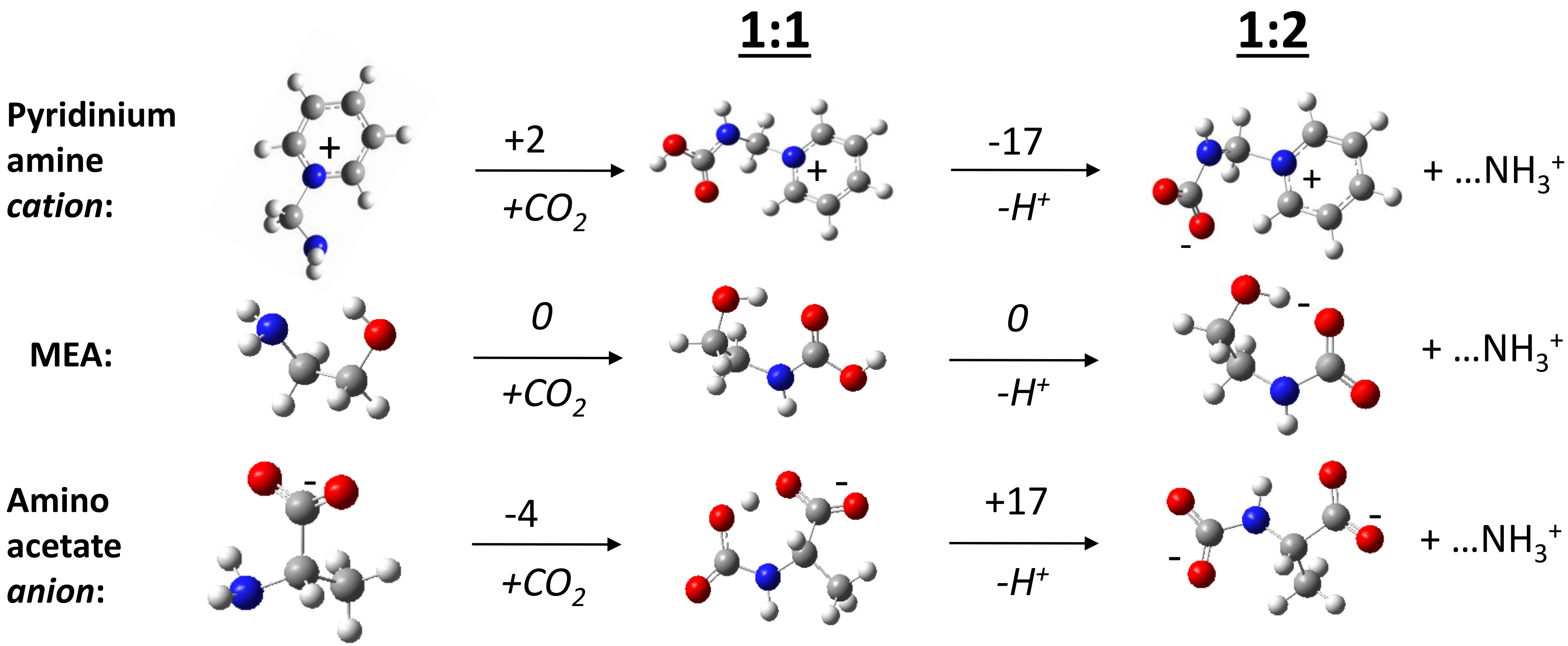
1 atm CO_2
Room temp.



- Results in 1:2 CO_2 to IL molar uptake
- Huge increase in viscosity

Can We Get Higher Capacity Than 1:2?

Reaction energies in kcal/mol relative to MEA

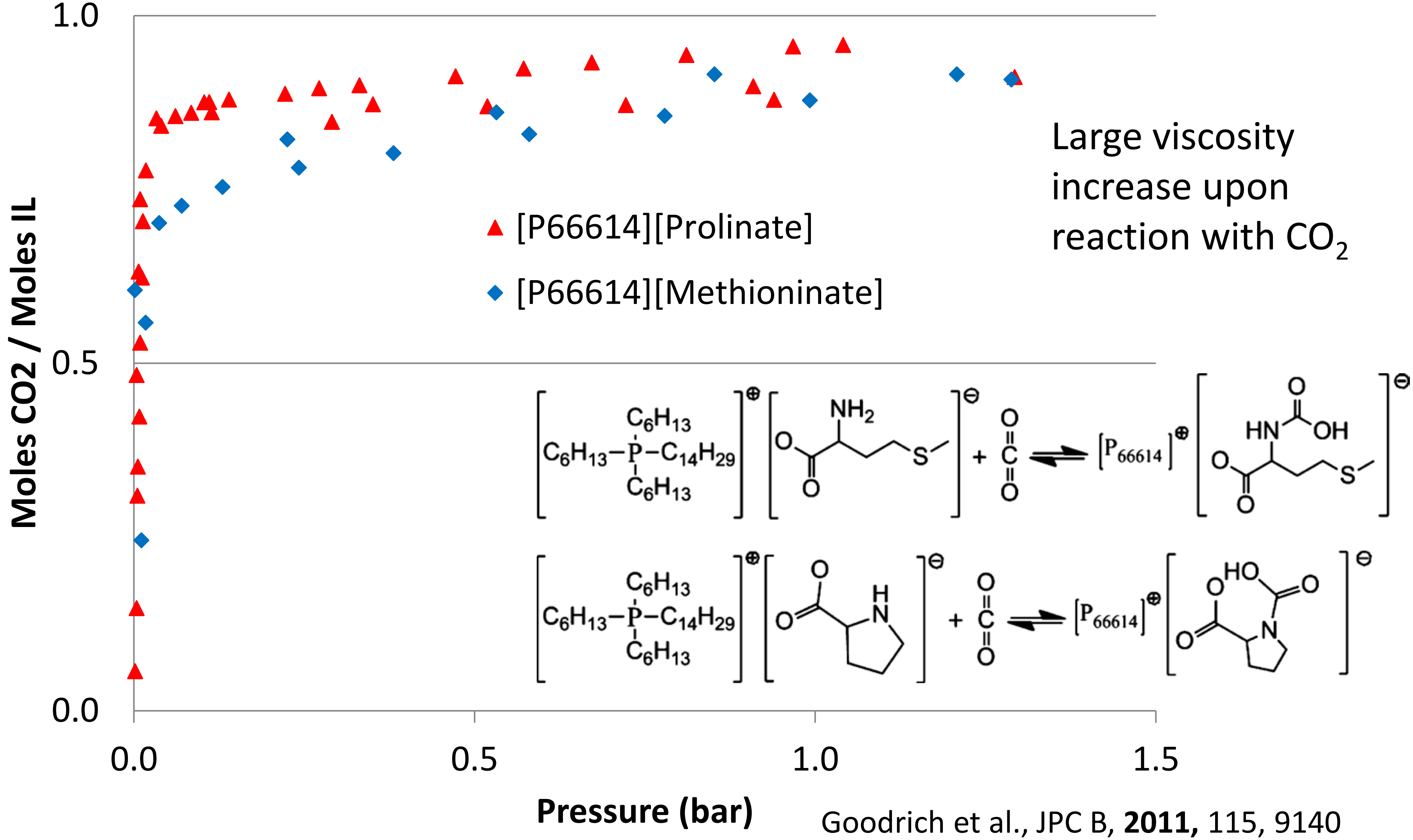


- Local cation tethering favors 1:2 binding
- Local anion tethering disfavors 1:2 binding
- Tethering ion and tethering point as important as functional groups in controlling CO_2 reactions

Mindrup and Schneider, *ACS Symp. Series* **2010**

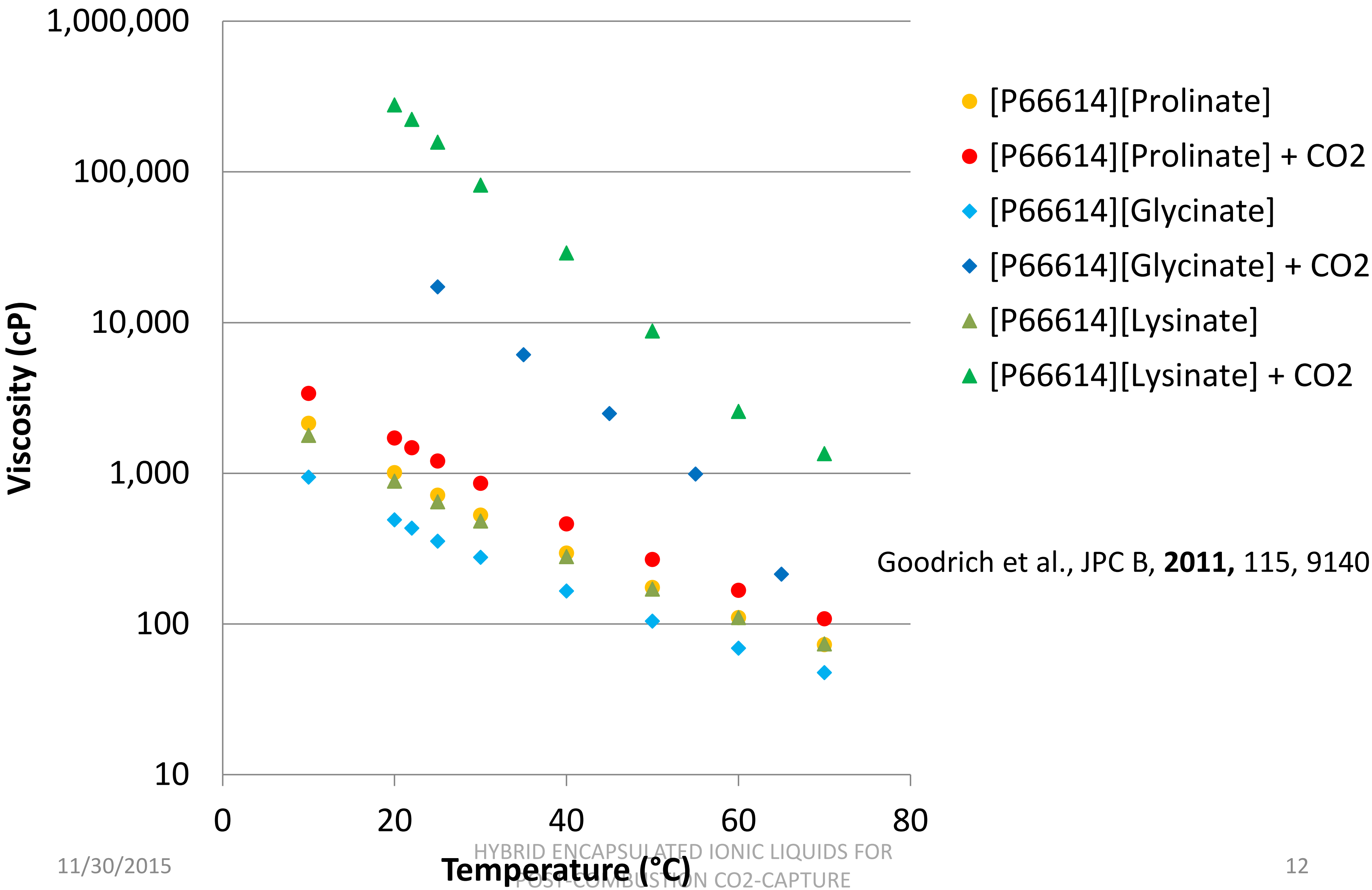
1:1 Uptake with Amine on Anion

Forms carbamic acid, not carbamate



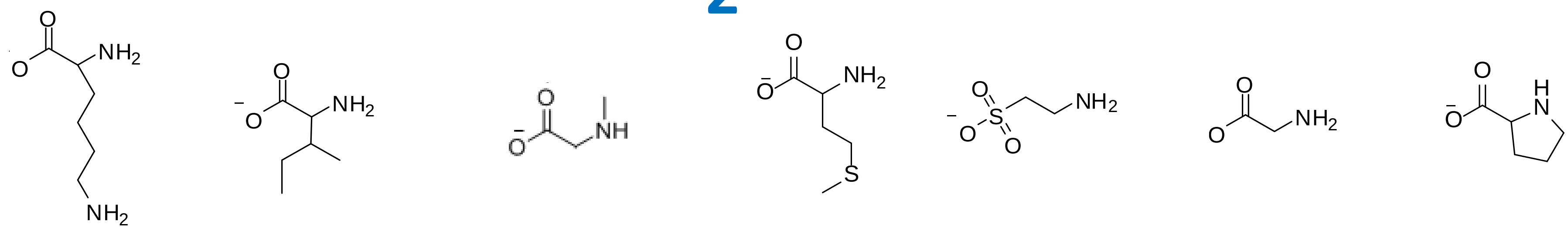
Goodrich et al., JPC B, **2011,** 115, 9140

Effect of CO_2 on Viscosity



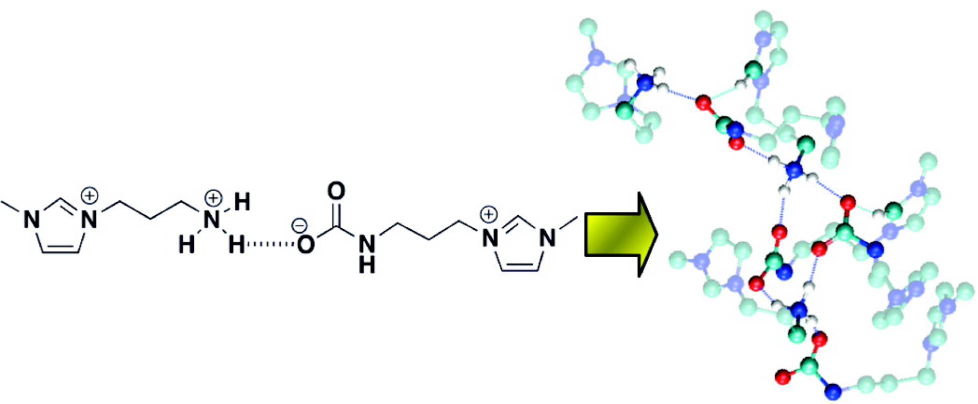
Goodrich et al., JPC B, **2011,** 115, 9140

Effect of CO_2 on Viscosities



Lysinate Isoleucinate Sarcosinate Methioninate Taurinate Glycinate Prolinate

Decreasing CO_2 Saturated Viscosity

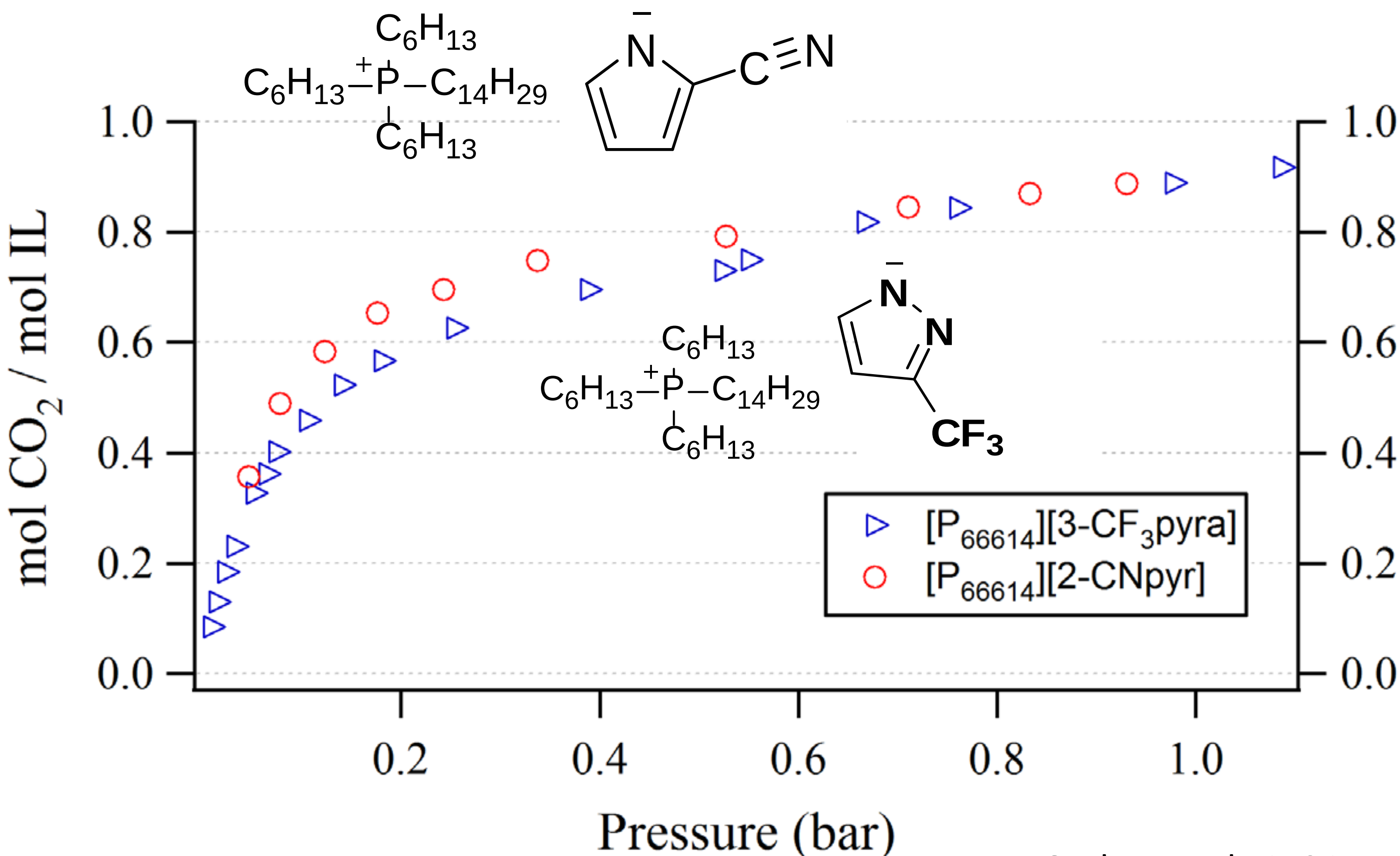


- Viscosity increases with CO_2 because of the formation of a hydrogen bonding network
- Prolinate, due to its ringed structure, has the least amount of free hydrogens able to participate in hydrogen bonding.

Gutowski, K. E.; Maginn, E. J., *J. Am. Chem. Soc.* **2008**, *130*(44), 14690-14704

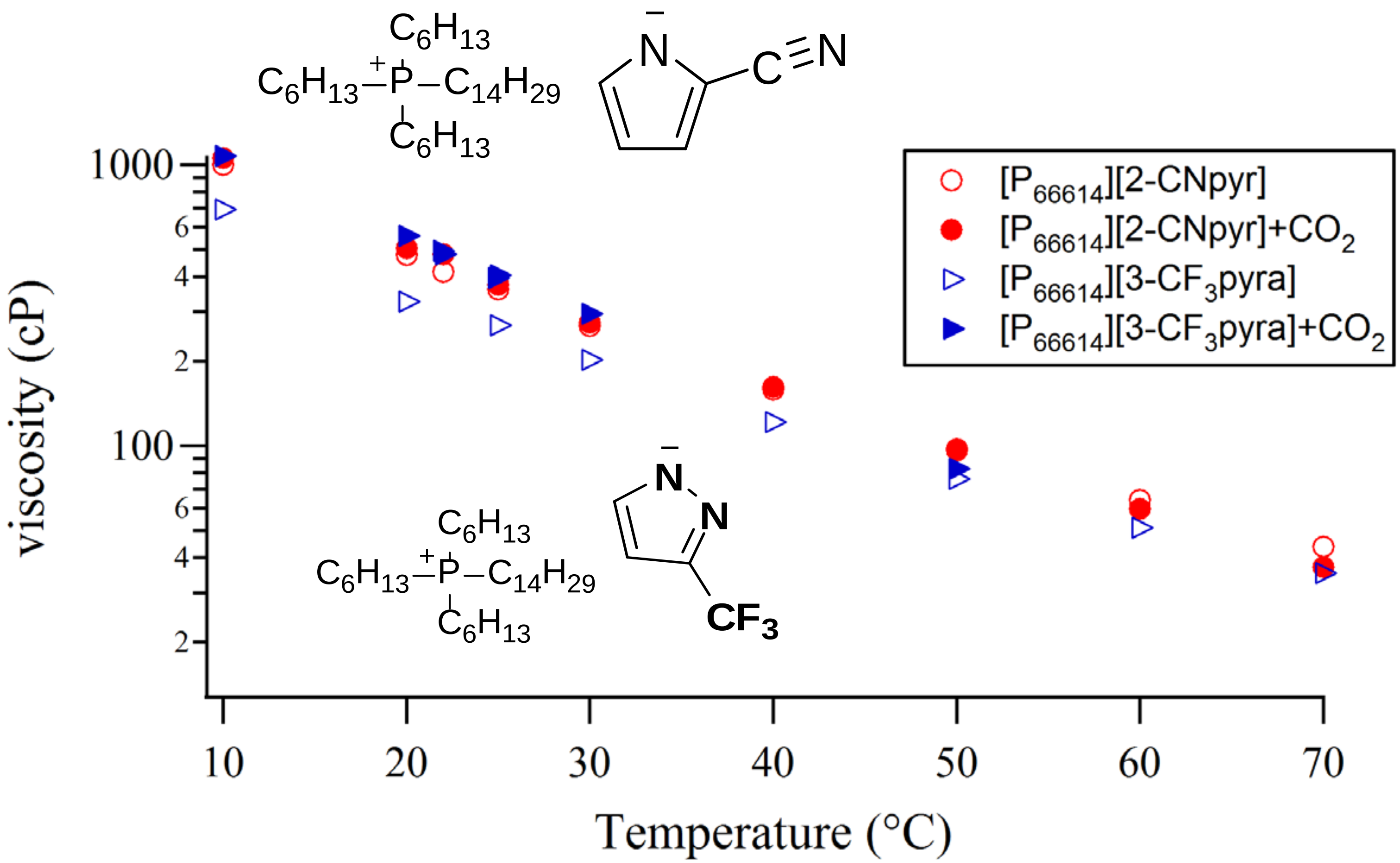
AHA – aprotic heterocyclic anions

- Retain amine in ring structure
- Further reduce free hydrogens to reduce hydrogen bonding



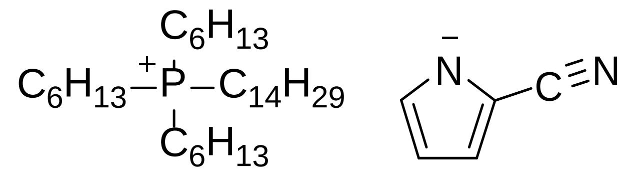
Gurkan et al., JPC Lett, 2010

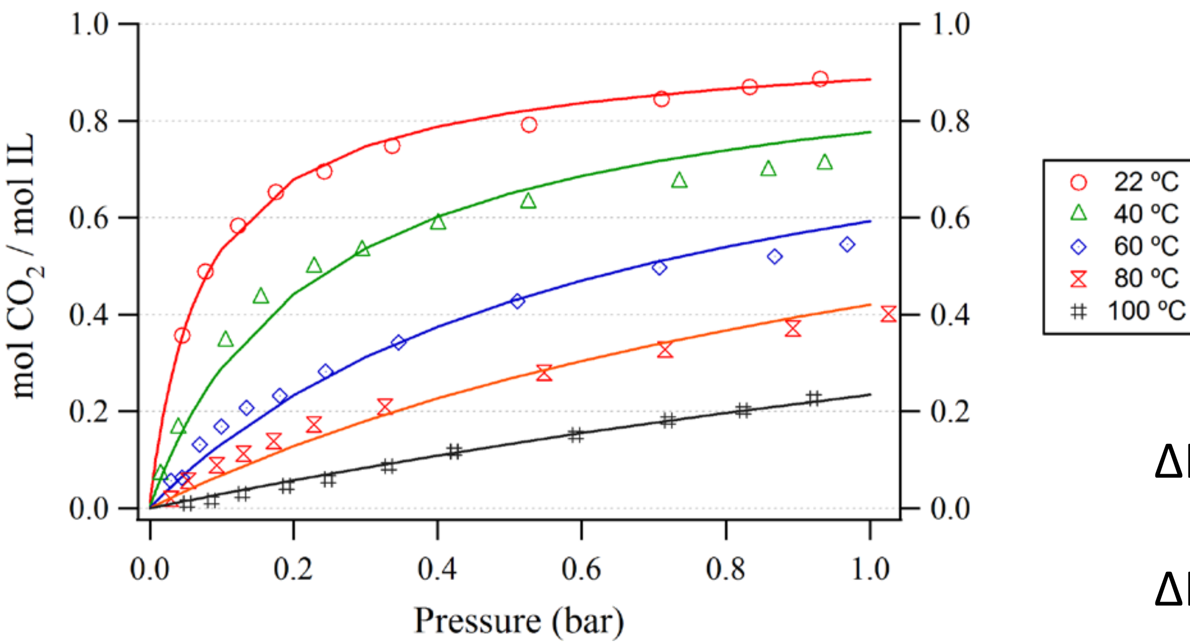
Eliminate Viscosity Increase by Using AHA – aprotic heterocyclic anions



Gurkan et al., JPC Lett, 2010

AHA CO_2 Uptake as Function of T





ΔH_{phys} = -10 kJ/mole CO_2

ΔH_{chem} = -43 kJ/mole CO_2

$CO_{2(g)} \rightleftharpoons CO_{2(phys)}$

$CO_{2(g)}$ + IL $\rightleftharpoons$ IL-CO_2

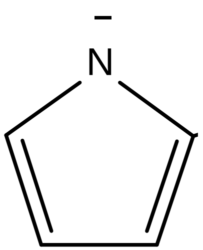
$$z = \frac{P_{CO2}/H}{1 - P_{CO2}/H} + \frac{k_1 P_{CO2} C_3}{1 + k_1 P_{CO2}}$$

Gurkan et al., JPC Lett, 2010

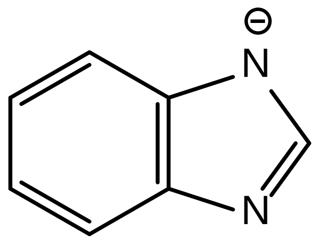
Different Aprotic Heterocyclic Anions

Adjust ΔH_{chem} with electron withdrawing groups

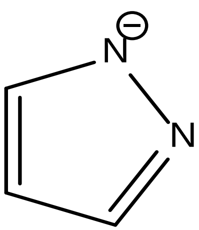
pyrrolides



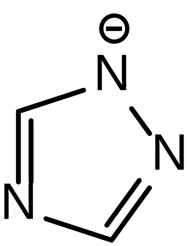
imidazolides



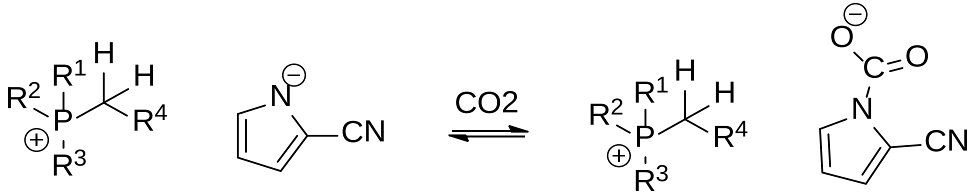
pyrazolides

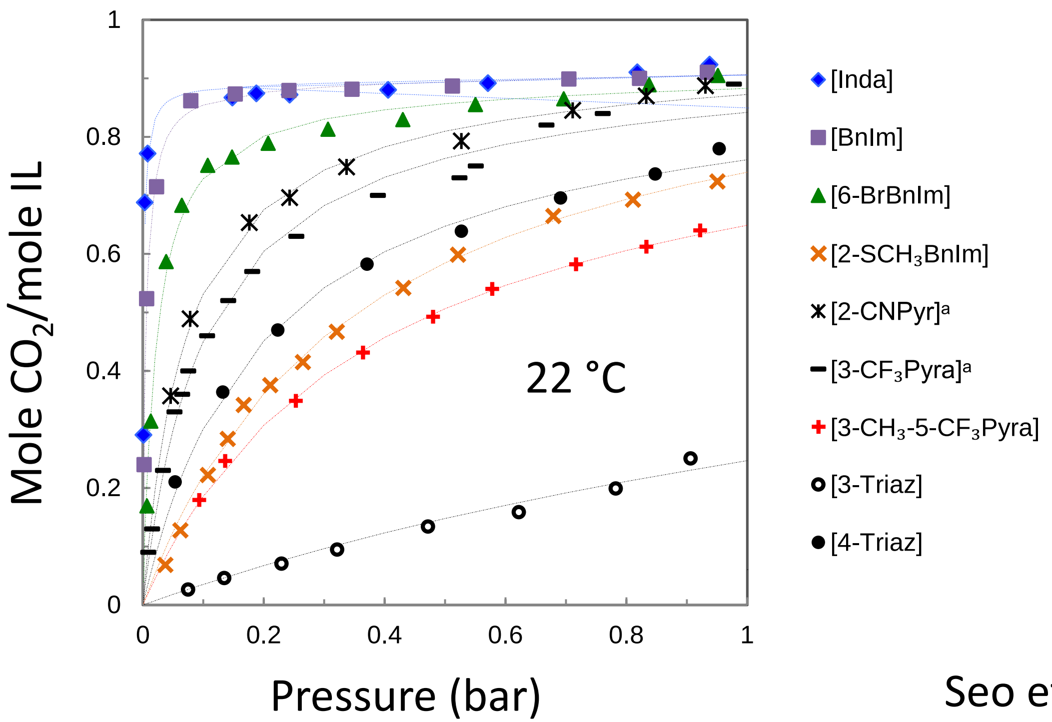


triazolides



Tuning Reaction Enthalpy of AHA ILs





ΔH_{rxn} (kJ/mol)

-54

-52

-48

-41

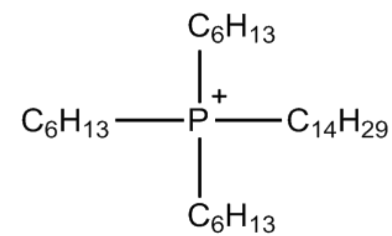
-45

-44

-41

-37

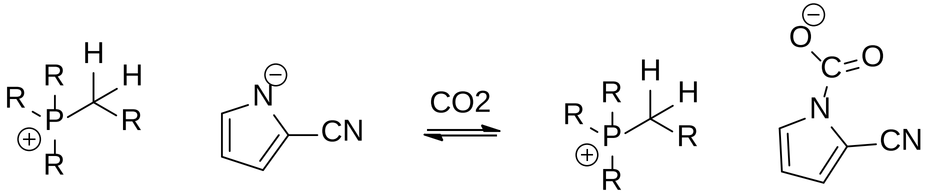
-42



Seo et al., JPC B, 2014, 118, 5740

Phosphonium Ylide Chemistry Challenges

- 2 reactions are taking place in parallel at higher temperatures
  - At low temperatures reaction 2 is kinetically limited
- Both reactions are reversible



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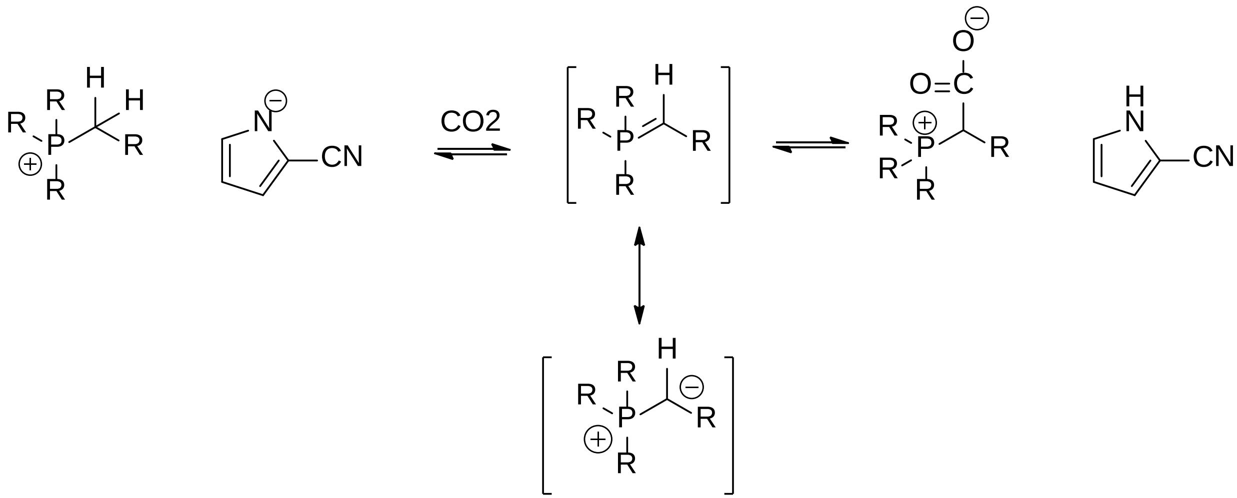
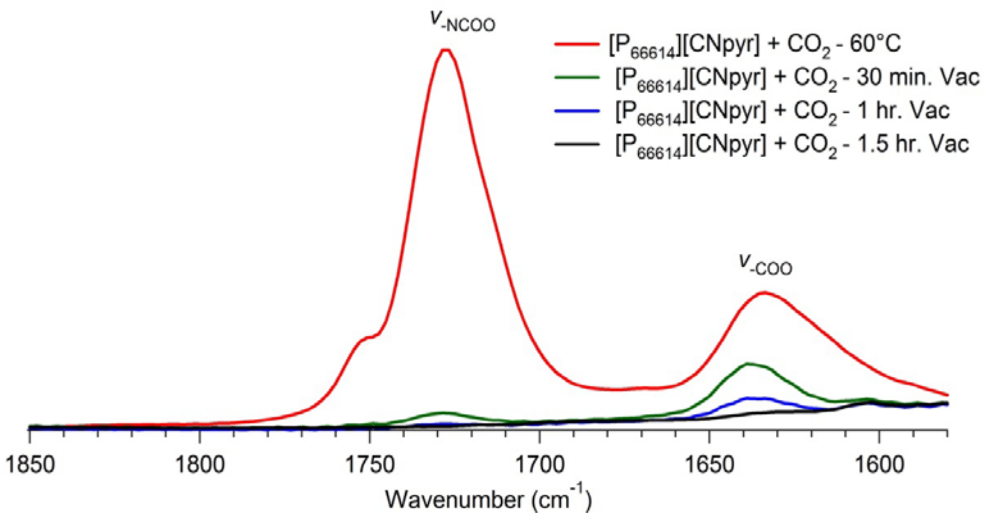
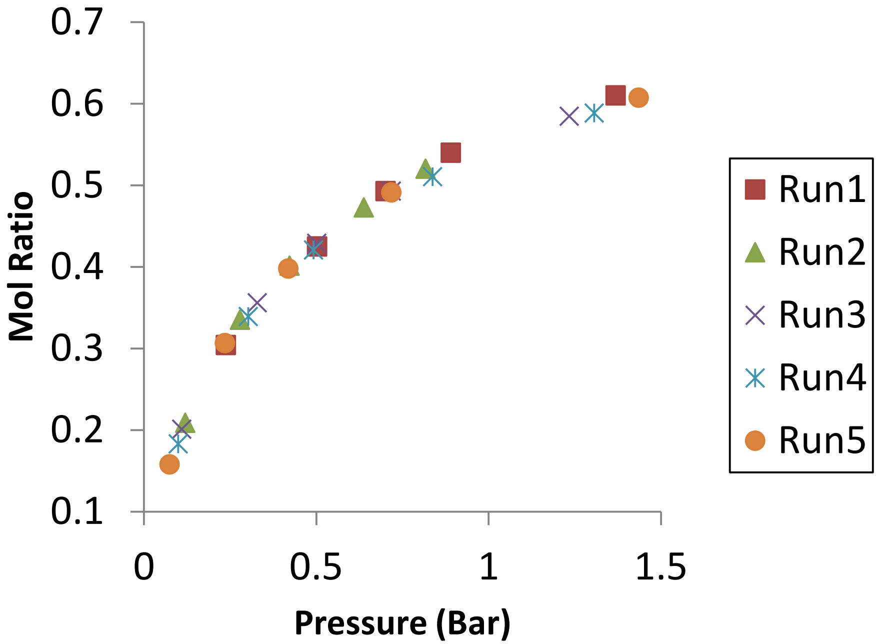


(2)

Ylide Reaction Completely Reversible

- Both anion-CO_2 and cation- CO_2 reactions reversible
  - Desorb under vacuum at 60°C
  - Process is fully reversible

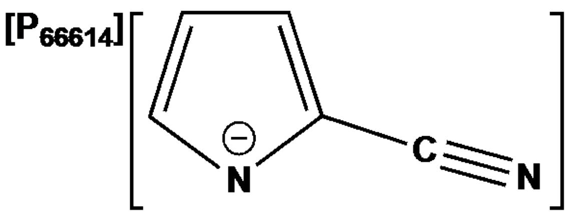




Possible irreversibility from evaporation of reprotonated anion completely eliminated if can't diffuse out of microcapsule!

Chemistry Challenges – Reprotonation?

$CO_2 + H_2O \longleftrightarrow H^+ + HCO_3^-$



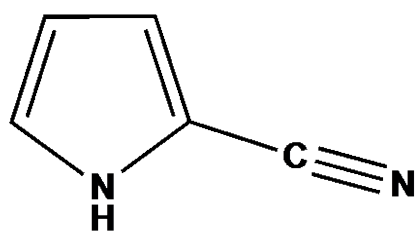
$+ \quad H_2O$

H^+ and/or CO_2

?

How fast?

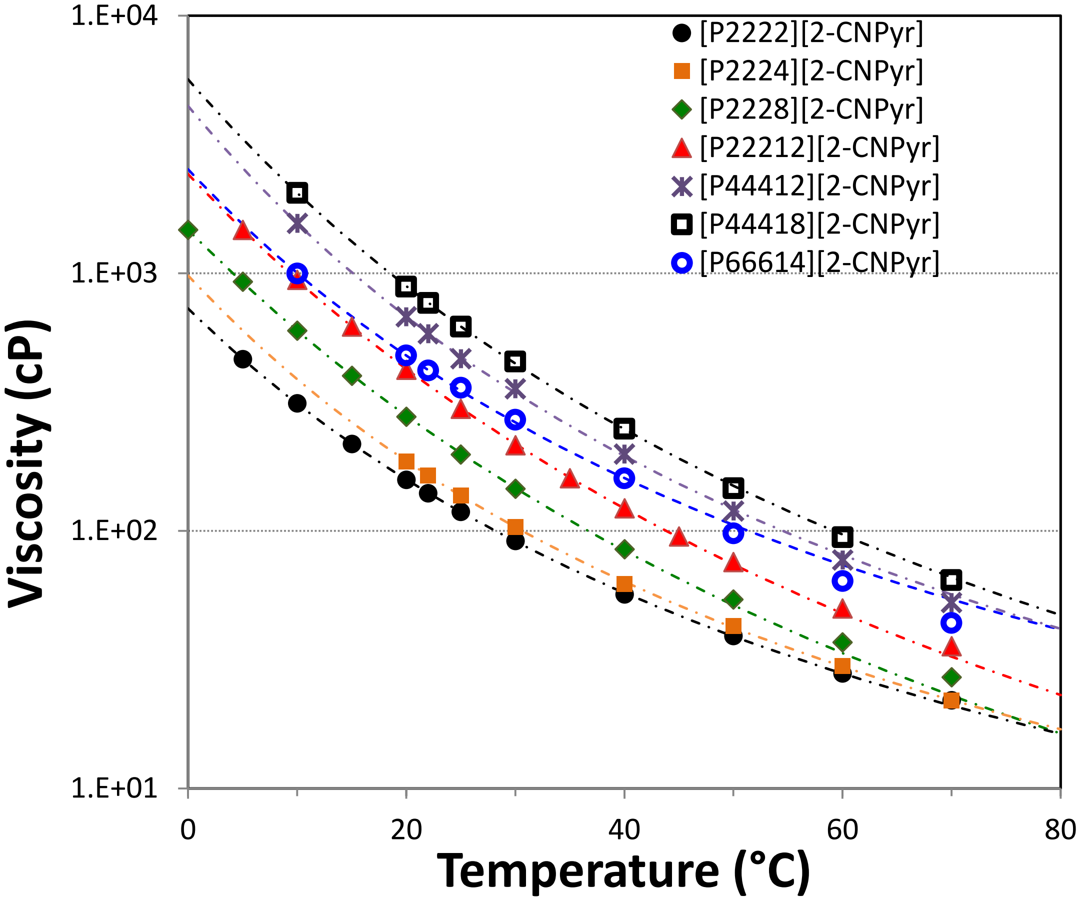
Reversible?



$+ \quad [P_{66614}]\,[OH]$

or $[P_{66614}][HCO_3]$

Effect of Cation – Viscosity



Shortening alkyl chains dramatically reduces viscosity

Other Effects of Shortening Alkyl Chains

Good

- Reduces molecular weight
  - Increases mass capacity
- Reduces heat capacity
  - Decreases sensible heat load

Bad

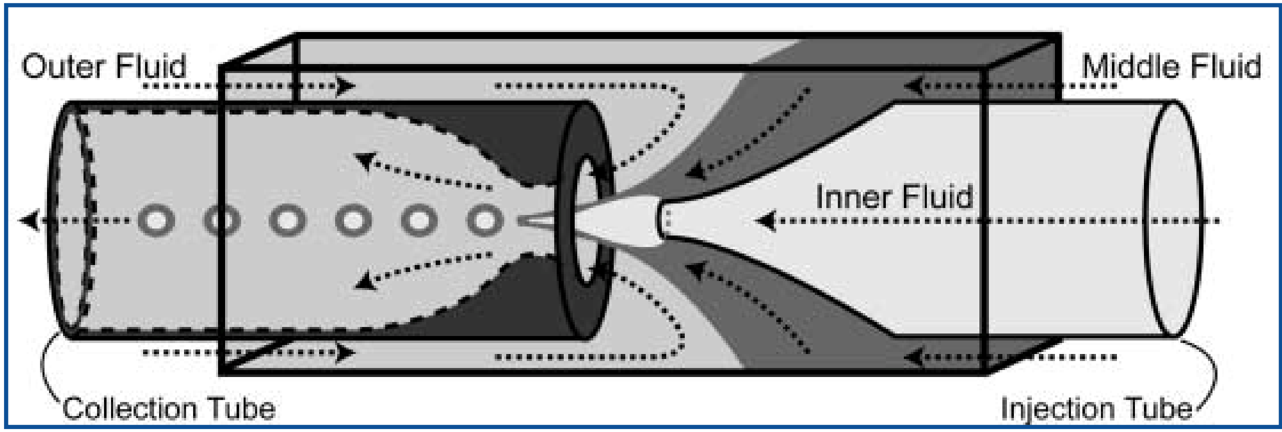
- More hydrophilic
  - Increases H_2O uptake
  - Potential reprotonation
- Appearance of melting points

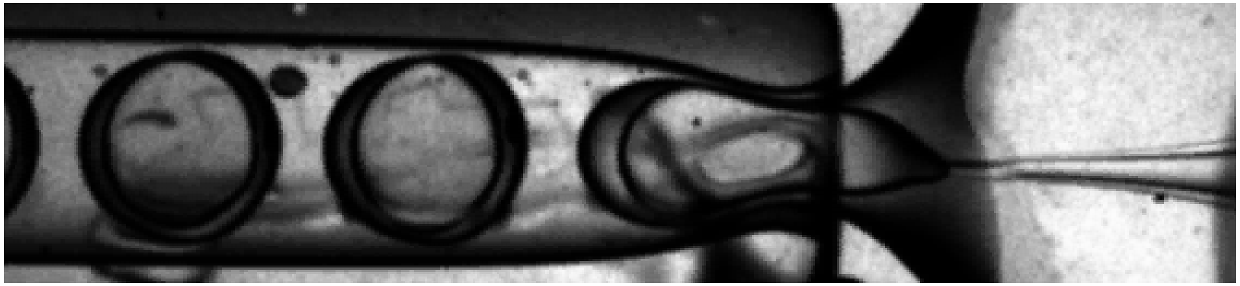
Microencapsulation Background

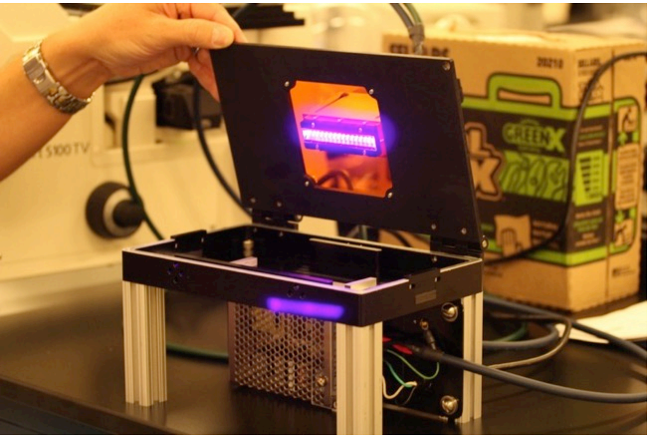
- Idea: improve mass transfer by increasing mass transfer AREA
- Successfully demonstrated by LLNL for other CO_2 sorbents

Microencapsulation Process

- 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



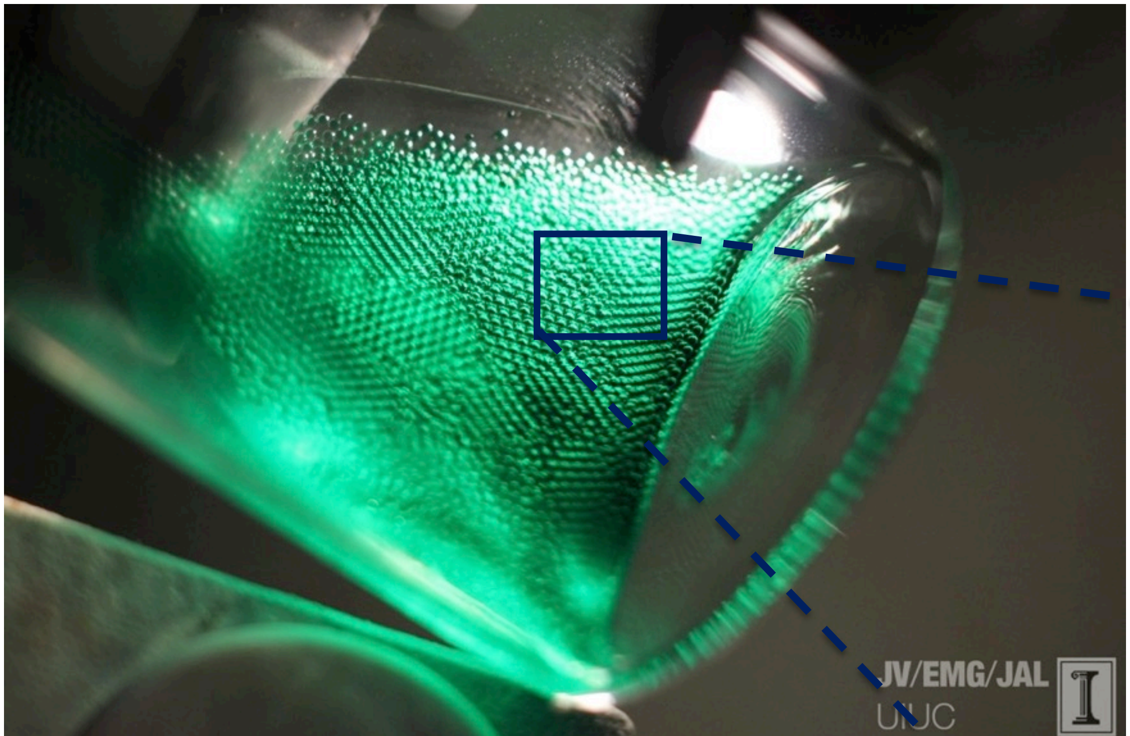




…and then cured with UV light.

Micro-encapsulated Carbon Sorbents (MECS)

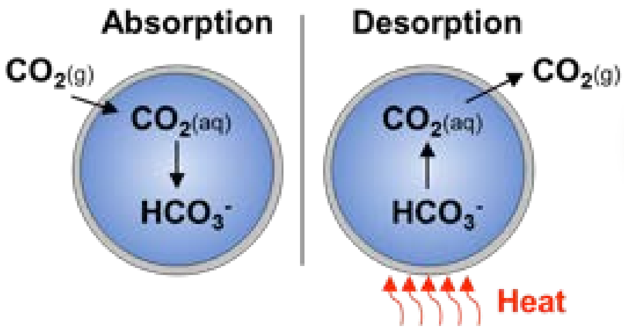
Liquid solvents or slurries encased in thin, permeable polymer shells

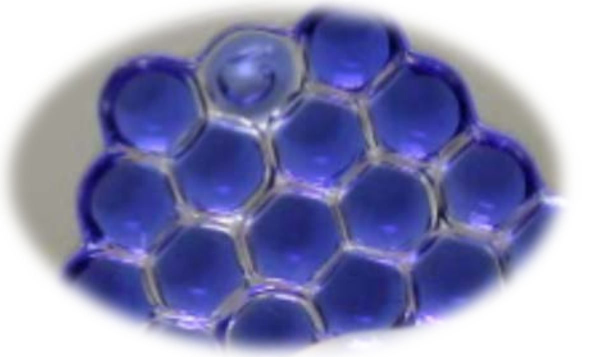


- Multiple solvents, shell materials, and sizes produced

Microencapsulation Enhances Absorption Rates

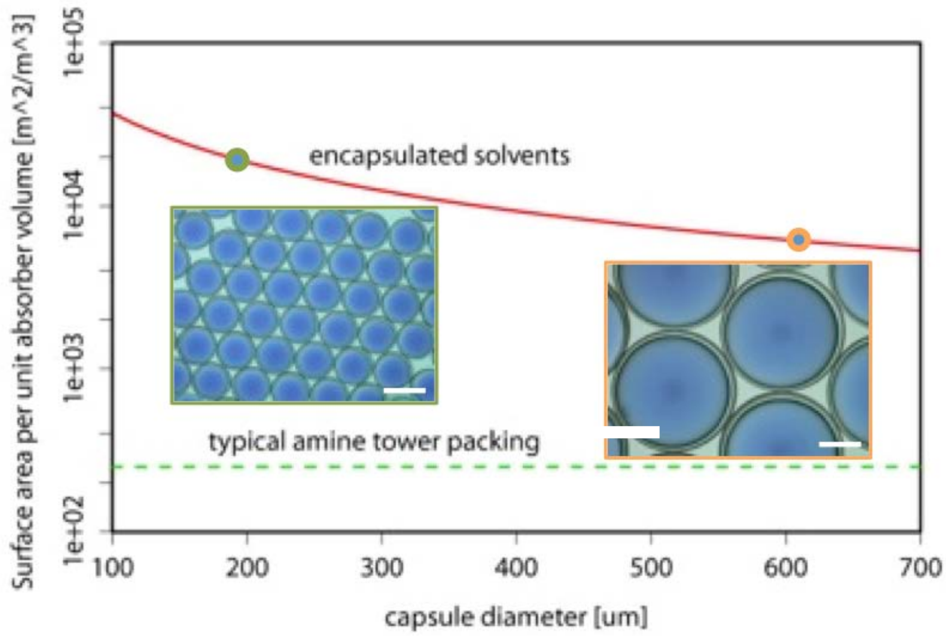
CO_2 absorbs through shell





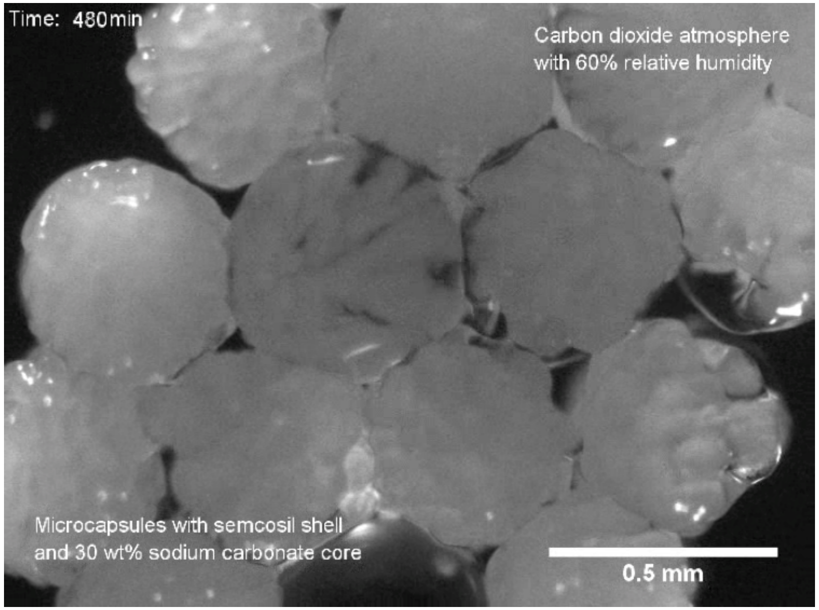
Mass transfer enhanced by increased surface area

Surface area formed by capsule, not a tower



Microencapsulation of Mixed Phases

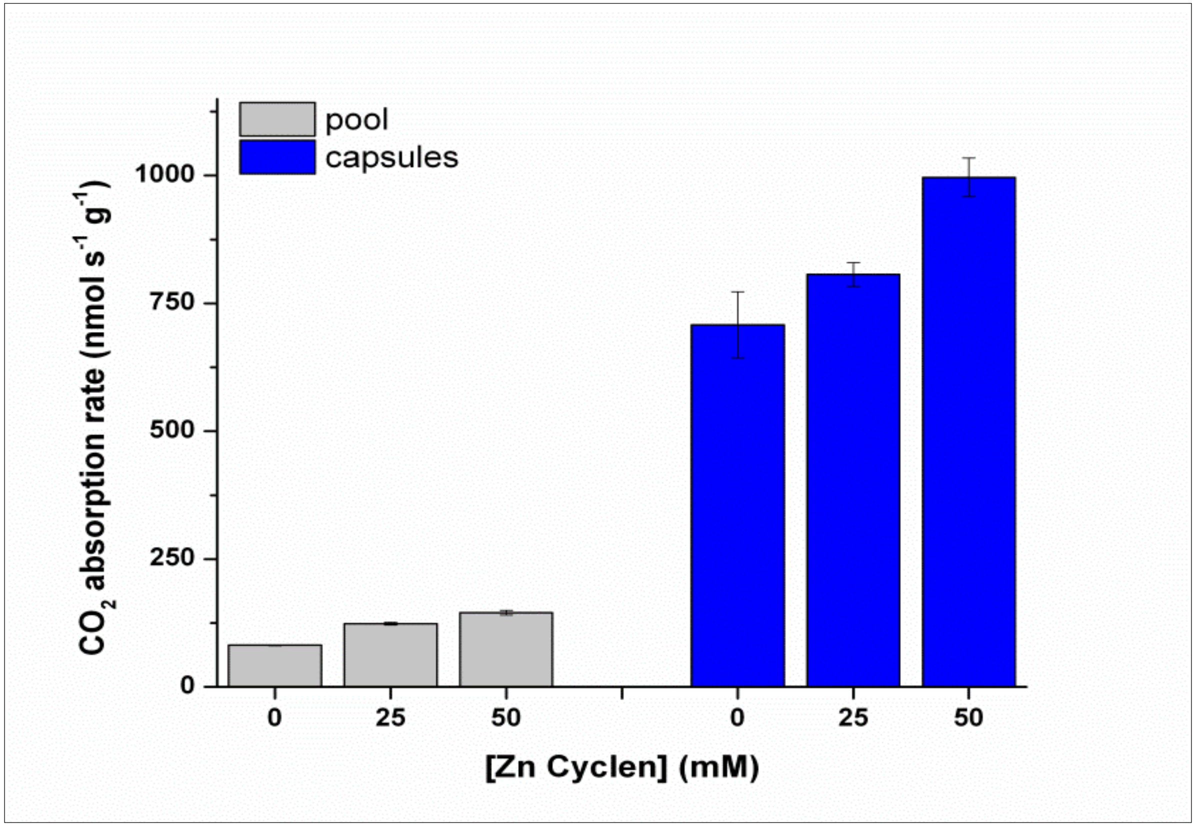
30 wt% Na_2CO_3 capsules exposed to CO_2 precipitating Nacholite ➞



Encapsulating slurry of glass bubbles ⬇

Microencapsulation Enhances Absorption Rates

Encapsulation increases capture rate of carbonates by 10x compared to same volume of liquid.



Microencapsulation

Process options same as for solids:

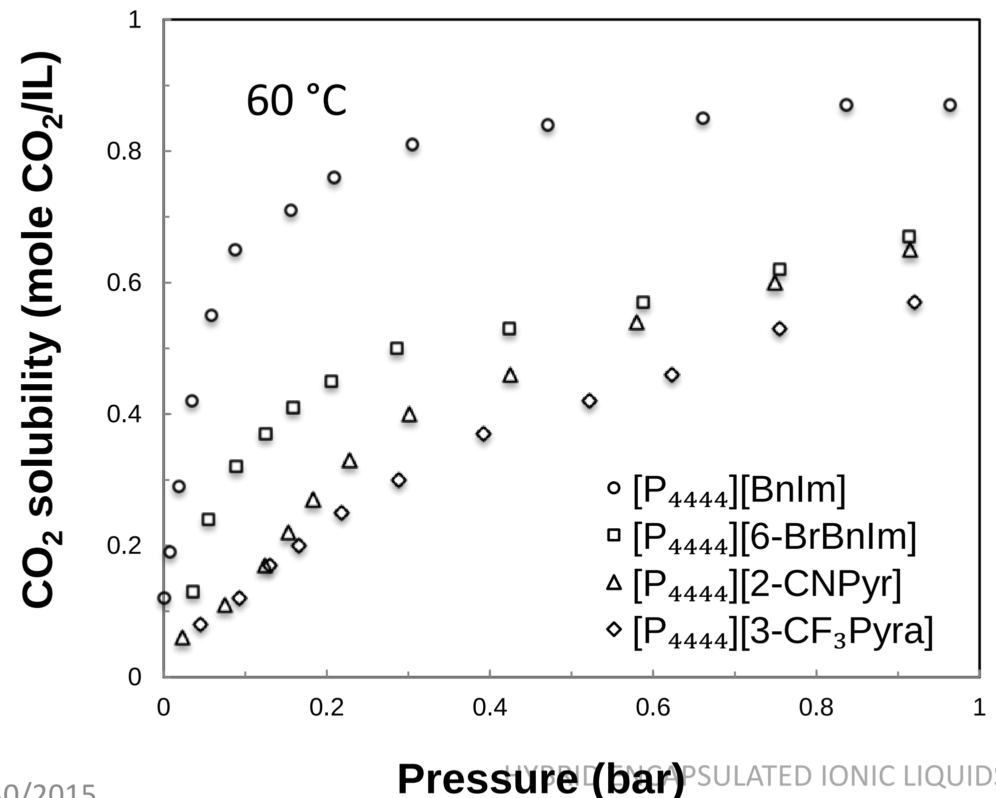
- Fluidized bed
- Moving Bed
- Fixed bed

Thermally regenerable for many cycles (80 tested).

Discovery of Phase Change Ionic Liquids

All T_m > 45 °C

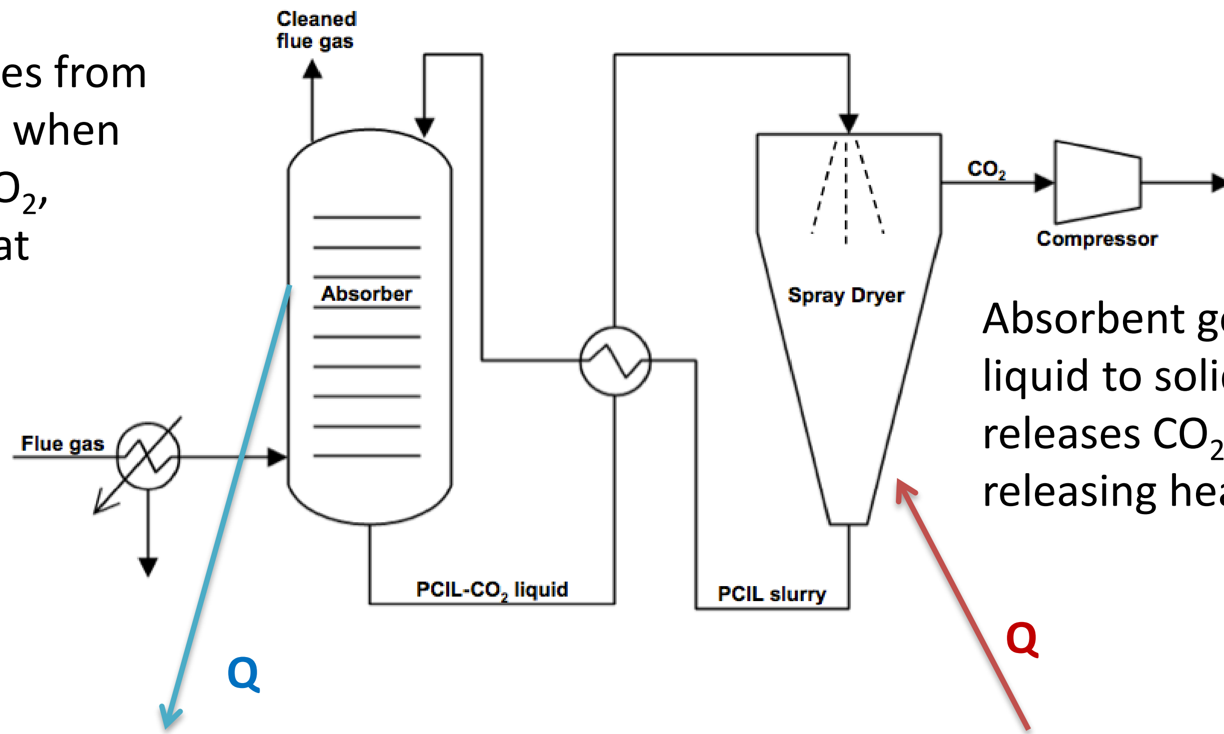
Remained liquid at 22 °C with 1 bar CO_2 pressure



$T_{m,\ complex} < T_{m,\ unreacted}$

CO_2 Capture with Phase Change Material

Absorbent goes from solid to liquid when reacts with CO_2, absorbing heat



Absorbent goes from liquid to solid when releases CO_2, releasing heat

‘Melting’ of absorbent reduces cooling duty

Heat duty in stripper reduced by the heat of fusion of the phase change material

CO_2 Capture with Phase Change Material

Absorber

Remove
50 kJ/mol

$[C^+][A^-]\ (s) + CO_2 \longrightarrow [C^+][ACO_2^-]\ (s)$

exothermic

$[C^+][ACO_2^-]\ (s) \longrightarrow [C^+][ACO_2^-]\ (l)$

endothermic

Add
20 kJ/mol

Q_{net} = Remove 30 kJ/mol

Regenerator

Add
50 kJ/mol

$[C^+][ACO_2^-]\ (l) \longrightarrow [C^+][A^-]\ (l) + CO_2$

endothermic

$[C^+][A^-]\ (l) \longrightarrow [C^+][A^-]\ (s)$

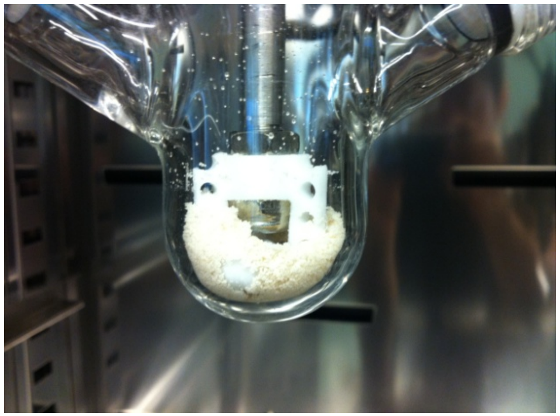
exothermic

Remove
20 kJ/mol

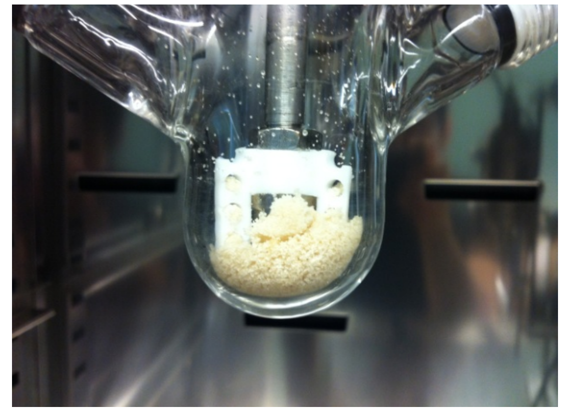
Q_{net} = Add 30 kJ/mol

Phase Change Ionic Material

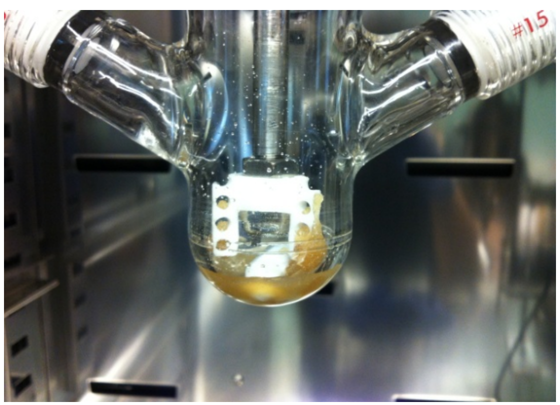
70 °C



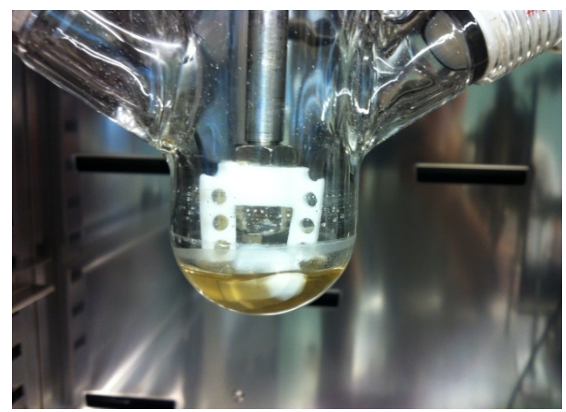
Pure material; T_m=166 °C; no CO_2



60 mbar CO_2

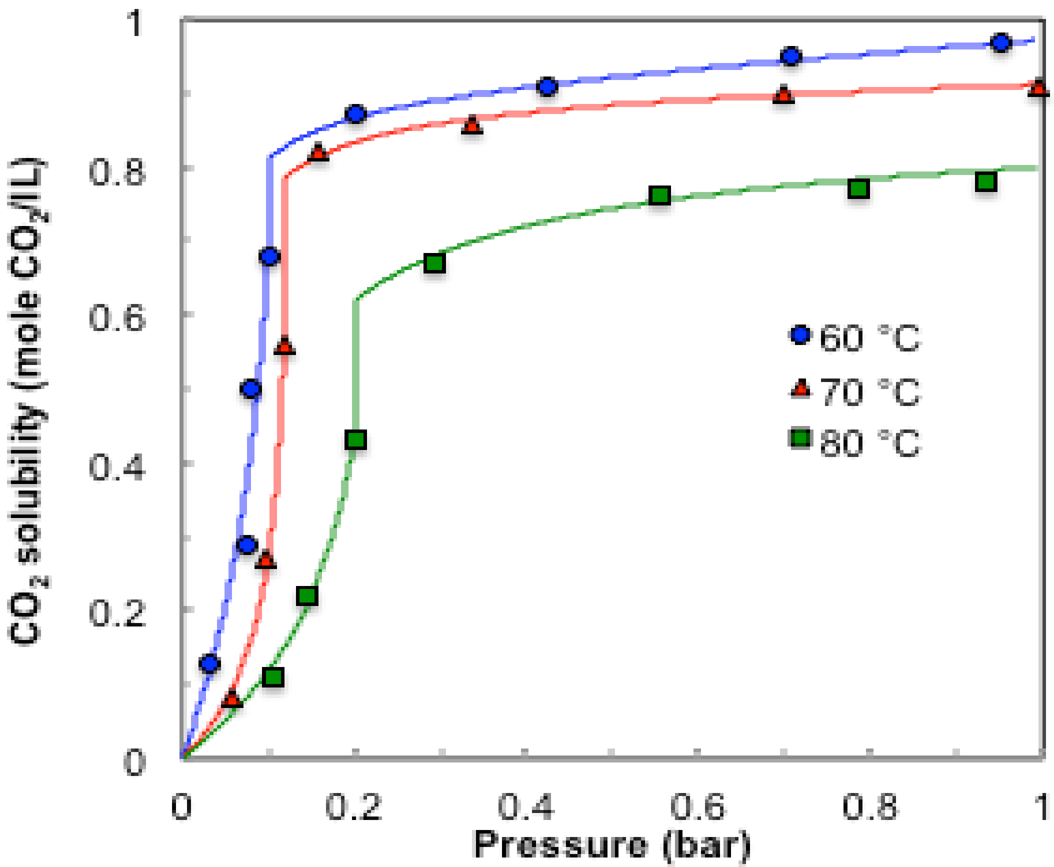


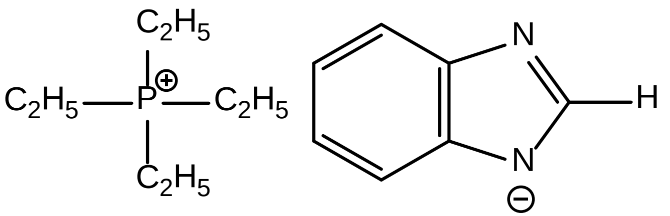
100 mbar CO_2



150 mbar CO_2

CO_2 Uptake Curves

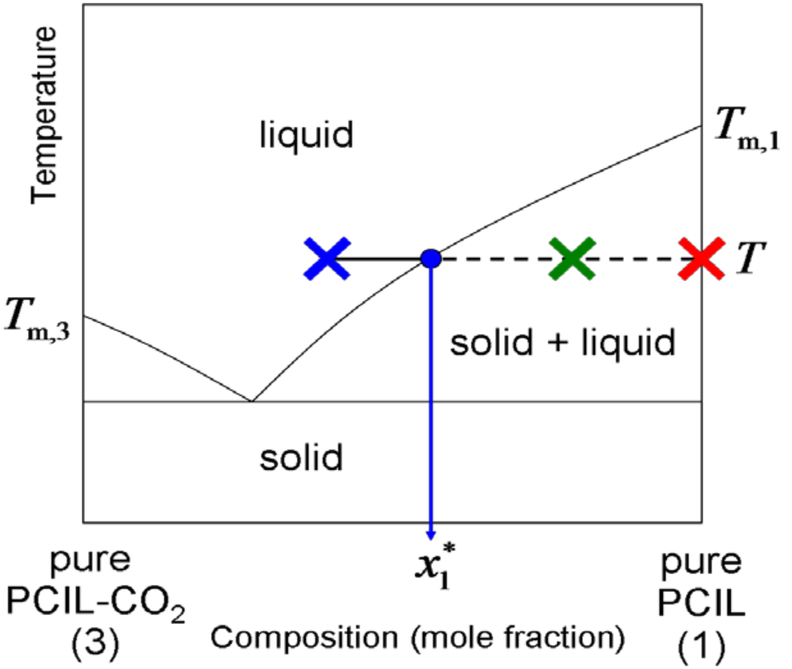




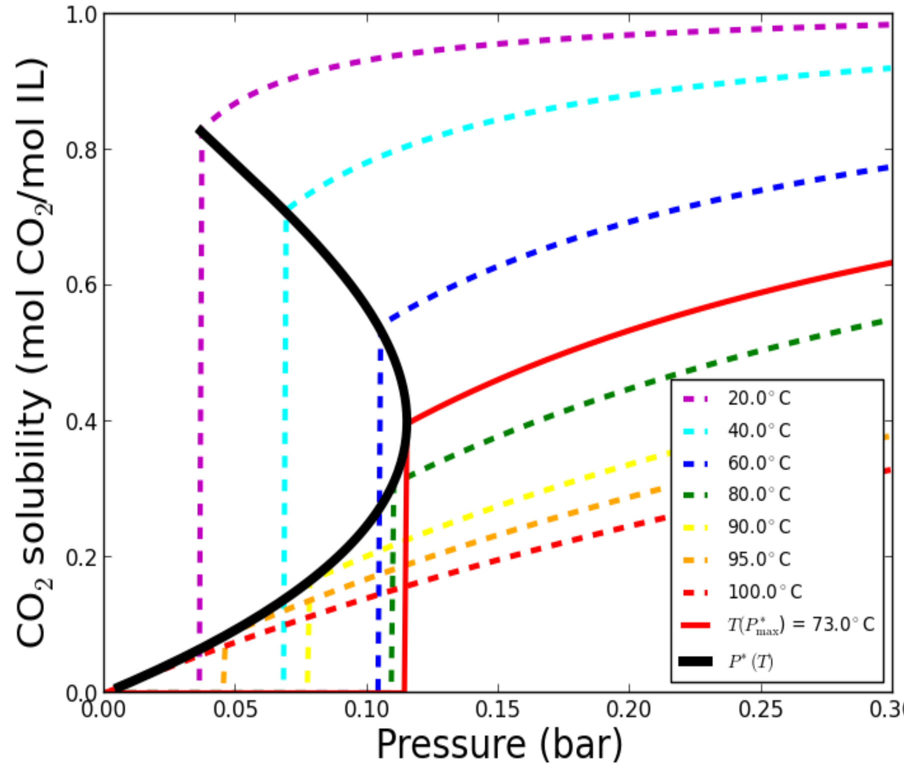
T_m = 166 °C
Δh_{fus} = -19.9 kJ/mole
Δh_{chem} = -52 kJ/mole

Seo et al., Energy & Fuels, 2014, 28, 5968-5977

Thermodynamic Model



Eutectic Model of PCIL System



Typical PCIL isotherms for idealized model, for the parameter values ΔH_{fus} = −20 kJ mol^{-1}, $T_{m,1}$ = 100 °C, ΔH_{rxn} = −50 kJ mol^{-1}, ΔS_{rxn} = −130 J mol^{-1} K^{-1}, ΔH_{phys} = −13 kJ mol^{-1}, ΔS_{phys} = −73 J mol^{-1} K^{-1}.

3 component, 3 phase, 1 rxt = 1 DOF
Fixed T, SVLE at one P*

Seo et al., Energy & Fuels, 2014, 28, 5968-5977

Process Modeling

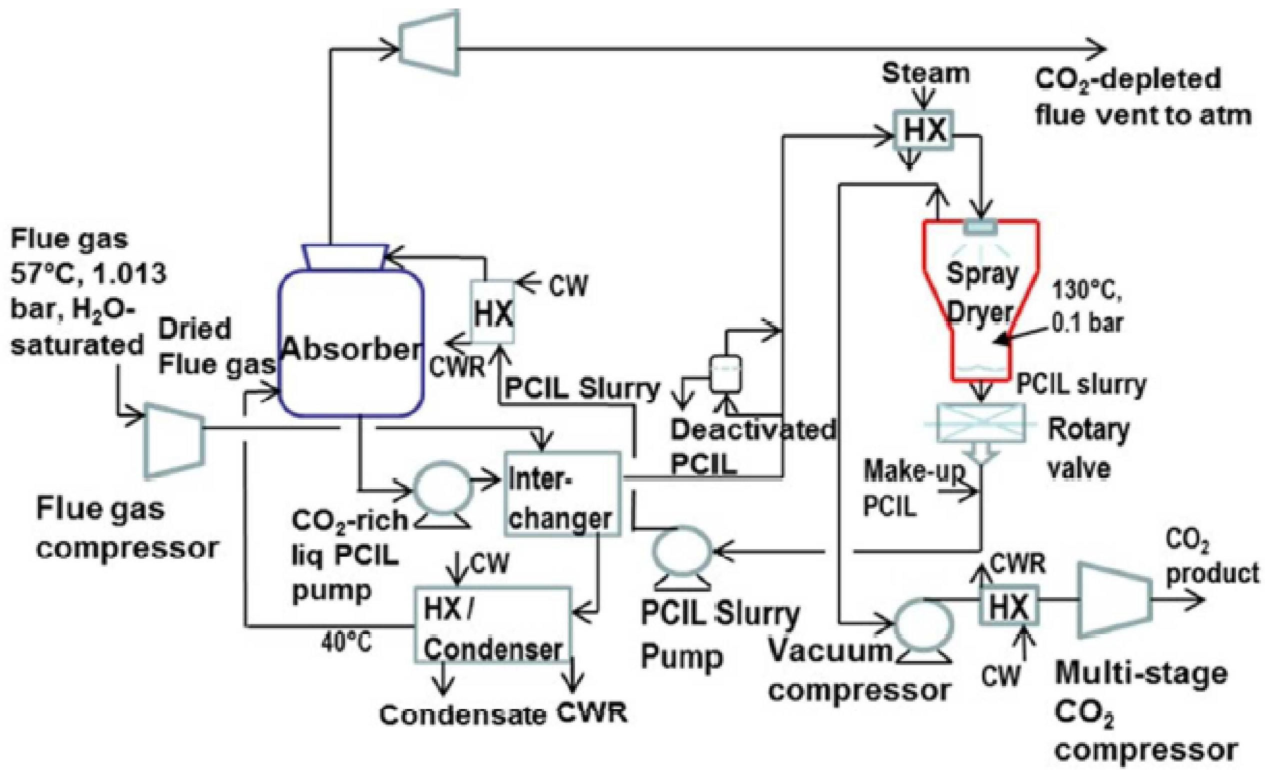


Figure 5. Process flow diagram for CO_2 capture in full-scale plant

Eisinger and Keller, Energy & Fuels, 2014, 28, 7070-7078

Laboratory Demonstration

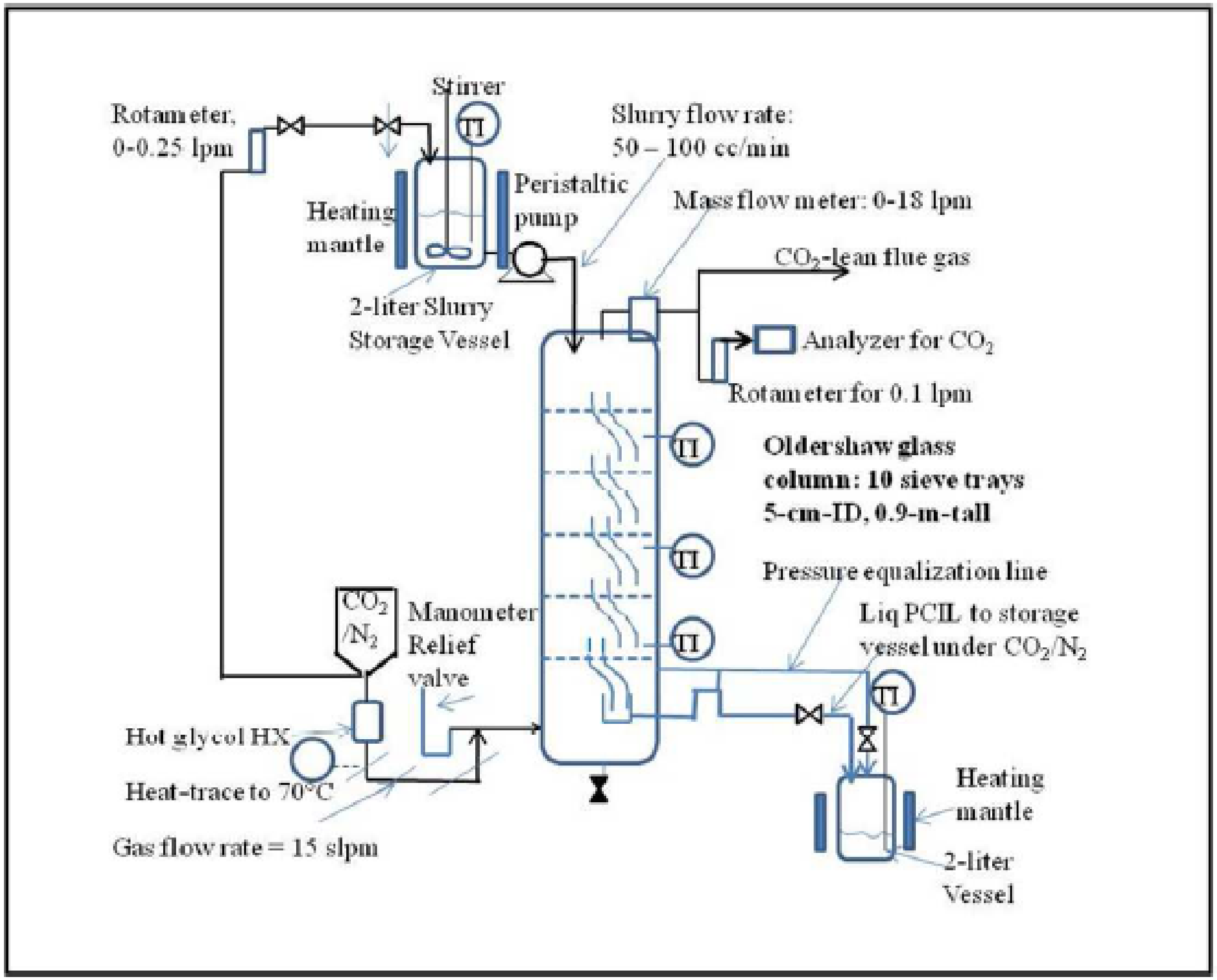


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Figure 7. Absorber for CO_2 capture

Laboratory Demonstration

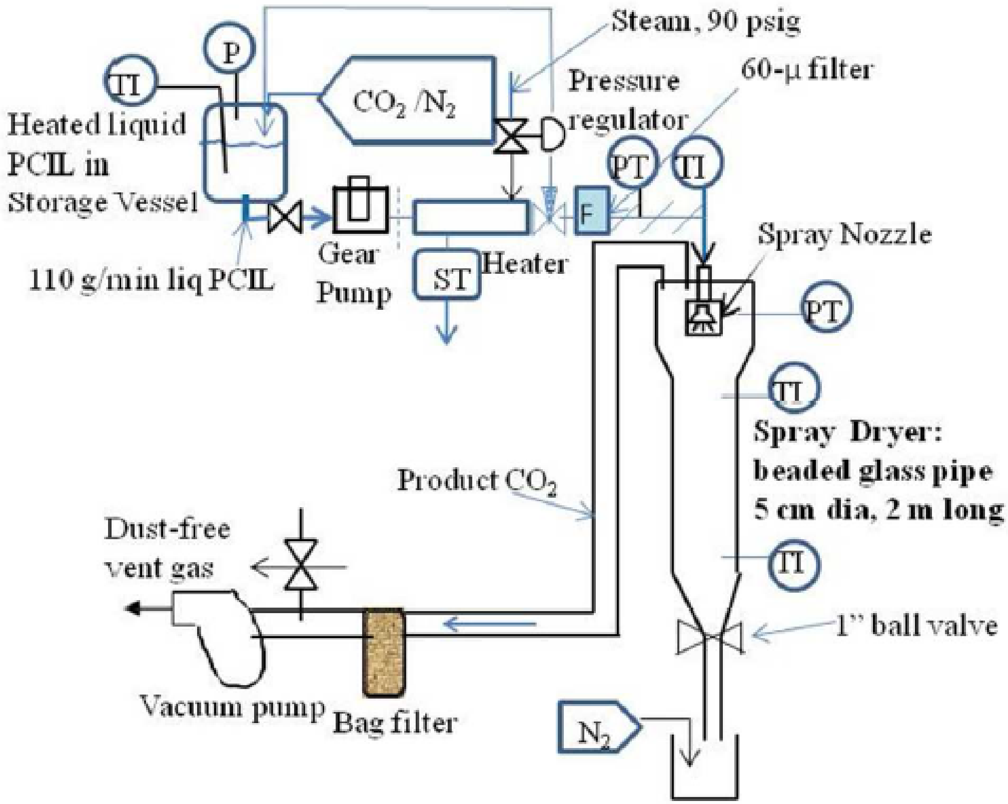

Figure 8. Spray dryer for regeneration of the liquid complex

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Process Modeling

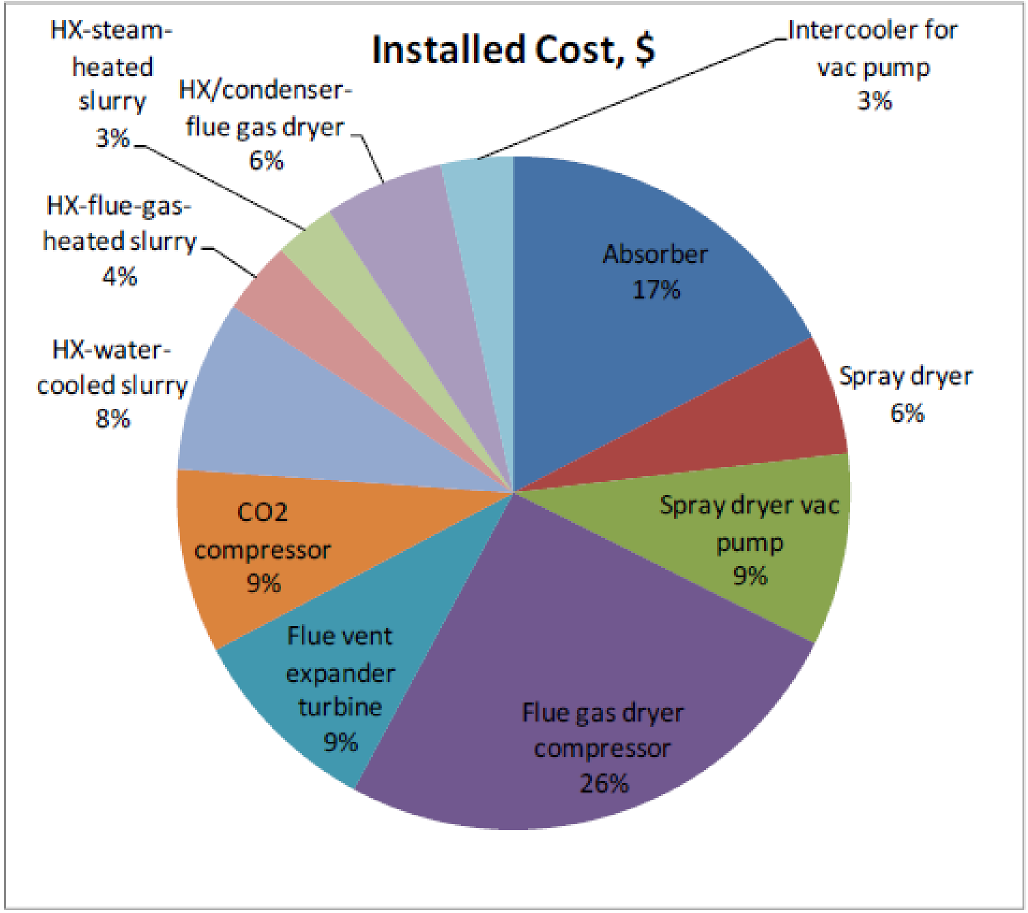

Figure 13. Contribution of major equipment to capital cost

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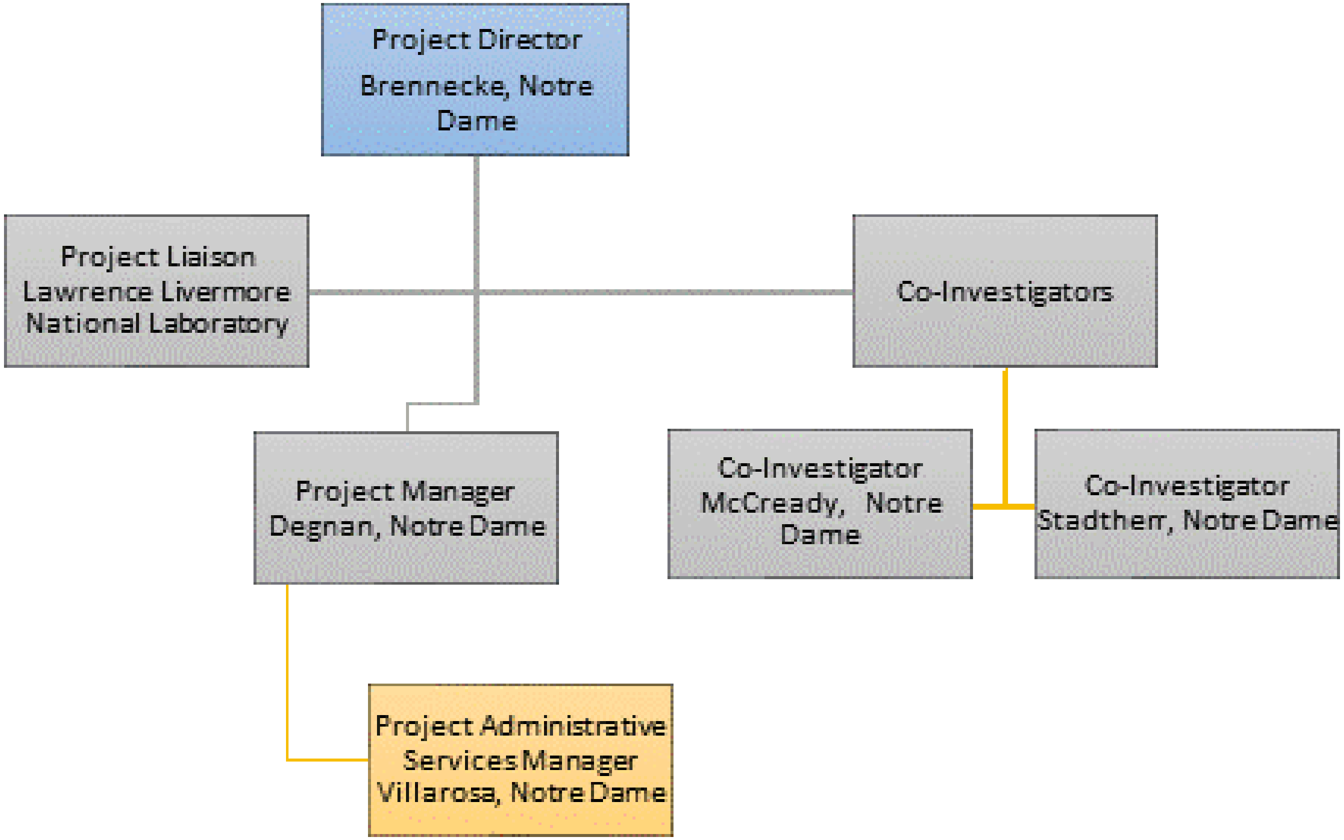
Project Team

Team Member	Background	Expertise	Role
Joan Brennecke	Ph.D. Univ. of Illinois, 1989, Keating-Crawford Professor	More than 25 years of experience with Ionic Liquids	Project Director; PI Materials Synthesis and Design
Mark McCready	Ph.D. Univ of Illinois, 1984, Professor and Sr.Assoc. Dean for Research and Graduate Studies	CO_2 adsorption and reaction in multiphase systems	PI, Process Development and Materials Evaluation
Mark Stadtherr	Ph.D. Univ. of Wisconsin, 1976; Keating - Crawford Professor	Mathematical modeling, optimization, and phase equilibria	PI, Physical Property and Process Modeling
Tom Degnan	Ph.D. Univ. of Delaware, 1977, Anthony Earley Professor of Energy and the Environment	Matertials development and commercialization; project management	Project Manager
Joshuha Stolaroff	Ph.D. Carnegie Mellon, 2006, Environmental Scientist	Carbon capture system design, mass transfer, advanced	PI, Microencapsulation
Barbara Villarosa	B.S. in Management and Administration, Indiana Univ., 2000	Accounting, compliance, project coordination	Administrative Services Manager

Project Organization



Project Objectives

Overall Objective : To demonstrate (TRL 3-4) the use of hybrid encapsulated ionic liquid (IL) materials for post-combustion CO_2 capture.

- **Budget Period 1 -** demonstrate: (1) that ILs and/or PCILs can be encapsulated, (2) that they retain high CO_2 capture efficiency and recyclability, and (3) that their use in a fluidized and/or packed bed is feasible.
- **Budget Period 2** – demonstrate: (1) high capacity and recyclability with a wet flue gas surrogate and (2) improved mass transfer over the bulk IL and/or PCIL system.
- **Budget Period 3** - demonstrate enhanced mass transfer for CO_2 capture and release in the laboratory scale unit using simulated flue gas.
  - The goal, consistent with the DOE target, is a 90% CO_2 capture rate with 95% purity and at least a 30% reduction in the COE compared to baseline technologies.

Technical approach/project scope

Technical Approach/Project Scope

1) Synthesis of ILs and PCILs (2,9,14)
2) Encapsulation of ILs and PCILs (3,10,15)
3) Test encapsulated and bulk ILs and PCILs for physical properties, capacity and cycling (2,4,14,16)
4) Develop a method to use the microcapsules in a real process (4,7)
5) Develop strategies for impurities (2,8,14,17)
6) Develop high-level rate based process model (5,12,21)
7) Laboratory scale demonstration (6,11,13,18,19)
8) Mass transfer measurements (7,18)

1) Synthesis of ILs and PCILs

2) Encapsulation of ILs and PCILs

- Encapsulation done at LLNL
- Compatibility tests
- Determine appropriate processing conditions (flowrates, stabilizers, surfactants, solvents)
- Range of diameters and thicknesses
- Development of superhydrophobic shells that are not completely permeable to water
- Bulk production

3) Test Encapsulated ILs and PCILs

Physical properties, capacity and cycling

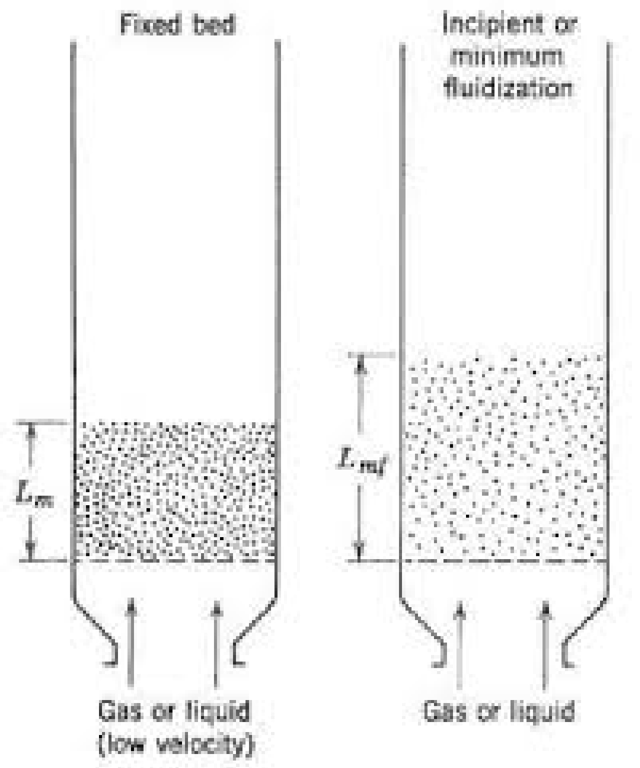
- All - T_g, T_m, T_{decomp}
- ILs
  - Densities, Viscosity neat and loaded
  - Capacity as f(T, P) and cycling
  - Uptake rates (i.e., diffusion coefficients)
- PCILs
  - Verify PCIL behavior and T range
  - Densities and viscosities loaded
  - Capacity as f(T,P) and cycling
- Encapsulated ILs and PCILs
  - Capacity as f(T,P) and cycling
  - Uptake rates relative to bulk

All Instrumentation Available

4) Method to Use Microcapsules in Real Process

To take full advantage of the large contact area of the encapsulated particles, we need to make sure that the external mass transfer resistance is much less than internal resistance

- Fluidized bed would give the best mass and heat transfer performance
- Within the flow systems, we will build a small test column that will use particles of the same size for initial test and then, the encapsulated particles once sufficient (~25 g) amounts become available.
- Fluidization behavior will be observed as a function of flow rate.
  - We will watch for “stickiness” and verify that the required superficial velocity for fluidization matches the predicted values for fluidized beds.



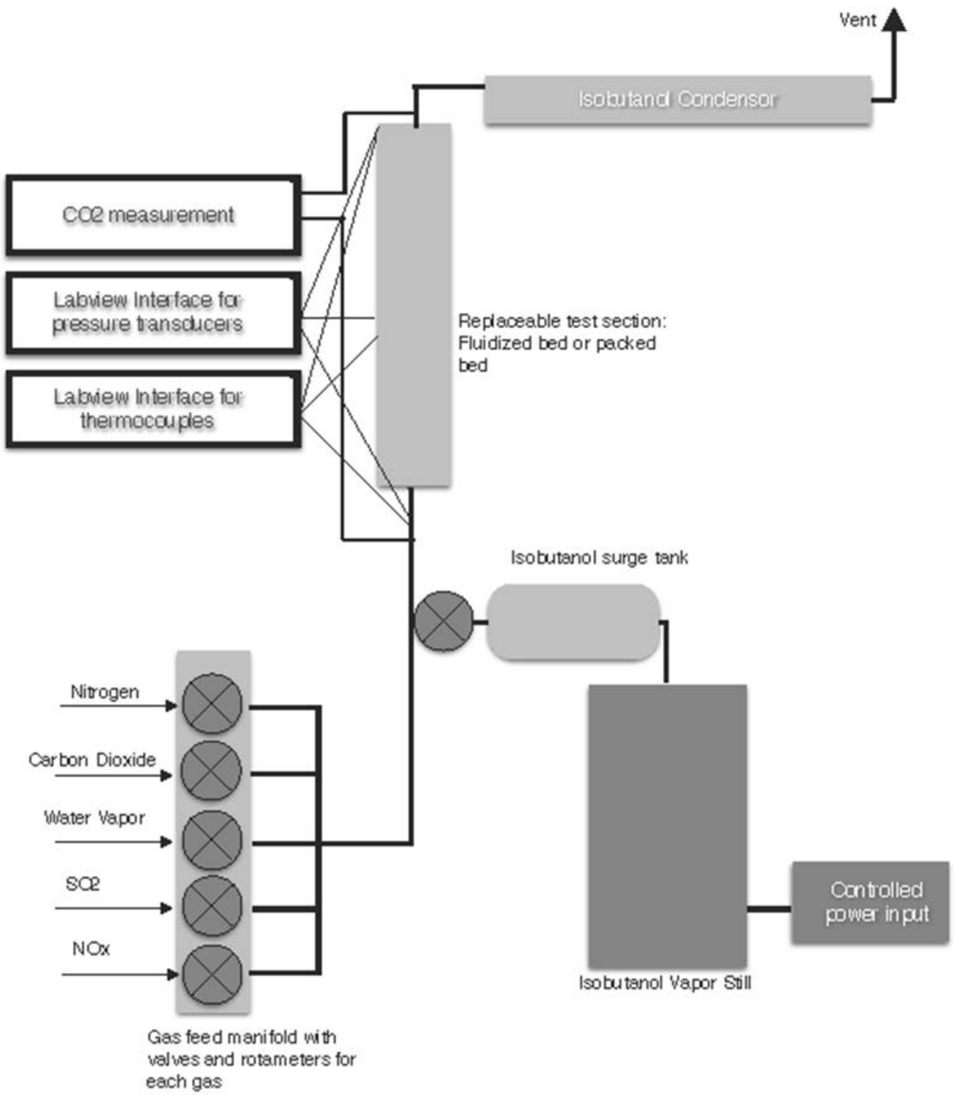
5) Strategies for Impurities

- SO_2, NO_x and water
- Predict that SO_2 will react irreversibly with ILs and PCILs
  - Measure uptake and analyze IL/PCILs by NMR
- Predict that NO_x will absorb/desorb physically
  - Measure uptake and analyze IL/PCILs by NMR
- Determine effect of water
  - Water uptake
  - Re-protonation equilibrium and rates

6) High Level Rate Based Process Model

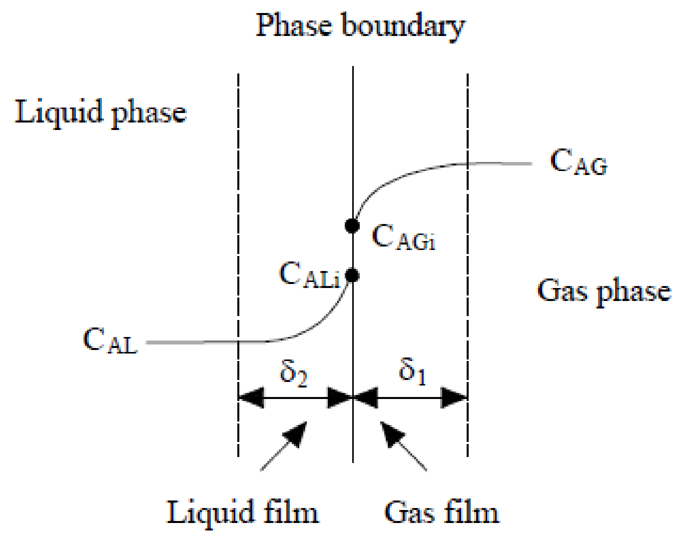
- Have previously used simple equilibrium-based process models to identify target chemical properties of ILs (e.g. ΔH_{rxn})
- Will develop simple rate-based process models that account for mass transfer rates and reaction kinetics
- Extension of standard design-oriented models (Seader et al., 2010; Kunii and Levenspiel, 1991) to account for encapsulated liquid phase, wall thickness and porosity, and the IL-CO_2 phase equilibrium
- Use to determine target microcapsule properties (e.g., diameter, wall thickness, porosity) and IL chemical properties in order to meet specified process performance goals
- Refine models as experimental fluidization and mass transfer rate measurements become available

7) Laboratory Scale Demonstration



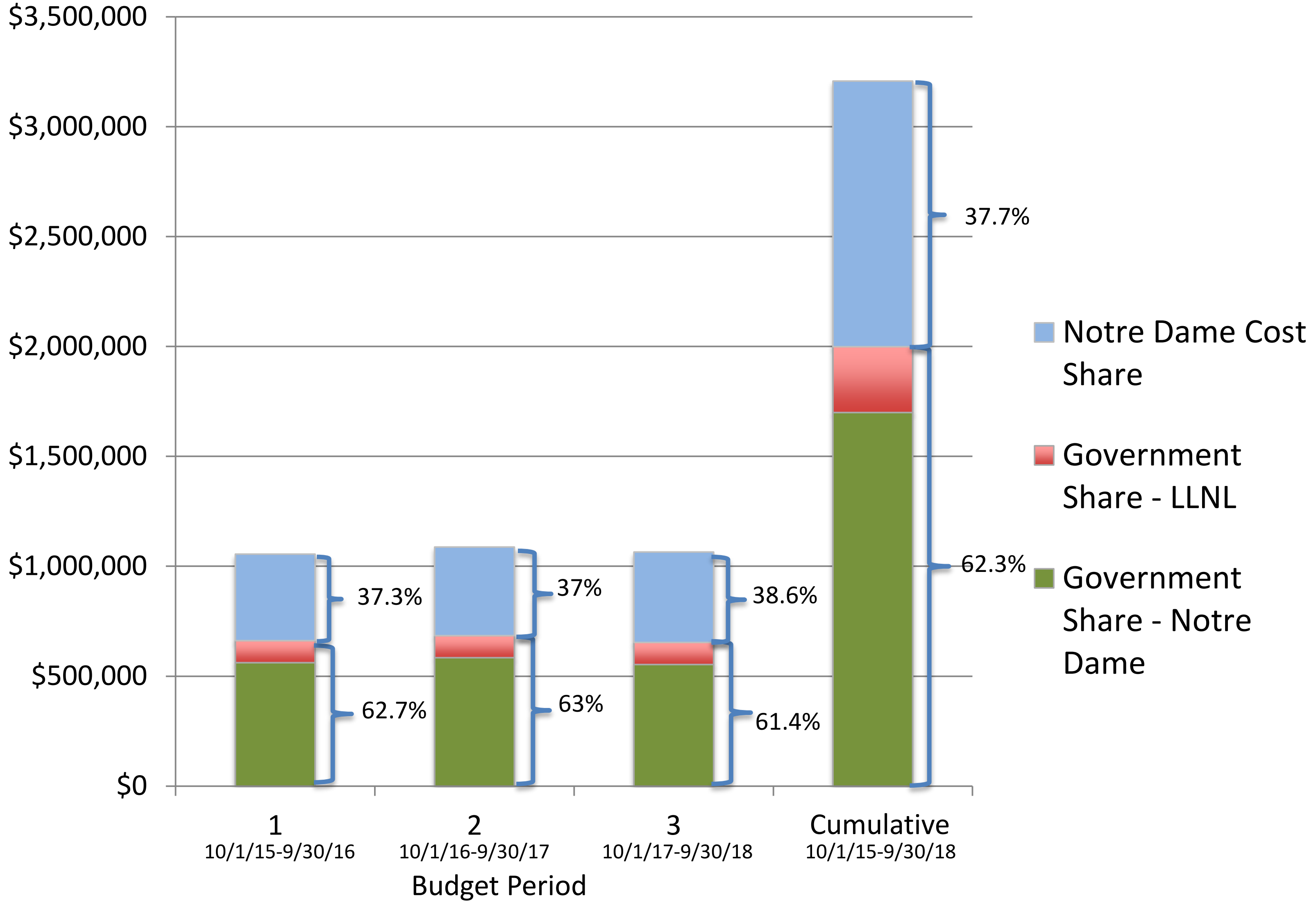
- Design
- Shakedown
- CO_2 capture and regeneration
- Effect of impurities
- Mass transfer

8) Mass Transfer Measurements

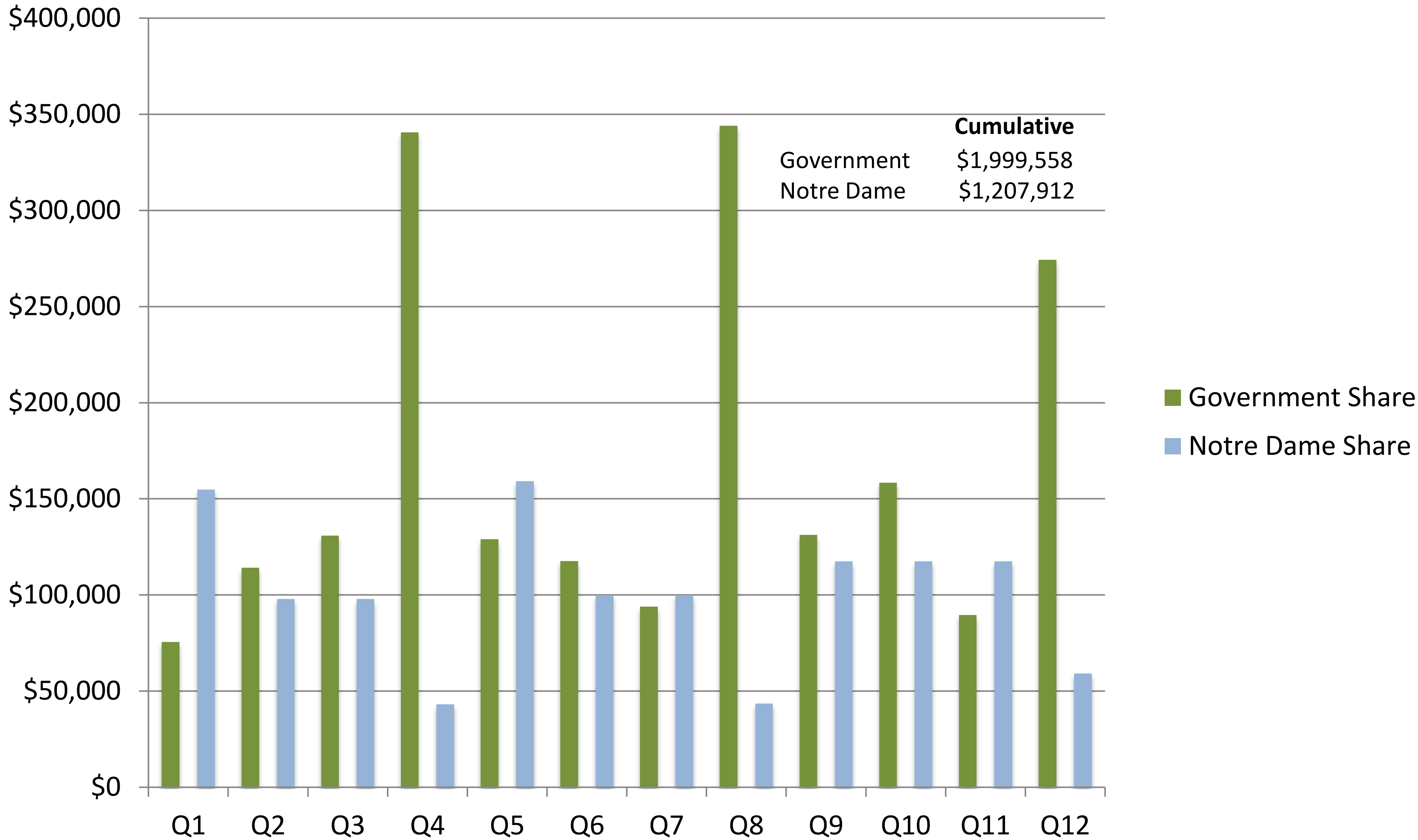


- Test regeneration with condensable vapor
- Verify external (gas side) resistance dominant (with packed bed and standard correlations)
- Measure mass transfer for fluidized bed (preferred configuration)
- Vary CO_2 concentration to eliminate gas side resistance
- Low CO_2 concentrations and freshly regenerated particles to study resistance external to particles
- Test effect of impurities on mass transfer

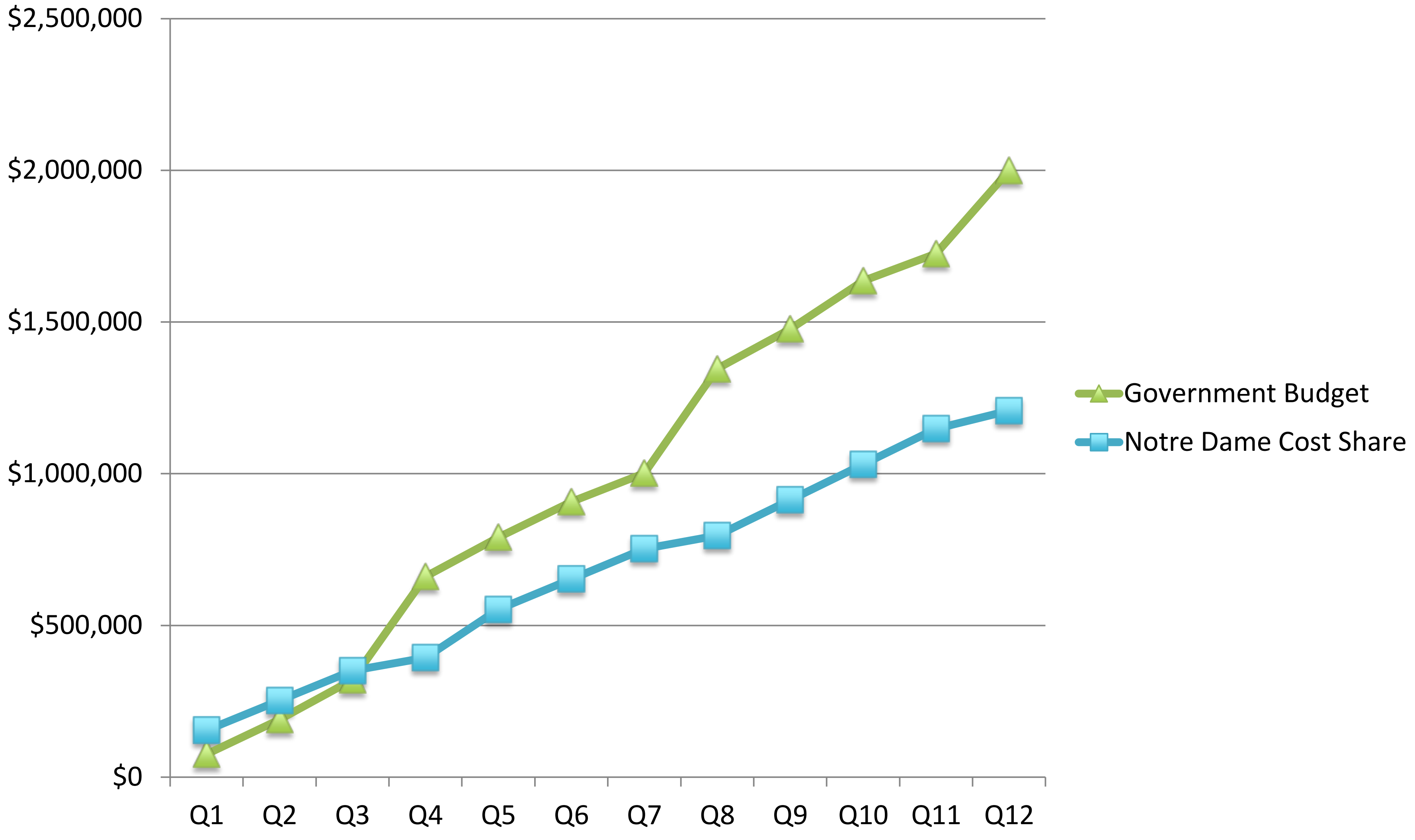
Project Budget



Project Budget by Quarter



Cumulative Project Planned Spend Profile



Project Schedule

Project Plan – Task Progression

Tasks 1 through 11

1 – Project Management & Planning

2 – Synthesize and Test IL and PCIL Candidates

3 – Encapsulate ILs

4 – Test Encapsulated IL Particles

5 – Develop Rate Based Process Model

6 – Design of Laboratory Scale Unit (LSU)

7 – Develop mass transfer Estimates

8 – Assess effects of impurities (for ILs in silicone IL microcapsules)

9 – Select top two ILs and synthesis of ~ 1 kg quantities of each

10 – Synthesize large quantities (~1 kg) of encapsulated ILs

11 - Construct and shake-down laboratory scale unit for absorption and regeneration of IL microcapsules

Project Plan – Task Progression

Tasks 12 through 20

12 - Modeling - using the rate-based models

13 - Initial testing of silicone IL microcapsules in fluidized bed or packed bed absorber with CO_2/N_2 mixture

14 – Synthesize additional small quantities of ILs for encapsulation for variable water permeability testing

15 – Encapsulate ILs in shells with selectivity against water

16 - Testing of encapsulated ILs in water-selective shells

17 - Produce additional large quantities of encapsulated ILs and small quantities of encapsulated ILs with limited water compatibility, as needed

18 - Test effect of impurities on encapsulated ILs in water-selective shells

19 - Conduct absorber studies: Mass transfer measurements of IL microcapsules with both dry and wet simulated flue gas

20 - Regenerator studies: Determine ability and conditions for regeneration of IL microcapsules

Project Plan – Task Progression

Tasks 21 through 23

21 - Analytical support for Laboratory Scale Unit

22 – Refine rate-based model and conduct initial economic feasibility study

23 – Prepare Final Report and Final Project review

Project Schedule

Task #1				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	**End Date**	**Cost**	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**	**Q8**	**Q9**	**Q10**	**Q11**	**Q12**
Task 1.0 – Project Management and Planning	10/1/15	9/30/18	$239,548												
Subtask 1.1 – Project management and planning	10/1/15	9/30/18													
Subtask 1.2 – Briefings and reports	10/1/15	9/30/18													
Milestones															
Submit Updated Project Management Plan				♦											
Conduct Kickoff Meeting				♦											
Conduct Annual Review							♦				♦				

Project Schedule

Task #2				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 2.0 – Synthesis and testing of IL and PCIL candidates	10/1/15	3/31/16	$239,881												
Subtask 2.1 – Synthesis and purification	10/1/15	12/31/15													
Subtask 2.2 – Physical property characterization	10/1/15	12/31/15													
Subtask 2.3 – CO_2 uptake measurements	1/1/16	3/31/16													
Subtask 2.4 – Recyclability testing	1/1/16	3/31/16													
Subtask 2.5 – Reprotonation equilibrium and kinetics investigations	1/1/16	3/31/16													

Project Schedule

Task #3				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 3.0 – Encapsulation of ILs	10/1/15	9/30/16	$114,341												
Subtask 3.1 – Identification of IL and PCIL-compatible shell material and/or curing process	10/1/15	6/30/16													
Subtask 3.2 – First production of small quantities (~25 g) of encapsulated Ils	1/1/16	6/30/16													
Subtask 3.3 – Production of a suite of small quantities of encapsulated Ils	4/1/16	9/30/16													
Milestones															
Successfully make encapsulated ILs						♦									
Deliver small samples of encapsulated Ils*						♦									

Project Schedule

Task #4				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	**End Date**	**Cost**	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**	**Q8**	**Q9**	**Q10**	**Q11**	**Q12**
Task 4.0 – Testing of encapsulated IL particles	4/1/16	9/30/16	$205,932												
Subtask 4.1 – Thermodynamic testing	4/1/16	9/30/16													
Subtask 4.2 – Mechanical and dynamic particle property testing	4/1/16	9/30/16													

Project Schedule

Task #5				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 5.0 – Rate-based process model	10/1/15	9/30/16	$184,682	■	■	■	■								
Subtask 5.1 – Develop rate-based model for IL liquid/gas packed bed absorber	10/1/15	3/31/16		■	■										
Subtask 5.2 – Develop rate-based model for fluidized IL microcapsules	4/1/16	6/30/16				■									
Subtask 5.3 – Develop rate-based model for packed bed of IL microcapsules	7/1/16	9/30/16					■								

Project Schedule

Task #6				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	**End Date**	**Cost**	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**	**Q8**	**Q9**	**Q10**	**Q11**	**Q12**
Task 6.0 – Design of laboratory scale unit	1/1/16	9/30/16	$117,287												
Subtask 6.1 – Design of fluidized bed absorber	1/1/16	6/30/16													
Subtask 6.2 – Design of packed bed absorber/desorber	1/1/16	6/30/16													
Subtask 6.3 – Design of condensable vapor regeneration system	1/1/16	6/30/16													
Subtask 6.4 – Selection and ordering of all system components	7/1/16	9/30/16													
Milestone															
Complete design LSU							♦								

Project Schedule

Task #7				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 7.0 – Mass transfer estimates	10/1/16	12/31/16	$43,008												
Subtask 7.1 – Mass transfer for fluidized bed of IL microcapsules	10/1/16	12/31/16													
Subtask 7.2 – Mass transfer for packed bed of IL microcapsules	10/1/16	12/3/16													

Project Schedule

Task #8				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 8.0 – Effect of impurities (for ILs in silicone IL microcapsules)	10/1/16	12/31/16	$92,933												
Subtask 8.1 - Measurements of solubility and chemistry of exposure of liquid ILs to SO_2, NO_x, and water	10/1/16	12/31/16													
Subtask 8.2 – Effect of SO_2 and NO_x on IL microcapsules	10/1/16	12/31/16													
Subtask 8.3 – Effect of water on IL microcapsules	10/1/16	12/31/16													

Project Schedule

Task #9				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 9.0 – Selection of top two ILs and synthesis of ~ 1 kg quantities of each	10/1/16	3/31/17	$111,304												
Subtask 9.1 – Synthesis and purification	10/1/16	12/31/16													
Subtask 9.2 – Physical property measurements	1/1/17	3/31/17													
Milestone Select ILs/PCILs for encapsulation and fluidization demonstration									♦						

Project Schedule

Task #10				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	**End Date**	**Cost**	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**	**Q8**	**Q9**	**Q10**	**Q11**	**Q12**
Task 10.0 – Synthesis of large quantities (~1 kg) of encapsulated Ils	10/1/16	6/30/17	-												
Subtask 10.1 – Identify scale-up method for ILs and PCILs	10/1/16	6/30/17													
Subtask 10.2 – Produce ~1 kg of encapsulated ILs for the top two ILs/PCILs	4/1/17	6/30/17													
Milestone Deliver kg quantities of encapsulated Ils*										♦					

Project Schedule

Task #11				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 11.0 – Construction and shake-down of laboratory scale unit for absorption and regeneration of IL microcapsules	10/1/16	6/30/17	$111,086												
Subtask 11.1 – Complete assembly of the test system, calibration and verification of all flow rate and pressure measurements, and operation of all analytical measurements	10/1/16	6/30/17													
Subtask 11.2 – "Cold Flow" experimental runs on inert particles	10/1/16	6/30/17													
Milestone Commission Lab Scale Unit										♦					

Project Schedule

Task #12				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 12.0 – Modeling	10/1/16	9/30/17	$181,405												
Subtask 12.1 – Refinement of rate-based models	10/1/16	3/31/17													
Subtask 12.2 – Use of rate-based models to identify targets for microcapsule properties	4/1/17	9/30/17													

Project Schedule

Task #13				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 13.0 – Initial testing of silicone IL microcapsules in fluidized bed or packed bed absorber with CO_2/N_2 mixture	7/1/17	9/30/17	$48,681												
Subtask 13.1 – CO_2 capture experiments in fluidized bed	7/1/17	9/30/17													
Subtask 13.2 – Regeneration of IL microcapsules	7/1/17	9/30/17													

Project Schedule

Task #13				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 13.0 – Initial testing of silicone IL microcapsules in fluidized bed or packed bed absorber with CO_2/N_2 mixture	7/1/17	9/30/17	$48,681												
Subtask 13.1 – CO_2 capture experiments in fluidized bed	7/1/17	9/30/17													
Subtask 13.2 – Regeneration of IL microcapsules	7/1/17	9/30/17													

Project Schedule

Task #14				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 14.0 – Synthesis of additional small quantities of ILs for encapsulation for variable water permeability testing	10/1/16	3/31/17	$132,596					■	■						
Subtask 14.1 – Synthesis and purification	10/1/16	12/31/16						■							
Subtask 14.2 – Physical property measurements	1/1/17	3/31/17							■						
Subtask 14.3 – CO_2 uptake measurements (if new ILs)	1/1/17	3/31/17							■						
Subtask 14.4 – Recyclability testing (if new ILs)	1/1/17	3/31/17							■						
Subtask 14.5 – Reprotonation equilibrium and kinetics investigations (if new ILs)	1/1/17	3/31/17							■						

Project Schedule

Task #14				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 14.0 – Synthesis of additional small quantities of ILs for encapsulation for variable water permeability testing	10/1/16	3/31/17	$132,596												
Subtask 14.1 – Synthesis and purification	10/1/16	12/31/16													
Subtask 14.2 – Physical property measurements	1/1/17	3/31/17													
Subtask 14.3 – CO_2 uptake measurements (if new ILs)	1/1/17	3/31/17													
Subtask 14.4 – Recyclability testing (if new ILs)	1/1/17	3/31/17													
Subtask 14.5 – Reprotonation equilibrium and kinetics investigations (if new ILs)	1/1/17	3/31/17													

Project Schedule

Task #15				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 15.0 – Encapsulation of ILs in shells with selectivity against water	10/1/16	9/30/17	$76,964												
Subtask 15.1 – Identification of hydrophobic membrane materials for selectivity against water with IL compatibility	10/1/16	12/31/16													
Subtask 15.2 – First production of small quantities (~25 g) of encapsulated ILs with water-selective shells	4/1/17	6/30/17													
Subtask 15.3 – Production of a suite of small quantities of encapsulated ILs with water-selective shells	7/1/17	9/30/17													
Milestone Deliver small samples of encapsulated ILs with variable water permeability shells*										♦					

Project Schedule

Task #16				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 16.0 – Testing of encapsulated ILs in water-selective shells	7/1/17	9/30/17	$111,005												
Subtask 16.1 – Thermodynamic testing	7/1/17	9/30/17													
Subtask 16.2 – Mechanical and dynamic particle property testing	7/1/17	9/30/17													

Project Schedule

Task #17				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 17.0 – Produce additional large quantities of encapsulated ILs and small quantities of encapsulated ILs with limited water compatibility, as needed.	10/1/17	9/30/18	-												

Project Schedule

Task #18				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 18.0 – Testing effect of impurities on encapsulated ILs in water-selective shells	10/1/17	12/31/17	$128,812												
Subtask 18.1 – Effect of SO_2 and NO_x on water-selective microcapsules	10/1/17	12/31/17													
Subtask 18.2 – Effect of water on variable water-selective microcapsules	10/1/17	12/31/17													

Project Schedule

Task #19				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 19.0 – Absorber studies: Mass transfer measurements of IL microcapsules with both dry and wet simulated flue gas	10/1/17	3/31/18	$119,563												
Milestone Measure mass transfer coefficients for microcapsules in LSU														♦	

Project Schedule

Tasks #20 and 21				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 20.0 – Regenerator studies: Determine ability and conditions for regeneration of IL microcapsules	1/1/18	6/30/18	$119,563												
Task 21.0 – Analytical support for Laboratory Scale Unit	10/1/17	9/30/18	$271,801												

Project Schedule

Task # 22				Budget Period 1				Budget Period 2				Budget Period 3			
				10/1/15 - 9/30/16				10/1/16 - 9/30/17				10/1/17 - 9/30/18			
	Start Date	**End Date**	**Cost**	**Q1**	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**	**Q7**	**Q8**	**Q9**	**Q10**	**Q11**	**Q12**
Task 22.0 – Modeling	10/1/17	9/30/18	$185,605												
Subtask 22.1 – Refinement of rate-based models	10/1/17	6/30/18													
Subtask 22.2 – Initial economic feasibility study	7/1/18	9/30/18													
Milestone Quantify mass transfer improvements by encapsulation															♦

Project Schedule

Task # 23				Budget Period 1 10/1/15 - 9/30/16				Budget Period 2 10/1/16 - 9/30/17				Budget Period 3 10/1/17 - 9/30/18			
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 23.0 – Preparation of Final Report and Final Project Review	7/1/18	9/30/18	$71,473												
Milestone Submit Final Report															♦

Project Milestones

Project Milestones

Budget Period	Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
1	1.0	Submit Updated Project Management Plan (PMP)	10/31/2015		PMP file
1	1.0	Conduct Kickoff Meeting	12/31/2015		Presentation file
1	3.0	Successfully make encapsulated ILs	6/30/2016		Quarterly Research Performance Progress Report
1	3.0	Deliver small samples of encapsulated ILs*	6/30/2016		Quarterly Research Performance Progress Report
1	6.0	Complete Design of LSU	9/30/2016		Quarterly Research Performance Progress Report
1	1.0	Conduct Annual Review	9/30/2016		Presentation file

Project Milestones

Budget Period	Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
2	9.0	Select ILs/PCILs for encapsulation and fluidization demonstration	12/31/2016		Quarterly Research Performance Progress Report
2	10.0	Deliver kg quantities of encapsulated ILs*	6/30/2017		Quarterly Research Performance Progress Report
2	11.0	Commission Lab Scale Unit	6/30/2017		Quarterly Research Performance Progress Report
2	15.0	Deliver small samples of encapsulated ILs with variable water permeability shells*	6/30/2017		Quarterly Research Performance Progress Report
2	1.0	Conduct Annual Review	9/30/2017		Presentation file

*Specified uniform particle diameters with known shell thickness; permeable to CO_2

Project Milestones

Budget Period	Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
3	19.0	Measure mass transfer coefficients for microcapsules in LSU	6/30/2018		Quarterly Research Performance Progress Report
3	22.0	Quantify mass transfer improvements by encapsulation	9/30/2018		Final Technical Report
3	1.0-23.0	Submit draft Final Report	9/30/2018		Presentation file

Decision Points and Success Criteria

Decision Points and Success Criteria

Budget Period #1

Decision Point	Date	Success Criteria
Completion of Budget Period 1	September 30, 2016	1. The successful identification and preparation of encapsulated IL or PCIL microcapsules. The shells of the ionic liquid microcapsules must be able to contain the ILs without leakage.
		2. The successful demonstration of CO_2 uptake by the encapsulated ILs or PCILs. They must have a CO_2 absorption capacity greater than 50% of the weight of the equivalent free IL/PCIL.
		3. The successful demonstration of the durability/recyclability of the encapsulated ILs/PCILs in pure CO_2. The test for this will be the maintenance of absorption capacity after multiple absorption – desorption cycles. There must be less than a 20% decline in CO_2 adsorption capacity after 5 cycles with pure CO_2.

Decision Points and Success Criteria

Budget Period #2

Decision Point	Date	Success Criteria
Completion of Budget Period 2	September 30, 2017	.4. The successful demonstration of the integrity and performance of the encapsulated ILs/PCILs in either a packed bed or a fluidized bed (or both). The integrity will be determined by the ability of the IL microcapsules to withstand the forces present in a fluidized or a packed bed without rupturing or leaking. The performance will be demonstrated by the ability of the ILs/PCILs to absorb pure CO_2 according to the criteria described in #2 and #3 above.

Decision Points and Success Criteria

Budget Period #3

Decision Point	Date	Success Criteria
End of project	September 30, 2018	1. The successful demonstration of the durability/recyclability of the encapsulated ILs/PCILs with a wet CO_2/N_2 mixture. The test for this will be the maintenance of absorption capacity after multiple absorption – desorption cycles. For this success criterion to be met there must be less than a 20% decline in CO_2 adsorption capacity after 5 cycles with wet CO_2/N_2 mixture
		2. The successful demonstration of CO_2 capture in a laboratory scale absorption unit with a wet CO_2/N_2 mixture. For this criterion to be met, the encapsulated ILs/PCILs must demonstrate the capture of greater than 50% of the CO_2 in an inlet stream comprised of a wet CO_2/N_2 mixture in the laboratory scale absorption unit.
		3. The successful demonstration of regeneration of the particles in the laboratory scale unit. For this criterion to be met, at least 80% of the absorbed CO2 must be removed by the hot vapor (/steam) without significant damage to the particles. The regeneration of particles will be sufficient to allow meeting criterion "6" for at least 5 complete cycles.

Project Risks and Risk Management

Technical Risks and Risk Management and Mitigation Strategies

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Technical Risks:			
Inability to identify ILs that have desired characteristics and which can be encapsulated by LLNL	Low	High	Active IL synthesis will continue during the span of this project. World-class experts in IL synthesis and characterization are engaged.
Encapsulation technology fails to produce a robust microcapsule prototype that has target CO_2 permeabilities and hydrophobicity	Moderate	High	Project will draw on silicone technologies from Dow Corning and specialty suppliers. Other encapsulation approaches will be evaluated.
90% post-combustion CO_2 uptake is not achieved by encapsulated IL/PCIL-based process	Low	High	Assembly of world-class team of IL experts best suited to tackle the technical challenges.
Fluid or particle degradation occurs because of contaminants in the flue gas stream	Moderate	Moderate	Assembly of world-class team of IL and silicone experts who have successfully resolved similar materials problems.

Technical Risks and Risk Management and Mitigation Strategies (cont'd)

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Technical Risks:			
Final process exceeds cost of electricity 30% less than baseline capture approaches	Moderate	Low	Best practices (e.g., http://www.ofm.wa.gov/budget/instructions/predesign/appendixE.pdf) will be used to develop DOE Class 5 (Order of Magnitude) cost estimate. If process estimate exceeds target, ideas will be solicited for means to further reduce capital, material, and operating costs. Additional funding may be required to commission a panel of external process experts aimed at further cost reduction.

Resource Risks and Risk Management and Mitigation Strategies

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Resource Risks:			
Insufficient access to unit necessary for IL encapsulation	Low	High	If LLNL equipment unavailable (unlikely), will replicate system at ND.
Insufficient access to instrumentation necessary for characterization	Low	Moderate	If the characterization instrumentation is unavailable, characterization will be subcontracted to a third party.
Unexpected costs associated with construction of LSU	Low	Low	Mitigation through detailed planning and accurate expense estimates
Prohibitive costs associated with the commercial production of the encapsulated IL's	Moderate	Moderate	Degnan, who has prior experience in commercialization of novel materials, will work with commercial providers to develop early cost estimates.

Management Risks and Risk Management and Mitigation Strategies

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Management Risks:			
Delays in construction of LSU	Moderate	Moderate	Ensure LSU construction plan follows aggressive timeline scheduling to achieve timely project completion

Recap and Next Steps

- Approval of Project Plan
- Summary of Action Items
- Schedule for resolution and response to Action Items

Questions?